Studies on the Extraction, Purification, and Analysis of Sugars and Sugar Juices with special reference to the Desiccation Process.

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INTRODUCTION.

Exactly two hundred years ago the German chemist Marggraf demonstrated the presence of sucrose in beet by drying the roots and then extracting the sucrose by alcohol.

Since his time there have been numerous attempts to perfect a process of desiccation with the main object of preserving the beet and thus allowing extension of the extraction season from the three months of the harvest to the full year.

The work here presented is a record of research carried out on various problems arising from the desiccation process of beet sugar manufacture,as follows :-

1. The composition of fresh and dried sugar beets :
2. The desiccation of sugar beets :
3. The design of a suitable apparatus for extracting sucrose from dried sugar beets;
4. Purification of the raw sugar juice thus extracted :
5. Methods of Analysis, with particular reference to the estimation of water in sugar products.

The problems arising in a desiccation process for sugar manufacture can be ascribed to a number of causes. There is first of all the concentration effect on other constituents due to the elimination of water ; there are the physical and chemical changes occurring during the drying process both naturally and by the use of furnace gases in the drying air ; and there is the danger of fracture and powdering of the dried cossettes if they are over-dried. Then there is the danger of deterioration during

storage over a period of 3 to 9 months.
In the extraction process, several difficulties appear, necessitating radical changes in the apparatus used. There is excessive frothing in the diffusion battery due to high concentrations of saponins, and there is often undue compression unless the amount of cossettes filled per cell is carefully regulated. The main difficulty in extraction however, is the risk of caramelisation and inversion, causing dark juices and loss of sucrose. This risk is even more evident in the ensuing purification process, which is further complicated by the high density and viscosity of the raw diffusion juice.

It was therefore necessary to make analyses of the various constituents of the fresh beets, the dried cossettes, and the raw diffusion juice, and to constrast these results with analyses of juices after purification. It will be clear that many of the methods of analysis used had to be modified to suit these concentrated products.

One of the most important of these analytical operations is the determination of water in materials sensitive to heat, and the latter part of this work deals with this problem.

STUDIES ON THE EXTRACTION, PURIFICATION, AND ANALYSIS OF SUGARS AND SUGAR JUICES, WITH SPECIAL REFERENCE TO THE DESICCATION PROCESS.

SUMMARY AND CONCLUSIONS.

SECTION 1

THE COMPOSITION OF FRESH AND DRIED SUGAR BEETS.

Detailed analyses have been made of fresh sugar beets and of the dried slices (cossettes) derived from them.

A spectroscopic examination has been made of the mineral matter in dried beets.

The dried beets analysed included samples dried - (a) by direct furnace gases, (b) by pure air, and (c) by air containing known quantities of sulphur dioxide.

Special attention was directed to the determination of harmful ("noxious") nitrogen in sugar beets.

SECTION 2

THE DESICCATION OF SUGAR BEETS.

SLICING :- An analysis has been made of the size distribution of fresh beet slices and dried cossettes, and from this study the profile of an "ideal" cossette has been drawn.

DRYING :- The process of drying has been described, and details given of the drier dimensions and the conditions of drying.

Analyses made by the author of the drying air and of the coal used have been of service in tracing the development of acidity in the dried beet cossettes. Analyses have been made of the beets in the various stages of drying.

CHEMICAL CONDITIONING OF DRIED BEET COSSETTES :- A summary is given of an extensive series of tests carried out by the author on the use of various neutralising agents in the drying process.

It was found that there was a wide choice of reagents with which the fresh slices can be treated so that neutral or slightly alkaline dried cossettes can be produced.

This avoidance of low pH values has important repercussions on the loss by inversion of sucrose during the extraction of the dried cossettes in a diffusion battery.

SECTION 3 . Part 1.

THE DESIGN AND OPERATION OF A DIFFUSION BATTERY FOR THE EXTRACTION OF DRIED SUGAR BEETS.

DESIGN :- The standard cell type of diffusion battery having failed to give even moderately satisfactory results when operating on dried beet slices, the author carried out a series of experiments to determine :-

(1) a suitable design of diffusion battery for this purpose :
(2) the percentage extraction obtainable with such a battery :
(3) the bahaviour of the constituents of the dried beet cossettes during extraction, and
(4) the effect of chemical conditioning of the cossettes in the diffusion battery.

After experience with six different pilot plant and large scale batteries the author has given a survey of the desirable features in a diffusion battery for the extraction of dried beet cossettes.

EXTRACTION :- Detailed results of extraction tests devised and controlled by the author are shown. They indicate that in a properly designed battery an extraction of over 97 per cent is possible when extracting dried beet cossettes, and that the inversion loss can be reduced to about 0.5 per cent on sugar.

SECTION 3 : PART 2

COMPOSITION OF DIFFUSION JUICES :- Detailed analyses made by the author are given for diffusion juices obtained from dried beet cossettes dried with (a) direct furnace gases, and (b) with pure air.

INVERSION DIFFUSION TRIALS :-

A series of diffusion trials made by the author sought to determine the conditions necessary to keep to a minimum the loss by inversion of sucrose in the diffusion of dried beets.

In these tests the effects of temperature and time of contact upon the extraction were also studied.

CONCLUSIONS

It was found that with pure-air dried cossettes there is some inversion of sucrose during diffusion, but much less than that occurring with cossettes dried by direct furnace gases.

Temperature increase caused an immediate rise in the rate of inversion.

The addition of alkali to reduce inversion was successful, but required exact control and careful supervision.

The author has discussed in this section some considerations regarding the formation of invert-sugar during the drying of sugar beets. The control of this loss by inversion of sucrose can be regarded as the key to the technical success of a beet desiccation process.

SECTION 4 : PART 1.

THE PURIFICATION OF DIFFUSION JUICES OF HIGH DENSITY FROM DRIED BEETS.

Introduction :- The general methods used in the purification of sugar juices are discussed in relation to the composition of these juices.

Special attention has been given to the colloidal matter in the juices, and the use of an electrophoresis method of estimating colloid content is described, and the experimental results obtained are recorded. The method has also been used to trace the removal of colloids from the juices in the several stages of purification. The relation between colloid content and the rate of filtration has also been studied.

PART 2 : Experimental :- A method developed by the author for the purification of diffusion juices of high density from dried beets is described. It involves the addition of alkali, and an electrolyte, such as aluminium sulphate in separate stages, followed by neutralisation with an acid reagent such as carbon dioxide or sulphur dioxide, the latter preferably in liquid form.

A comprehensive study has been made of the variable factors in this purification process especially in regard to quantities of reagents used, times of contact, temperatures, times of filtration, and improvement of colour and purity. The experiments were controlled primarily by purity, colour, and pH value determinations.

In the final testing of the process, more complete analyses were made of all the products derived from a pilot plant working of the process, and from this scheme a balance of ash and invert-sugar was drawn up. The elimination of impurities in the stages of this process is shown by these analyses.

SECTION 5

METHODS OF ANALYSIS : PART 1

DETERMINATION OF THE POLARISATION AND REDUCING SUGAR CONTENT OF FRESH BEETS AND DRIED BEET COSSETTES.

Methods developed for the analysis of dried beet cossettes from the work described in Part 2 of the present Section are given in detail.

PART 2 :- The experimental work carried out by the author on the perfection of suitable methods for determining polarisation and reducing sugars is described. The tables shown here record this experimental work.

The factors investigated included :-

(a) Adsorption of sucrose by the insoluble marc :

(b) The influence of temperature upon digestion :

(c) A comparison of polarisation methods- e.g., alcoholic and aqueous digestion ; cold and hot digestion ; comminution of the sample by saw, mincer, rasp, or special mill:

(d) The influence of concentration of solutions :

The methods evolved for dried beet analysis as a result of this work were used throughout the investigations recorded in Section 1 to 4,(composition, extraction, and purification).

The determination of reducing sugars forms Subject 4 of the Research agenda of the International Commission for Uniform Methods of Sugar Analysis, under the Presidency of Dr. Frederick Bates, U.S. National Bureau of Standards. The author is an Associate Referee for Subject 4 : he hopes to present the results here recorded at the Tenth Session of the Commission.

SECTION 5 : PART 3

THE DETERMINATION OF RAFFINOSE, MARC, AND SPECIFIC GRAVITY.

The specific gravities of fresh beets, dried beet cossettes, and dried marc have been determined by the author.

An investigation has been made of the problem of determining insoluble marc in dried beets, and the results are here presented.

The presence of raffinose in dried beets does not appear to have been investigated previously : the author's experimental figures are recorded with the reservation that they merely indicate that raffinose may provide the largest proportion of the percentage here called "raffinose".

Bibliographies are included for marc and for raffinose.

PREVIOUS WORK :- So far as the author is aware little or nothing has been published on the composition and methods of analysis of dried beets.

Similarly no detailed research on the problems of extracting dried beets has appeared, and there is little or no recorded data regarding the purification of beet juices of high density.

SECTION 5 : PART 4.

THE DETERMINATION OF WATER AND TOTAL SOLIDS IN SUGAR PRODUCTS.

A survey has been made of the literature relating to - (a) the presence of water in solid materials ; (b) its determination ; (c) oven methods in general.

The influence of humidity on moisture determinations has been discussed, and the importance of the determination of water has been recognised.

A general comparison of methods has revealed a multiplicity of these, often very diverse in character and accuracy.

A summary has been made of various reasons for discrepancies and poor agreement in oven methods of determining water.

A graph has been constructed showing the solubilities of Various carbohydrates

PART 5 :- OVEN METHODS FOR THE DETERMINATION OF WATER.

This part serves as an introduction outlining the scope of the work.

Detailed consideration has been given to the many factors involved in the use of the various types of oven-drying, and it has been shown that, on account of these factors, oven drying is far from being the simple operation it appears to be.

An attempt was made to establish :-

1. The best type and quantity of absorbing medium and its preparation.
2. The best type and dimensions of drying dish :
3. The optimum time and temperature of drying :

4. The best type of oven :
5. The influence of atmospheric pressure :
6. The effect of drying at a pre-determined pH value.

SECTION 5 : PART 6.

THE RATE OF EVAPORATION IN THE DETERMINATION OF WATER.

The rate of evaporation of water from open vessels in "still" air has been investigated by several workers, but the conditions of evaporation of water in a closed compartment of a steam or vacuum oven are markedly different from those in open evaporation systems.

The experimental work of the author on this subject is summarised on page .

It has been shown that the rate of evaporation of water in a ventilated closed compartment of an oven is very much lower than the rate of evaporation from an open pan in "still" air, and that the rate of supply of heat to the vessel is probably the most important factor influencing this rate.

SECTION 5 : PART 7.

THE DETERMINATION OF WATER IN GOLDEN SYRUP.

On account of its very high content of reducing-sugars and its very low proportion of mineral matter, golden syrup is very sensitive to heat, and it therefore forms an excellent test-material in comparing methods of determining water.

Factors influencing this determination in golden syrup have been studied, and several methods have been compared, A full analysis of two samples of golden syrup has been made.

An acid-washed kieselguhr (Celite) has been found suitable as an absorbent for the syrup, yielding more concordant results than sand.

A method is recommended for the estimation of water in such thermally sensitive substances as golden syrup.

SECTION 5 : PART 8.

THE DETERMINATION OF WATER IN KNOWN SOLUTIONS OF GLUCOSE, SUCROSE, AND LEVULOSE.

In these experiments the solutions were dried on sand, Celite, paper, and asbestos. Crushed pumice was also used.

Analyses were made of various acid-washed kieselguhrs. Much of this experimental work was conducted at pre-determined pH values.

CONCLUSIONS :-

Levulose in Vacuum oven :- Levulose can be dried without appreciable loss in the vacuum oven at 70°C., at pH values of 4, 5, or 6 for periods up to 4 hours. Drying at pH values above 7.0 is slower, and there appears to be more decomposition of the sugar.

Drying on pumice gave good results : drying on sand and Celite gave slightly low results.

For vacuum oven drying, 60°C. is definitely preferable to 70°C., but the optimum time of 4 hours at 70°C. becomes 7 to 9 hours at 60°C.

When drying on paper rolls there is danger at this lower temperature that water will not be expelled from hydrated forms of the sugars.

Levulose in Steam Oven :- In all the steam-oven tests there was considerable loss of solids even after only 3 hours heating at approximately 98°C.

Glucose in vacuum oven :- No decomposition was seen after 28 hours heating at 70°C. In tests with regulated pH values, drying at 2, 5, and 11 pH was satisfactory at 70°C., with faster drying in the acid region.

Glucose in steam oven :- Results were good : the rate of drying appears to be faster than for levulose. Glucose was relatively stable at 98°C. with an optimum heating period of just over 3 hours.

Sucrose in vacuum oven :- Drying on Celite or on paper rolls gave remarkably constant results at 70°C. Sand gave slower drying, the known percentage solids being reached in 28 hours, compared with 3-6 hours for Celite or paper rolls. Drying with buffer solutions gave good results at 5 to 12 pH, but not below 5 pH.

Sucrose in steam oven :- Very consistent results were obtained, but in no case was the known percentage of water reached. Sucrose seems to be very reluctant to part with the last trace of water. This may be due to very close atomic binding of part of the water, or it is possible that partial inversion occurs, taking up a minute quantity of water, and thus increasing the apparent solids.

SECTION 5 : PART 9

THE DETERMINATION OF WATER IN RAW SUGARS.

In this work the factors investigated included a study of replication, of optimum time and temperature of heating, of the influence of the weight of sugar taken, and of the type of dish used. The effect of position in the oven was also studied. Analyses are given of the various raw sugars tested.

The effect of heat on the reducing sugars was also observed by determining the reducing sugars in the dried residues.

SUMMARY OF CONCLUSIONS. (See page 411).

Time of Heating :- There is higher apparent loss as the time of heating is increased : the vacuum oven gives lower results than the steam oven.

Weight taken :- It is recommended that not less than 5 g. nor more than 20 g. of sample be weighed for each determination.

Effect of Dishes :- Glass dishes and nickel dishes give somewhat higher results than aluminium dishes. The bottom of the dish must maintain good contact with the oven bottom. Aluminium dishes of small diameter tend to give higher results than those of larger diameter.

Replication :- Similar dishes have similar results : the position of the dish in the oven was a much more important factor.

Temperature of Heating :- In the vacuum oven there was little difference in results at 50, 60, or 70°C.

In the steam oven a departure of one or two degrees from 100°C. had considerable effect on the moisture content recorded.

Decomposition of Reducing Sugars :- This was found to occur even after only 30 minutes heating in the steam oven. There is a likelihood that inversion of sucrose, oxidation of organic matter, and actual destruction of reducing sugars - in particular of levulose- are going on simultaneously during the heating.

SECTION 5 : PART 10.

DETERMINATION OF WATER USING THE SPENCER OVEN.

In this oven, air heated electrically is continously drawn through the sample to be dried. Four series of tests were carried out.

SUMMARY OF TESTS AND CONCLUSIONS.

(1) Drying of a known levulose solution :- Using a 38.27 per cent solution of levulose at average temperatures of 53, 66, 77, 80, and 85°C. the following results were obtained :-

At 53°C. it was found that the temperature was too low for the driving off of the last traces of water from the levulose.

At 66°C. the drying was completed in about 4 hours, and there was little change in 16 hours.

Temperatures above 75°C. should not be used in the Spencer oven when drying a sensitive sugar like levulose.

(2) Comparison of Spencer oven and steam oven for Raw Sugars :-

In the Spencer oven at 70°C. 0.72 per cent, at 77°C., 0.73 per cent, and at 91°C., 0.75 per cent water was found compared with an average of 0.84 per cent in the steam oven at 99°C.

(3) Moisture in different sizes of Raw Sugar crystals :- The differences found were not significantly great.

(4) Effect of Spencer oven heating on reducing sugars :-

Using a Cuban raw sugar, heating above 115°C. for over 20 minutes caused a progressive decrease in the reducing sugar content.

General Conclusion :-

The Spencer oven can yield comparable results in routine testing, but it cannot be regarded as an accurate means of determining water in thermally sensitive substances.

A note is appended on the Serbia drying oven.

SECTION 5 : PART 11.

THE DETERMINATION OF WATER BY DESICCATION METHODS.

Introduction :- Various types of drying agents and their mode of action are discussed, and factors which the author found significant in chemical desiccation methods are described.

Experimental Results :- See summary on page 469.

Solutions of sucrose, glucose and levulose were dried at room temperature, (a) in a static atmosphere, (b) in a stirred atmosphere, using concentrated sulphuric acid as drying agent.

Celite and sand were used as dispersing and absorbing media. Similar tests were made using golden syrup, and vacuum drying was also used for this material, both at room temperature and within the temperature range 36-50°C.

The moisture content of a raw sugar was estimated at room temperature with stirring : this served as a contrast to the estimations made on solutions as above.

CONCLUSIONS REGARDING THE DESICCATION METHOD.

Time of Drying :- This was found to be excessively long, and only in a few tests was a satisfactory result obtained.

Stirring :- This considerably shortened the drying time when "free" water was present, but the effect of stirring was much less marked when the sample was nearly dry.

Vacuum :- The drying time was greatly reduced in vacuum conditions at room temperature, but the vacuum oven at 50°C. was found to give satisfactory results in much less time.

RECOMMENDATION :-

(a) The use of stirring and vacuum is recommended when desiccation at room temperature is found desirable. Adequate ratios of absorbing medium to sample must be maintained.

(b) The use of a vacuum oven at low temperature is generally more satisfactory than desiccation at room temperature, and should be preferred when conditions permit.

ANALYSIS : SECTION 5 : PART 12.

THE DETERMINATION OF WATER BY DISTILLATION METHODS.

Introduction :- A critical survey of the literature has been made. The advantages and disadvantages of the distillation method are reviewed. The types of liquids used in the method are discussed, and a description is given of the various types of apparatus used.

Summary of Experimental results :-

(1) Levulose Solution :- Tests were made on a 48.16 per cent levulose solution with three diverse types of apparatus using benzene, heptane, toluene, and xylene, and with one type of apparatus using carbon tetrachloride and tetrachlorethylene.

Conclusions :- The results that the distillation method with the types of apparatus used is not suitable for the determination of water in thermally sensitive media like levulose solution. There was progressive decomposition as the distillation proceeded.

(2) Golden Syrup :- Ten different types of apparatus were tested with golden syrup using a wide range of solvents.

Conclusions :- The results bore out those obtained with levulose solution in series (1), but showed that with careful standardisation the method might be adapted for routine comparison purposes where the materials being tested are not unduly sensitive to heat.

The use of ignited Celite in the distillation flask to "blanket" the solution from the source of heat is recommended.

(3) Known sugar solutions :- A comparison was made between the Dean and Stark distillation method, the vacuum and steam oven methods, and the refractometric method of determining water in known solutions of sucrose, glucose, and levulose.

The Dean and Stark method gave comparable results for these sugars only after 8 hours heating, and tended to give low results for sucrose and levulose.

(4) Levulose Solution with special apparatus and mixed liquids :-

Various mixtures of solvents were made of suitable boiling points and densities, and these were used in testing levulose solutions in various types of apparatus.

In some of these tests the recovery of water was slightly lower than the amount of water known to be present, but in several cases the recovery was very satisfactory.

It seems clear that for levulose the temperature of distillation should be kept below 100°C., and that the time required for complete distillation of the water present is between 2 and 3 hours.

Special types of Apparatus :- Several types of distillation apparatus were devised by the author which could be used with solvents both lighter and heavier than water. This type of apparatus was found useful in finding a mixture of solvents which was of suitable density and boiling-point, and also non-inflammable.

(5) Distillation with Buffer Solutions of known pH value :-

The object of these tests was to find (a) the best conditions for a clear meniscus, and (b) the variation in pH caused by the solvents.

It was found that in general toluene gave less emulsification than benzene or xylene.

The most permanent emulsions occurred with alkaline buffer solutions, but paradoxically, the two cases found of a perfect meniscus were from alkaline solution.

The acid buffer solutions caused a greater clinging of water to the condenser walls.

(6) Vacuum Distillation :- A series of tests was made using a vacuum technique with the object of preventing the destruction of the more heat-sensitive sugars such as levulose.

The vacuum method was found to be difficult to apply owing to the surging and "bumping" properties of the mixtures involved, and the results obtained were not considered to be sufficiently accurate to justify the extra care and time necessary.

THE DISTILLATION METHOD : FINAL SUMMARY.

A technique is recommended for the distillation method with the use of electric hot plate heating by radiation, and the employment of a dispersing medium (Celite) in the flask.

For satisfactory results all apparatus used should have glass joints and stoppers.

The washing-down of water from the condenser is most important.

Three types of dual purpose apparatus are described.

SECTION 5 : PART 13.

THE DETERMINATION OF WATER BY CHEMICAL METHODS.

Introduction :- A summary is given of methods for determining water, including a note on the carbide method.

The experimental work deals with the Fischer method, which is described in detail.

Experimental :- Two series of tests were made - one on refined white sugars and samples of solid sugars other than sucrose, the other on golden syrup.

(1) Solid sugars :- These were found to require up to 3 hours contact time at 18°C., compared with 1 hour at 60°C.

In general the results were lower than those obtained in the vacuum oven at 70°C., or the steam oven at 99°C.

(2) Golden Syrup :- In twenty tests made at 60°C., the previously discovered contact time of 10 minutes was given.

The results again tended to be lower than those found by vacuum oven or steam oven methods.

Conclusion :- The Fischer method is well adapted for use where a large number of moisture estimations is to be performed daily. Otherwise the frequent standardisation and care required to exclude water render the method tedious. It is not necessarily more accurate than other methods, as side-reactions may occur.

BIBLIOGRAPHIES.

Extensive selected bibliographies for the determination of water have been compiled and are given in the form of an appendix.

SECTION 1.

THE COMPOSITION OF FRESH AND DRIED SUGAR BEETS.

A knowledge of the nature of the non-sugar constituents of the sugar beet is important with regard to the subsequent purification of beet juices which will contain at least part of these non-sugars.

Analyses have been made using well-known methods and modifications of these, both of fresh beet slices and of the dried slices (cossettes) derived from them.

The methods of analysis used for the dried beet have been modified to suit this concentrated product : a spectroscopic examination has been made of its mineral matter.

1. Introduction :
2. Composition of the Sugar Beet :
3. Constituents of plants :
4. Objects of the present work :
5. Methods of analysis :
6. Analyses of fresh and dried beet cossettes :
7. Spectrodcopic examination of the ash :
8. Nitrogen in the Sugar Beet :
9. References and Bibliography.

INTRODUCTION :-

Scientific methods of plant improvement are well illustrated by the modern sugar beet. By methods of modifying the conditions of growth of the plant and breeding new varieties the sugar content of the beet has been raised from 5 to 7 per cent to 15 - 20 per cent. The yield of sugar per acre and the disease-resistance of the plant have also been substantially improved.

COMPOSITION OF THE SUGAR BEET :-

The soluble solids of the beet are dissolved in about 80 per cent of water, giving approximately 95.5 per cent of juice. The remaining 4.5 - 5 per cent consists of cellulose with other carbohydrates and is known as the 'marc!

There has been a progressive change in the non-sugar content of the plant as the sugar percentage has increased : this is shown in the table below :-

TABLE I. Per cent

Source	Water	Sucrose (apparent)	Ash	Organic Non-sugars	Fibre
Voelcker[1]	83.0	9.3	1.1	2.3	4.3
Heriot[2]	78.0	15.0	1.0	1.5	4.5
Present work	76.5	16.7	0.7	1.3	4.8
		Per cent on dry basis			
Voelcker	~~54.7~~	54.7	6.5	13.5	25.3
Heriot	~~62~~	68.2	4.6	6.8	20.4
Present work	---	71.1	3.0	5.5	20.4

CONSTITUENTS OF PLANTS :- WATER :-

Water is present in all plants,and the exact amount present is not easily found, since it may be held very tenaciously, and the organic matter of the plant may decompose at a temperature well below that necessary to drive off all the water.

Protein :- Protein is usually calculated as total nitrogen multiplied by the factor 6.25. Since the nitrogen may be present partly in non-protein form, and since the nitrogen content of vegetable proteins ranges from 15 to over 19 per cent, this calculation can be only ~~be~~ approximate.

Fats and Oils :- These consist mainly of the glycerides of fatty acids, with small amounts of free fatty acids, and are often referred to as "ether extract". Ether will also dissolve chlorophyll, lecithin, cholesterol, and some alkaloidal substances, so that this extract may vary widely in nature and may be most unlike fat or oil.

Crude Fibre :- The fibre content of a plant is taken to mean that part of the structure which defies solution on boiling with dilute acid and/or dilute alkali. This estimation can have great error, particularly when the fibre content is high due to such substances as the lignin of sclerenchymatous fibres, the subenin of cork, or the cutin of cuticles.

Ash :- The ash is usually taken as the residue obtained when the material is ignited to whiteness at a temperature just below red-heat. Relatively volatile substances such as sulphur and chlorine may escape in part during the ignition, and there is scant knowledge of how mineral bodies are bound up in plant tissues, so that the ash figure thus obtained is only approximate, and efforts to re-combine the elements in ash analyses are therefore difficult.

Nitrogen-free Extract :- Winton[3] refers to this as a numerical expression of our ignorance and errors. In cereals it consists principally of starches, sugars, and dextrins : with non-starchy vegetables a large proportion is composed of substances not yet thoroughly investigated. Organic acids, glucosides, and tannins will also appear in this extract.

Pentosans :- The pentose sugars in plants occur mainly as polysaccharides. Pentosans for example, may be present as gums such as araban or xylan. These sugars are also present in the nucleic acids and seem to be of vital physiological importance. They are intensely hydrophilic, having a major part in the water relations of many plants. In the sugar cane, pentosans are the principal constituents of cane-gum.

Pectins :- These are colloidal carbohydrates of high molecular weight and rather complex composition. At present three of these substances are generally recognised - protopectin, pectin, and pectic acid. Pectin itself is a mixture of polysaccharides including an araban, a galactan, and a polygalacturonide known as pectic acid. The proportions of these constituents vary widely with the source of the pectin. Protopectin is regarded as the mother - substance of the group : it occurs in the cell walls of most plant tissues. It was formerly named pectose.

The protopectin of sugar beet juice has been shown by Ehrlich and Sommerfeld[4] to consist of an araban together with the Ca-Mg salt of pectin combined with the cell wall. This protopectin can be freed from the cell wall by hydrolysis and converted to hydro-pecti which pass into colloidal solution in the extracted beet juice.

It is evident that the average composition of vegetables such as sugar beets is merely suggestive, and should not be considered to be anything more than an approximation for individual samples. All comparisons should be made on the basis of dry matter, or on the basis of a calculated uniform water content.

Objects of the present work :-

In the purification of beet sugar juices the behaviour of the constituents other than sugar is of the greatest importance, especially if these are of colloidal character. It is thus necessary to have a comprehensive knowledge of the composition of the original beets. This knowledge is also essential for adequate understanding of the process of drying sugar beet slices, which aims to extend the manufacturing season from the three months of the normal harvesting period to the full year. Analyses were therefore made of fresh beet samples and of dried cossettes which had been dried (a) with direct furnace gases, (b) with hot air without adulteration, and (c) with air containing a known amount of sulphur dioxide. The results are shown in Tables II. to V.

METHODS OF ANALYSIS

Polarization - Fresh beet slices :-

The hot digestion method was used at 88°C. taking a normal weight of 26 g. in a 200 c.c. flask, and digesting for 30 minutes with 160-170 c.c. water, and for a further 30 minutes after completing to the mark without cooling. Basic lead acetate solution (5-7 c.c) is added before digestion. The marc volume allowance is 1.2 c.c. per normal weight of fresh beets.

Polarization - Dried cossettes :-

As for fresh beet, using 13 g. in 200 c.c.

Determination of Reducing Sugars :-

For fresh beets 60 g. are taken and for dried cossettes 15 g. in 200 c.c. flasks, and digestion is carried out as for the polarization and preferably at the same time, but using neutral lead acetate solution as required. The marc volume allowances are 2.8 c.c. for fresh beets, and 0.7 c.c. for dried cossettes.

The filtrate is de-leaded with dry potassium oxalate and filtered. For the estimation, 50 c.c. of this de-leaded filtrate is placed in a 150 c.c. conical flask, 20 c.c. of mixed Bertrand-Saillard[5] copper reagent added, and the flask heated for exactly 22 minutes in a water bath maintained at 62-63°C. The cuprous oxide is filtered off, and after washing, dissolved in ferric sulphate solution, and is finally titrated against a standard potassium permanganate solution 1 c.c. of which is equivalent to 2.5 mg. copper. The percentage of reducing sugars is found from specially prepared tables. Note :- The marc volume allowances are based on experimental average figures for both fresh beets and dried cossettes.

Total Nitrogen :- Kjeldahl method : digestion with conc. H_2SO_4 and iodine catalyst in presence of $CuSO_4$, followed by distillation in presence of MgO into N/10 H_2SO_4, and titration with N/10 NaOH using methyl red as indicator.

Ammoniacal Nitrogen :- Distillation in presence of excess MgO into N/10 H_2SO_4 and titration with N/10 NaOH.

Soluble Nitrogen :-Cold :- The cossettes were extracted with cold water and an aliquot portion digested by Kjeldahl method as above.

Soluble Nitrogen :- Hot :- The cossettes were extracted with hot water followed by Kjeldahl digestion.

Protopectin :- Finely ground cossettes (1 g.) were heated on a boiling water bath with 100 c.c. N/20 HCl under reflux for two hours. The mixture was filtered through cloth, and 40 c.c. N/10 NaOH added to 50 c.c. of filtrate. After 2 hours (or preferably overnight), 25 c.c. of N-acetic acid were added, followed by 25 c.c. M-calcium chloride, and the solution boiled. The calcium pectate precipitated was filtered through a sintered glass crucible and dried at 100°C.

Soluble pectin :- Finely ground cossettes (2-3 g.) were diffused with 100 c.c. cold water and filtered. An aliquot portion of the filtrate was treated as for protopectin using only 35 c.c. N/10 NaOH. (For these pectin estimations see Farnell[6]).

Pentosan :- Tollens-Krober method[7], the distillation being made from 0.5 - 1.0 g. material. The method converts the pentose sugars into fufural by distillation with HCl. The furfural is then converted to phloroglucide by precipitation with phloroglucinol and weighed.

pH values:- By glass electrode :(Cambridge Instrument Co.)

Ash :- By direct incineration in platinum capsules.

Moisture :- Vacuum drying at 70°C. for 5 hours was the method most commonly used.

ANALYSIS OF THE ASH

Insoluble matter :- Acid extraction and baking at low temperature followed by weighing.

Carbonaceous matter :- Free carbon was estimated by igniting the acid-extracted insoluble matter and was found to be negligible- in most cases below 0.02 per cent.

Sulphate :- Gravimetric estimation as $BaSO_4$.

Chloride :- Volhard titration[8].

Aluminium and Iron:- Gravimetric estimation by ammonia precipitation and weighing.

Phosphate :- Colorimetrically by coeruleo blue - molybdate method[9].

Calcium :- Precipitation as calcium oxalate and ignition to calcium carbonate.

Magnesium :- Precipitation as magnesium ammonium phosphate and ignition to magnesium pyrophosphate.

Sulphite :- Monier-Williams distillation method[10].

Alkalis :- By difference.

Preparation of Ash for Spectroscopic Analysis :-

(1) Fifty grams of dried cossettes were ashed below red-heat in a large silica basin, 3.59 per cent ash resulting.

(2) Fifty grams of dried cossettes were slowly ashed as in (1), with the addition of "Analar" sulphuric acid. In this way the loss of volatile salts was minimised : the sulphated ash was 3.77 per cent.

TABLE II.

COMPOSITION OF THE ASH OF THE SUGAR BEET

PER CENT ON ASH

CONSTITUENT	NEES 1933[1] DISTRICT 1.	2.	3.	4.	DAHLBERG 1920[2]	ANDRLIK, 1908[3] 1.	2.	1.	2.
PURITY	90.7	89.4	87.8	85.9	---	---	---	---	---
SUGAR	18.28	18.22	17.23	14.97	---	15.7	12.8	18.28	17.14
ASH	2.75	3.27	3.31	4.45	---	---	---	---	---
SILICA	0.92	0.46	0.54	0.33	2.64	---	---	---	---
R_2O_3	0.57	0.32	0.50	0.38	---	2.6	7.6	4.2	4.5
Fe_2O_3	0.20	0.14	0.14	0.10	1.84	---	---	---	---
MnO	0.12	0.16	0.12	0.13	---	---	---	---	---
CaO	6.02	4.62	3.98	3.68	0.59	15.4	12.3	15.2	14.8
MgO	10.65	10.87	9.21	8.52	2.05	12.6	8.8	10.8	10.7
K_2O	33.18	34.21	36.92	37.77	30.35	20.4	17.3	37.9	36.1
Na_2O	11.22	15.00	14.90	15.02	11.28	27.7	33.4	7.2	11.2
Cl'	5.74	12.65	7.88	17.16	6.87	2.6	7.6	1.0	1.1
SO_3''	2.79	2.41	3.20	2.32	3.61	6.5	6.6	6.7	6.8
P_2O_5	8.08	7.43	7.05	6.58	7.42	17.5	16.7	16.4	14.8
N_2O_4	2.62	2.23	3.71	3.96	---	---	---	---	---
CO_3''	---	---	---	---	30.98	---	---	---	---
UNDETERMINED	---	---	---	---	2.17	---	---	---	---

[1] Ind. Eng. Chem., 25, 426, 1933.

[2] Chem. Metb.Eng., 23, 421. 1920

[3] O. Wehryzek,"Chemie der Zuckerindustrie", p. 170, 1914.

TABLE III.

ANALYSIS OF FRESH BEET SLICES AND DRIED BEET COSSETTES

PER CENT ON DRY SUBSTANCE.

	FRESH BEET	DRIED COSSETTES		
		Best Quality	Average Quality	
Method of Drying	1. ---	2. Direct gases	3. Direct gases	4. Direct gases
CONSTITUENTS				
Dry Substance	23.56	92.74	92.16	91.73
Sucrose	70.91	68.58	68.14	69.34
Reducing Sugars	1.27	1.43	0.87	0.82
Ash	2.91	2.56	3.18	4.44
Albuminoid Nitrogen	2.19	2.38	7.31	4.19
Ammoniacal Nitrogen	0.29	0.18	0.20	0.19
Pentosans	9.13	12.51	6.51	8.18
Protopectin	4.67	6.51	5.59	5.41
Soluble pectin	Nil	0.20	0.33	0.68
Other Organic Matter (By difference)	8.63	5.65	7.87	6.75
ASH CONSTITUENTS :-				
Insoluble Matter	0.33	0.24	0.32	0.50
Sulphate - as SO_3''	0.20	0.54	0.49	0.84
Chloride - Cl'	0.16	0.02	0.03	0.04
Phosphate - as P_2O_5	0.34	0.15	0.11	0.30
Al_2O_3 Fe_2O_3	0.21	0.26	0.35	0.71
CaO	0.17	0.39	0.55	0.28
MgO	0.08	0.21	0.24	0.21
Alkalis (By diffce.)	1.42	0.75	1.12	1.57

5.	6.	7.	8.	9.
Pure Air	Pure Air	Pure Air	Air with 0.016% SO_2	Air with 0.028% SO_2
93.57	92.47	90.56	93.12	93.18
70.33	71.15	67.47	69.49	68.69
1.07	1.17	0.59	0.96	0.77
4.65	3.72	3.76	5.22	3.93
3.06	2.90	3.94	3.31	5.06
0.25	0.22	0.19	0.30	0.17
9.62	7.79	9.83	8.81	8.48
5.77	5.41	5.30	5.26	5.58
1.39	1.51	0.22	1.07	0.54
3.86	6.13	8.72	5.58	6.86
0.56	0.57	0.77	0.53	0.46
0.60	0.67	0.22	0.36	1.15
0.03	0.04	0.05	0.03	0.04
0.39	0.19	0.35	0.37	0.11
1.03	0.76	0.75	1.39	0.73
0.16	0.13	0.09	0.28	0.15
0.17	0.15	0.01	0.13	0.16
1.72	1.21	1.52	2.13	1.13

TABLE IV.

COMPOSITION OF THE ASH OF FRESH BEET SLICES AND DRIED COSSETTES

PER CENT ON ASH.

	Fresh Beets	Dried Cossettes						
	1.	2.	3.	4.	5.	6.	7.	8.	9.
Mode of Drying	-	Direct gases			Pure Air			Air with SO_2 0.016%	0.028%
Per cent ash (on dry)	2.91	2.56	3.18	4.44	4.65	3.72	3.76	5.22	3.93
Insoluble Matter	11.34	9.38	10.07	11.27	12.04	15.32	20.42	10.15	11.70
Sulphate as SO_3''	6.87	21.10	15.48	18.82	12.80	17.96	5.85	6.90	29.26
Chloride-Cl'	5.49	0.78	0.94	0.90	0.65	1.08	1.33	0.57	1.02
Phosphate-as P_2O_5	11.69	5.86	3.46	6.76	8.41	5.11	9.31	7.09	2.80
Al_2O_3 Fe_2O_3	7.22	10.16	10.13	15.90	22.15	20.38	19.95	26.63	18.58
CaO	5.84	15.24	17.30	6.31	3.44	3.49	2.39	5.36	3.82
MgO	2.75	8.20	7.55	4.73	3.57	4.03	0.27	2.49	4.07
Alkalis, etc., By diffce.	48.80	29.28	35.07	35.31	36.94	32.63	40.48	40.83	28.76

TABLE V.

Spectroscopic examination of the Ash of Dried Cossettes

Samples of the ash obtained with and without sulphation were removed from the silica basins, taking care not to include ash adhering to the sides of the dish.

Spectrograms were taken using a Hilger Medium quartz spectrograph, the samples being placed in a bored graphite cathode. Pure iron and graphite spectra were included for comparison.

After the standard checking of the iron spectrum, the unknown lines were obtained by comparison with standard plates of the elements, and the "raies ultimes" of the elements were checked from wave-length tables for spectrum analysis[11].

The results are summarised below :-

Elements present	Elements probably present	Inconclusive Evidence	Absent
Al	As	Co	Ag
B	Ba	La	Au
Ca	Cu	Mo	Be
Fe	Rb	Nb	Bi
K	Sr	Ni	Cb
Li	V	Rh	Cd
Mg	W	Sn	Ce
Mn		Yt	Cr
Na		Zn	Cs
P		Zr	Ge
Si			In
Ti			Ir
			Os
			Pd
			Pt
			Sb
			Tl

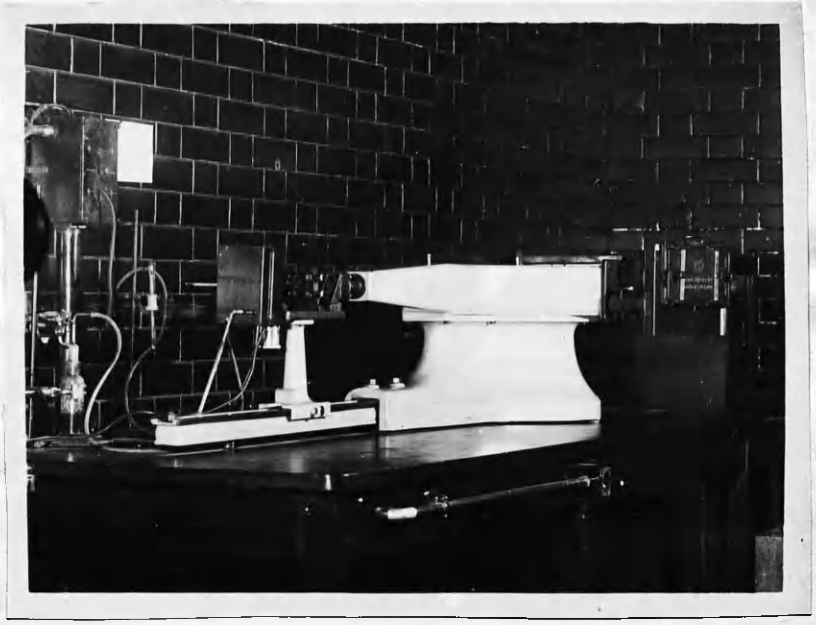

Figure 1 : Hilger E.498 Medium Quartz Spectrograph.

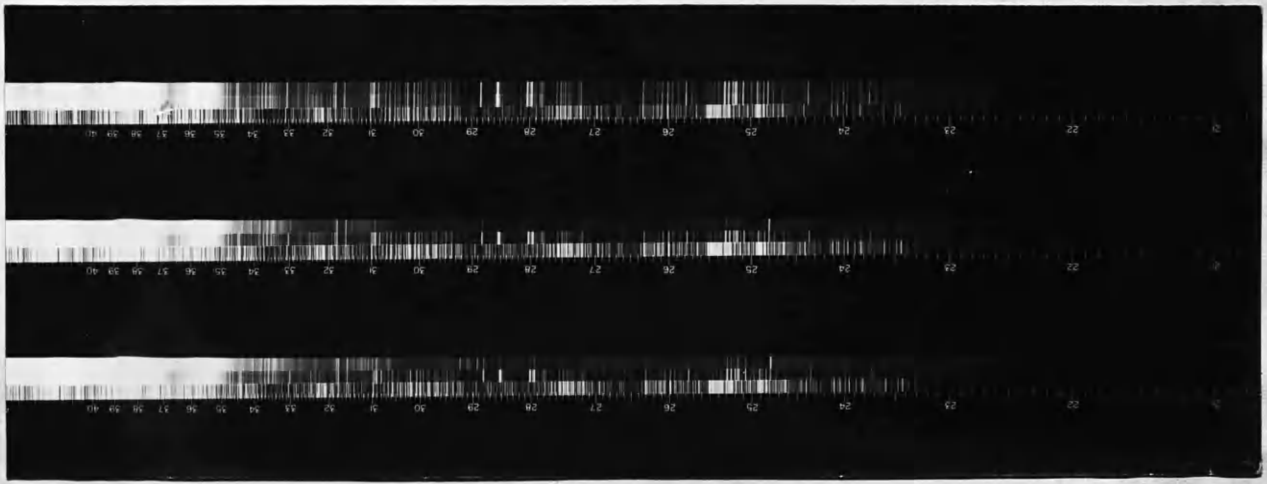

Figure 2 : Positive Spectrogram of Ash of Dried Beet.

NITROGEN IN THE SUGAR BEET.

Certain non-sugars occurring in the sugar beet are known to hinder the crystallisation of sugar and thus increase the amount of molasses produced. Among these are chlorides, organic potassium salts, and various compounds of nitrogen. Protein nitrogen is not considered to be detrimental since it is almost completely precipitated by the reagents used in the purification process, but all forms of nitrogen not thus eliminated have been termed 'noxious' or 'harmful nitrogen.

Such compounds of nitrogen include the decomposition products of proteins, betaine, glutamine, asparagine and aspartic acid, xanthine, adenine, hypoxanthine, guanine, allantoin, arginine and vicine, with many other related compounds. This objectionable nitrogen varies in amount in the sugar beet depending upon many factors such as the soil, its cultivation, the method of manuring, the length of the season, and the time of harvesting. These factors can be controlled to some extent, but others, such as the choice of a situation, the climate, or the local weather conditions, cannot be controlled. Dry warm weather and small rainfall are known to cause great increase in the content of harmful nitrogen.

About 90 per cent of the harmful nitrogen in the beet passes over almost unchanged into the molasses. In addition, the protein nitrogen narmally precipitated during purification may be re-dissolved unless the conditions for working are rigidly followed.

The determination of harmful nitrogen in the beet is thus of importance from the technological standpoint.

DETERMINATION OF 'NOXIOUS' NITROGEN.

It has been commonly accepted that harmful nitrogen is to be considered as the amount found by subtracting the protein and ammonia plus amide nitrogen from the total nitrogen found in the beet by the Kjeldahl method. In Stutzer's[12] original method, the substances not precipitated by cupric hydroxide - mainly ammonia, amides, and nitrates - were called objectionable nitrogen.

Andrlik[13] precipitated the protein with copper sulphate and sodium hydroxide solutions, leaving the ammonia and amide nitrogen in solution together with the harmful nitrogen. Since the ammonia and amide nitrogen are not considered harmful, the nitrogen present in amide form is converted to ammonia in an aliquot portion and distilled from ignited magnesia along with the original ammonia. The harmful nitrogen is then the residue left by subtracting the protein, amide, and ammonia amounts from the total nitrogen. This method is lengthy, and has been replaced by a procedure due to Friedl[14], based on the colour intensity produced by the copper sukphate and sodium hydroxide. This method was used in the present work, in conjunction with a modification of Andrlik's method.

It has been pointed out by Hart and Bentley[15] that all the protein is not precipitated by cupric hydroxide, so that the results obtained for albuminoids will tend to be low.

Friedl (ibid) holds that amide nitrogen is harmful on the basis that the amides break up and form salts, and there is thus as yet no definite information regarding the exact rôle of nitrogenous substances as molasses-formers in sugar manufacture.

DISTRIBUTION OF NITROGEN IN THE SUGAR BEET.

Results for nitrogen in continental sugar beets are shown in the following table :-

TABLE VI.

	Kleinwanzleben[16] (Germany)				Dr. E. Rosenbluh[17] (Czechoslovakia)	
	1921		1922		1933-34	
Form of Nitrogen	**Min.**	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**
Total Nitrogen	0.145	0.180	0.133	0.179	0.150	0.287
Nitrogen not pptd. by $Cu(OH)_2$	0.047	0.078	0.035	0.067	0.067	0.210
Albuminoid N_2	0.092	0.113	0.096	0.118	0.014	0.132
(NH_3 & Amide Nitrogen)	0.006	0.114	0.003	0.010	0.005	0.038
Noxious Nitrogen	0.041	0.064	0.031	0.060	0.040	0.130

The results obtained by the author are here summarized :-

TABLE VII.

Nitrogen Content of Fresh Beets grown in Southern England, and of Dried Cossettes derived from them :-

FRESH BEETS :- Average Water Content 76.45 per cent

No. 666	Total Nitrogen	Nitrogen not pptd. by $Cu(OH)_2$	Protein Nitrogen	Ammonia and Amide Nitrogen	Noxious Nitrogen	Noxious Nitrogen % of Total Nitrogen
1.	0.150	0.093	0.057	0.007	0.086^x	57.3
2.	0.223	0.129	0.094	0.015	0.114^x	51.2
3.	0.195	0.072	0.123	0.019	0.053	27.2
4.	0.163	0.081	0.082	0.027	0.054	33.1
5.	0.190	0.069	0.121	0.020	0.049	25.8

x Harvested in aearly September : others in mid-October.

TABLE VII. (continued).

DRIED COSSETTES:- Average water content :- 7.5 per cent

No.	Total Nitrogen	Nitrogen not pptd. by $Cu(OH)_2$	Protein Nitrogen	Ammonia and Amide Nitrogen	Noxious Nitrogen	Noxious Nitrogen % of Total N_2
1.	0.74	0.41	0.33	0.17	0.24	32.5
2.	0.91	0.52	0.39	0.21	0.31	34.1
3.	0.63	0.36	0.27	0.16	0.20	31.8
4.	1.26	0.73	0.43	0.18	0.55	43.6
5.	0.96	0.40	0.56	0.16	0.24	25.0

Note :- These samples do not correspond exactly to the Fresh Beet samples above although they were from the same harvesting period.

The variability of the noxious nitrogen content shown by these samples emphasises the need to know more about the non-sugars in the sugar beet, and their behaviour during the manufacturing process.

It is evident that of two beets giving equal yield per acre and of equal sugar content, the one with a higher content of noxious nitrogen will be less valuable since this nitrogen will lower the potential yield of sugar. Similarly beets with more nitrogen and other non-sugars present generally have less natural alkalinity and lower purity.

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SECTION 2.

THE DESICCATION OF SUGAR BEETS.

1. The Desiccation Process in Sugar Manufacture :
2. Bibliography of Drying Processes :
3. The Slicing of Sugar Beets :
4. The behaviour of Sugar Beets during Drying :
5. Description of the Drier for Sugar Beet Cossettes :
6. Typical Results of Beet Drying :
7. The Chemical Conditioning of Dried Beet Cossettes.

THE DESICCATION PROCESS IN SUGAR MANUFACTURE.

The German chemist Marggraf can be credited with the first mention of the extraction of sucrose from the sugar beet. In 1847 he described the drying of two pounds of beet cut into small pieces yielding half a pound of dry matter from which he obtained by extraction with alcohol a half-ounce of good sugar.

F.C.Achard, a pupil of Marggraf's, erected the first beet sugar factory at Cunern in Silesia in 1799, and in the same year a well-known chemist, Gotting, of Jena, conceived the idea of drying the beets and extracting the sugar with cold water.

Schützenbach in 1836 improved a cold maceration process due to Pelletan, and in 1837 proposed the preliminary drying of the beet and its extraction with water at 90°C. Dumas exhibited in Paris in 1838 dried beet and refined sugar obtained from it by the methods of Schutzenbach. M. Lirac of Carpentras had employed sun-drying for beets in France in the same year.

A paper by Gotting in 1811 described a scheme for drying and storing beets for subsequent extraction of sugar, and patents with similar objects were taken out by Crossly (7469,1837), and Newton in 1848 (12053). Daubrée imported dried sugar cane in Paris in 1850 and reported little effect on the sugar content during transit.

Frémy gave a full account of Schützenbach's work in his book published in Paris in 1875. Schützenbach put his process into practice at a large factory in Galicia, comprising a Central factory with fourteen small drying stations placed at moderate distances from it. In these drying stations the beet from the neighbourhood was dried in large kilns. The resultant dried cossettes were carried to the central factory and extracted in closed vessels. The juices reached 42°Brix. They were treated with lime and then with boneblack, filtered, and passed to the evaporators. In the campaign of 1849-50, 1,116,000 hundredweights of beets were treated in this way. The lime treatment took place in the macerating vessels, using 6 per cent of lime on dried beets.

The next large scaletests on beet drying were made by J.C.F. Lafeuille (1901-5) who experimented in Egypt, Spain, Italy, and France, and tried several methods of drying such as sun drying, drying with heated air, and drying with carbon dioxide. His tests were not satisfactory, mainly due to invert sugar formation and the very dark juices produced. Lafeuille has since enggged in beet drying for other purposes, but in 1924 wrote to the Journal des Fabricants de Sucre saying he had confirmed De Vecchis' results. His patents included 301,206 and 147,576 (U.S.), and Fr.pat.326,035.

Daubreband (French patent 414,329, 25/3/1910) described the drying of whole beets : this was not primarily for sugar making.

In 1908 G.W.McMullen of Chicago took out British patent No. 18237 to shred and dry sugar cane, extract the sugar and use the bagasse for paper manufacture. He also worked with beet but considered cane drying to be more economical on account of the paper manufacture.

G. H.Benjamin (1914) proposed drying beet at fairly low temperature until 90 per cent of the water had been removed with the object of coagulating albuminoid substances without causing cell rupture. The sugar was then extracted in diffusion vessels.

Benjamin made the claim that his process actually increased the amount of sucrose present, by stimulating enzyme action.

De Vecchis conducted large scale tests of beet drying and extraction for the Romano sugar Company at Viterbo in Italy, commencing in 1923. He claimed diffusion juices of 45-50°Brix and of 86-88.3 Purity Quotient. The juices were treated with powdered lime and superphosphate and gave massesuites of 89.9-90.2 Purity.

Weichmann stated in 1915 that beets could be dried without the formation of reducing sugars, and mentioned the advantages due to dehydration of a longer running season and the high purity juices of higher density.

Haseltine (1919) estimated the cost of drying a ton of beets by his process at 75 cents.

The De Vecchis process was investigated by a Commission from the Institute of Agricultural Engineering under British Government auspices in 1925-6, and this enquiry resulted in the setting up of an experimental drying station and sugar factory at Eynsham, near Oxford. The process was ultimately transferred to the commercial scale, and factories using this process were erected in France and in Russia. Those in Russia appear to be still in active operation as the geographical conditions in the northern portions of European Russia are peculiarly favourable for the development of a Central factory surrounded by feeder drying stations.

The desiccation process was investigated by practically every country in Europe during the experimental work at Oxford, and the literature of the period deals fairly fully with the process.

THE DESICCATION PROCESS IN SUGAR MANUFACTURE.

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THE SLICING OF SUGAR BEETS.

DIMENSIONS OF BEET COSSETTES :-

Type of Knife :- Knives of various types and sizes were tested and the optimum dimensions were found with a knife 9 mms. deep containing 20 divisions in a length of 14 cms.
This type of knife cuts a cossette which is considerably larger than is usual for the ordinary wet beet diffusion process, but this larger slice has been found necessary owing to the difficulty of drying a mass of small slices which tend to cling together. This problem is particularly apparent when the beets have been damaged by frost, or are insufficiently washed. Smaller cossettes also lead to more fine particles and dust.

To facilitate drying and diffusion each cossette should present as large a surface area as possible in proportion to its volume ; the ideal cossette therefore would seem to be one resembling a thick "V" in cross-section. The 'roof-ridge' or 'Splitter' knife appears to be the only type which will produce a large proportion of cossettes of this shape, and was adopted as the standard type. Experiments were made using specially constructed Königsfeld knives producing square-section slices. It was found that these knives had to be changed more frequently and that square-section cossettes could not be dried as efficiently as the V-shaped cossettes. Unfortunately the 'roof-ridge' knives cannot be sharpened in one operation, but this drawback is more than balanced by the better drying and the less frequent changing of the knives. These V-section cossettes are sometimes called butterfly section cossettes. They favour free circulation of the cell flux, since the slices lie loosely one over the other, so that the circulating liquid is able to flow around them and can thus more easily penetrate the walls of the cells.

The 'Splitter' knives have a dividing rib under each corrugation of the cutting edge, whereas Königsfelder and Goller knives merely have a corrugated edge. The knives are made with varying pitches, the pitch being the distance between the centres of the corrugations. The Königsfelder and Goller knives in general use are 6 or 7.2 mms. pitch : pitches of 5 or 8 mms. are less frequently used. 'Splitter' knives are used with widely varying pitches-e.g. 8,7,6,5,5,5,4.5, 3.5, and 3 mms.,the wider pitches being used for poor quality or 'woody' beets. Pitches of 5 and 5.5 mms. are most generally used with an edge depth of 9 mms. Below 4 mms. pitch, the edge depth is usually 7 mms. Typical beet knives are shown in Figures 1 and 2.

BEET KNIVES.

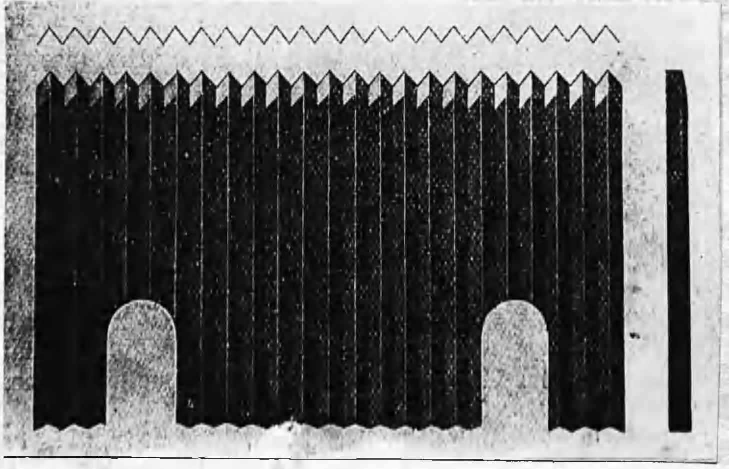


Fig.3 GOLLER KNIFE.

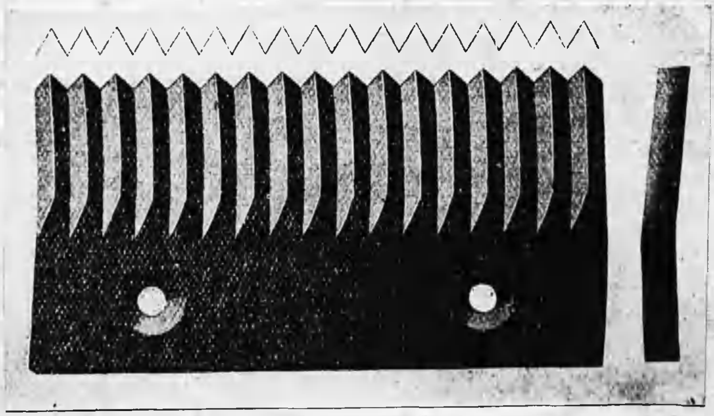


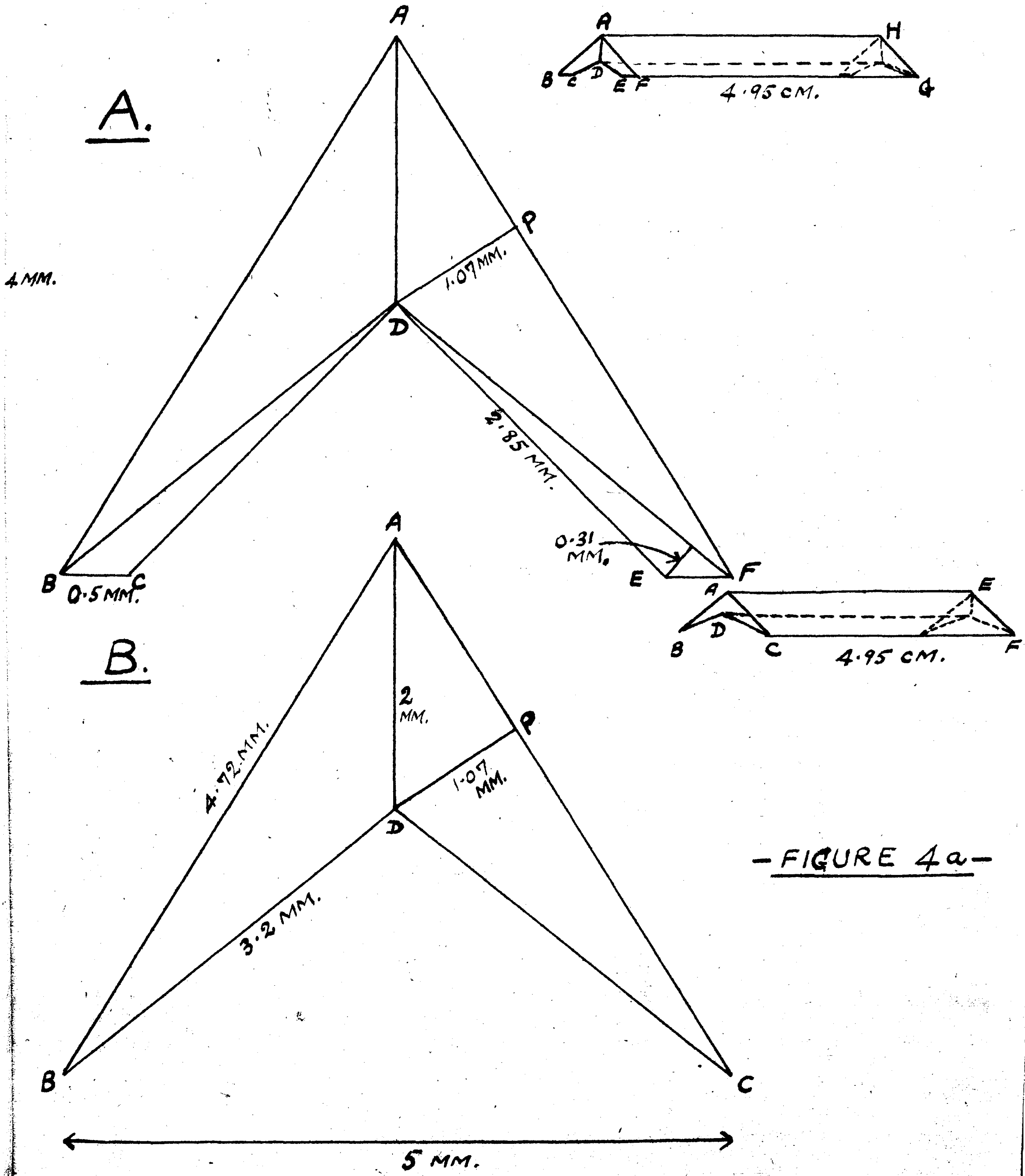
Fig.4 KÖNIGSFELDER KNIFE.

DIMENSIONS OF COSSETTES.

Rangeof Length mm.	Fresh Beet Av.	Dried Cossettes 1.	2.	3.	4.
0-10	15	3	24	2	4
11-20	6	36	56	25	15
21-30	9	62	44	42	31
31-40	18	74	98	81	69
41-50	48	59	65	88	90
51-60	53	51	136	62	60
61-70	32	22	22	30	34
71-80	56	18	15	21	17
81-90	25	11	2	20	15
91-100	31	14	3	18	14
101-110	4	3	3	12	9
111-120	3	1	0	9	6
121-130	5	1	1	6	3
131-140	6	-	-	-	-
141-150	6	-	-	-	-
151-160	3	-	-	-	-
Max. Length,mm.	160	126	112	132	129
Min. " mm.	5	8	12	7	9
Average " mm.	74	45	57	49	47
Width mm.	3-5	3-6.5	3-6.5	3-6.5	3-6.5
Av. Width mm.	4	5	5	5	5
Residue (dust) gm.	Nil	0.39	0.82	0.46	0.36
Thickness mm.	2-3	3-4	3-4	3-4	3-4
Gms. taken	165	100	100	100	100
No. of pieces	320	355	440	416	367

PROCEDURE :- A random sample was taken and weighed in the case of the fresh beets. The dried cossettes samples represented the average of cossettes in storage. Each piece was measured for length,width, and thickness.

— PROFILE OF IDEAL COSSETTE —



— FIGURE 4a —

<u>Dimensions of Beet Knives used in normal practice and in the present Experimental work :-</u>

TYPE	DEPTH MM.	APPROX. DIVISIONS PER 14 CMS. LENGTH	HEIGHT OF KNIFE ABOVE PLATE	DISTANCE FROM EDGE OF KNIFE TO PLATE
Standard wet diffusion knives	9	26	5	2-4
As used for Dried Cossettes	9	20	5½	1½
Special Königsfelder knives	7	16	5-5¾	0-2
Normal Königsfelder knives	7.2	20	6	3

THE IDEAL COSSETTE.

As seen in Figure 1a the cossettes produced by the "Splitter" type of knife are tent-shaped in section : they tend to be of the two shapes shown, in about equal proportions.

From the figures, the total surface area of cossette B is 7.27 sq. cm. while that of cossette A is 8.26 sq. cm. The volumes are 0.673 cu. cm. for A, and 0.625 cu. cm. for B.

Claassen ("Beet-Sugar Manufacture", Wiley, 1911, p. 7.) states that the average diameter of the beet cells in the plant is 0.04 mm., and the volume 0.000033 cu. mm. with a proportion of 2 to 5 per cent of broken or ruptured cells.

It is clear that the ideal cossette would offer considerable surface area for contact with the circulating liquid, and that it would have a long smooth surface with uniform section throughout its length. In practice about one-fourth of the cossettes will have about this ideal shape and size, the remainder being irregular due mainly to non-uniformity of the roots and defects in the knives.

Behaviour of Sugar Beets during Drying :-

The success of the drying process as applied to layers of vegetable matter in relatively small layers is primarily affected by the temperature and time of treatment. Ignoring exothermic reactions occurring within the beet slices, the drying efficiency will depend upon certain specific factors which arise from the composition and properties of the beet itself.

These factors are :-

1. Consolidation and porosity or penetrability :
2. Volume and pressure of the drying air :
3. Time of Drying :
4. Thickness of the layer of material :
5. Temperature of the air at varying ranges of moisture.

Tests showed that to avoid caramelisation and inversion the moist material must not be heated above 220°F.

The rate of formation of invert sugar is a product of temperature and moisture, and the amount of invert sugar formed is a product of temperature, moisture, and time.

It was found that so long as the beet slices contained more than 20 per cent of water the temperature of the drying air (100 to 260°F.) had little effect on the sugar in the beet, but above 235°F. there was a loss of sugar with slices containing less than 20 per cent of water.

The normal acidity of the beet which is largely due to partially dissociated organic acids, increases during the drying period due to concentration of the juice present, and high temperature is then much more harmful. It is evident that the reactions occurring within the slices during the temperature rise from 50°F. to 150°F. are of an involved nature and will include oxidation and enzyme action. The moist faintly acid material offers, at the lower ranges of temperature at least, a favourable medium for such enzyme action and bacterial metabolism with their accompanying sugar loss.

During drying, the resistance offered by the material to the drying air is greatly affected by the shrinkage of about 50 per cent in the bulk of the slices. The penetrability of the material is further increased by slicing the beets into cossettes of "V" cross-section.

Summary of desirable conditions for Drying.

1. The layer of slices to be dried must have a pre-determined thickness.
2. The beets must be dried in a limited time.
3. The layer of beet must not be broken or interrupted during the period.
4. The velocity and volume of the drying air must be exactly determined so that the beet is not disturbed or blown away during drying.
5. The layer must pass through definite heat zones within definite ranges of moisture content and humidity, since the exothermic effect has a critical point above which destruction of sugar occurs. This point must be properly determined and controlled.

The Drying of Sugar Beets.

The beet cossettes are treated in a mass 7 to 8 inches deep, which remains undisturbed during the whole course of drying, but passes in continuous progression through a multi-stage drier; the temperature, volume, and velocity of the drying air are controlled.

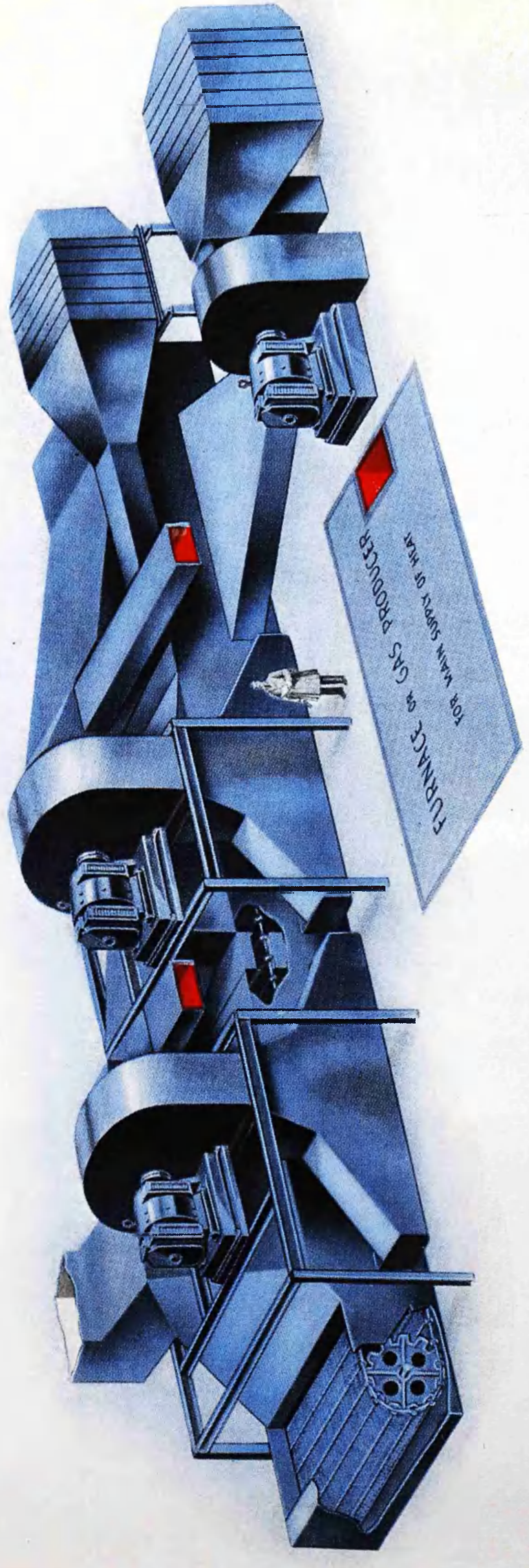
Description of the Drier for Beet Cossettes.

The beet cossettes are treated in an undisturbed mass which is in continuous motion on a conveyor belt. The furnace gases and hot air which form the drying medium are passed through the material so that it is dried progressively in three stages, separated from one another by air locks. In each of these stages the material is subjected to a temperature constant for that stage.(Figure 2a).

The first air enters the drier at a temperature of 190°F. at the end where the beet is undergoing its third stage of drying. It then passes upwards through the cossettes and is afterwards reheated by the addition of furnace gases to 230°F., and by means of a second fan is forced through the material in stage two,and is then in turn reheated to 250°F. by the addition of more furnace gases.This reheated drying air then passes through the fresh beet cossettes in the first stage of the drier, and is finally exhausted to the atmosphere.

In the first stage (fresh beet cossettes) about 65 per cent of the water is removed in 15 to 20 minutes. Owing to the cooling effect due to evaporation, an air temperature of 260°F. is not harmful in this stage. (Figure 2b).

In the second stage a further 25 per cent of the water is removed : the remainder is lost in the third stage. The time of passage through the drier varies slightly according to the initial moisture content of the beet.For beets containing 74-78 per cent water the drying time varies from t50 to 60 minutes,the final product containing 5-10 per cent water.



Type "C" Dryer.

Figure 4b

The exact temperatures used in each stage are obtained by easily regulated dampers controlling the flow of furnace gases.
The air passing through the fresh cossettes has been used three times, having passed upwards through the material in each of the three stages. It is discharged completely saturated with water at a temperature of 110-120^{O}F. The volume of air at each stage is so regulated that it is sufficient to rempve the required amount of water ; it is greatest for the fresh cossettes in the first stage.

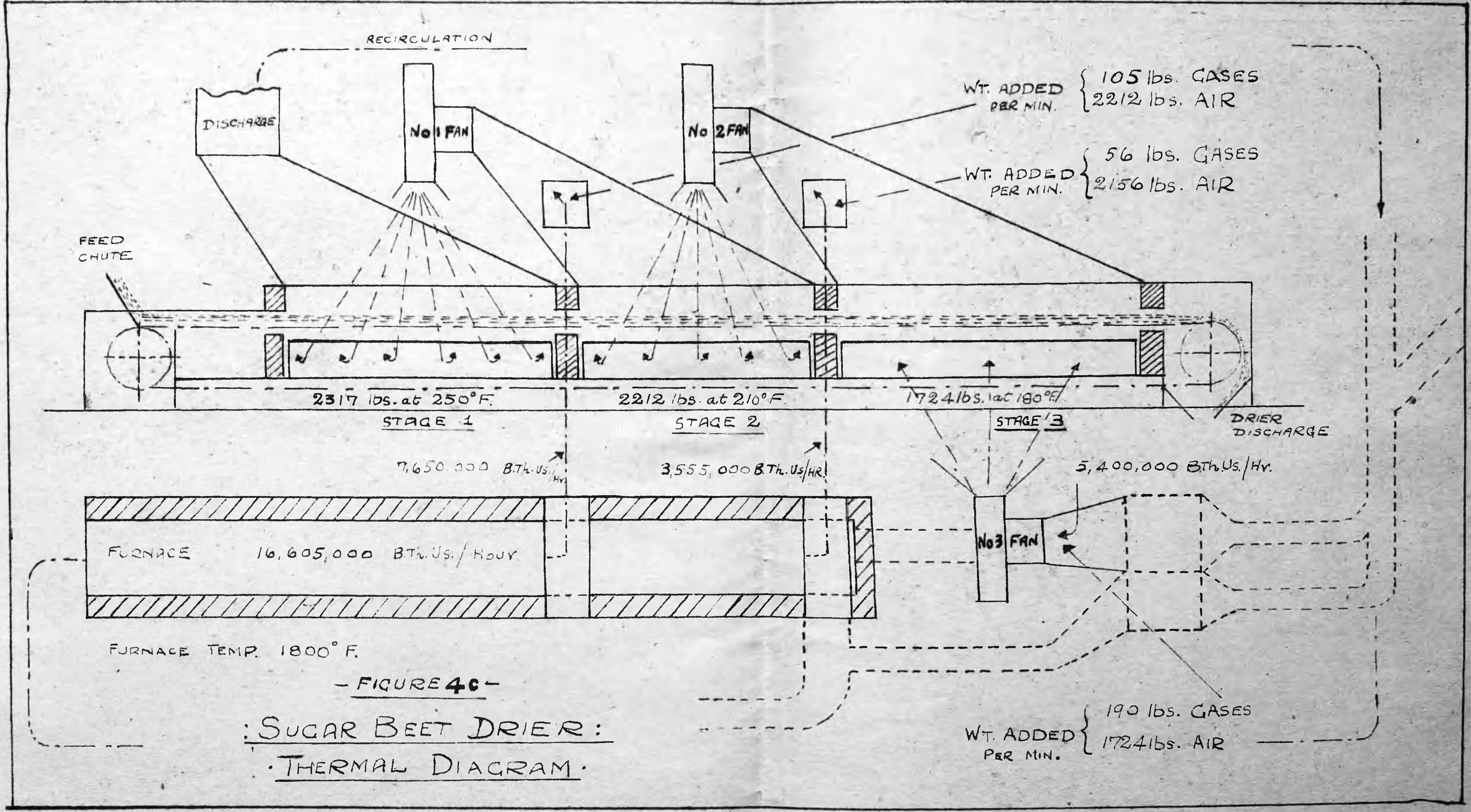
The length of conveyor exposed at each stage diminishes from the fresh cossette stage to the dried cossette stage, the velocity of the air likewise diminishing, since too high a velocity in the dried stage would blow the material off the conveyor. The velocity of the drying air is also limited by economic considerations since an increase in velocity involves a disproportionately greater increase in the power required.

The conveyor belt is an endless perforated steel band driven through a four-speed gear box and worm reduction gearing by a variable speed electric motor, this permitting a wide variation of the conveyor speed. The three drying compartments consist of a steel framework covered with steel plates :each compartment has a separate fan. A levelling device is provided at the feed end to distribute the material evenly before it enters the first drying compartment. At the discharge end the dried material falls on to a conveyor or elevator and passes to the storage warehouse.

The correct size and condition of the material entering is vitally important for drying efficiency, involving the factors of reduction of air resistance, uniform drying, and exit air saturation.

FIGURE 4c.

SUGAR BEET DRIER - THERMAL DIAGRAM.



– FIGURE 4c –

: SUGAR BEET DRIER :

· THERMAL DIAGRAM ·

PARTICULARS OF DRIERS FOR SUGAR BEET COSSETTES.

DIMENSIONS :-

Drying Area of Belt...61' x 10' :- 610 square feet :

" " " Stage 1...21' x 10' :- 210 " "

" " " " 2...19' x 10' :- 190 " "

" " " " 3...21' x 10' :- 210 " "

Centres of Belt......................:- 78' 9"

Area of Grate..........11'3".x 5'3¾":- 59 square feet.

POWER REQUIREMENTS :-

STAGE	1.	2.	3.
Velocity of Gases : ft./min.	350	345	270
Inches water gauge:-			
Discharge side : static	1.77	0.92	0.25
" " : dynamic	0.76	0.71	0.91
Suction side : static	0.80	0.65	0.40
" " : dynamic	0.42	0.38	0.45
Total	3.75	2.66	2.01
Gas volume, cu.ft. at 250°F.	73,400	65,625	44,200
" " " " " 40°F.	51,420	47,250	34,600
Theoretical H.P. at 50% Fan Efficiency	60.5	39.1	22.5
Equivalent amps. at 105 volts	400	265	147
Average amps. recorded	390	270	160

Total Horse-Power estimated from volume and water-gauge :- 122.1

Equivalent amps.)- 812

Average amps recorded :- 820

ANALYSIS OF GASES CIRCULATING INSIDE DRIERS......(BY VOLUME).

CONSTITUENT	1.	2.	3.	4.	5.	6.	7.
CO_2 & SO_2	1.2	0.8	1.5	1.4	1.2	1.5	0.8
O_2	19.6	19.7	19.5	19.7	19.6	19.5	19.7
CO	0.0	0.1	0.0	0.0	0.0	0.0	0.1
N_2 (Diffce.)	79.2	79.4	79.0	78.9	79.2	79.0	79.4
SO_2	.023	.014	.026	.037	.015	.039	.009
TEMPERATURES :-							
1st. Stage							
Inlet	245	240	235	245	240	225	240
2nd. Stage							
Inlet	230	230	220	225	225	215	230
Discharge	145	140	145	150	150	165	140
3rd. Stage							
Inlet	180	180	180	190	190	180	180
Discharge	170	165	170	180	185	170	165
Drying Belt Speed :ft./m.	0.8	0.8	0.8	1.02	1.02	0.7	0.8

FANS AND AIR VELOCITIES:-

Stage	Fan Capacity Cu.ft./min.	Speed r.p.m.	Total Water gauge"	Air Velocity Ft./min.	Lbs. gases per min.		
					Air	Furnace	Total
1	54520	450/620	2.9"	350	2212	105	2317
2	46620	300/475	1.9"	345	2156	56	2212
3	26160	425/625	1.75"	270	1724	190	1914

Total Furnace Gases :- 351 lbs. per minute.

The absorption of Sulphur Dioxide by Beets during Drying.

1. Analysis of Coal used in Drier Furnaces :-

Screened Nuts of 1/2 to 1 1/2 inch size : hard, with a bright splintering resinoid fracture : the volatile matter burned with a long smoky flame and the coke was dark grey, hard, compact, and dull.

Analysis	As Received	As Dried
Sulphur - combustible	0.75	0.82
Sulphur - incombustible	0.06	0.07
Volatile Matter	33.91	37.15
Coke	57.38	62.85
Ash	4.04	4.42
Fixed Carbon	53.34	58.43
Free Moisture	-	-
Hygroscopic Moisture	8.71	-
Thermal Values		
Calorific Value Gross B.Th.Us.	12,539	13,735
Nett	12,029	
Carbon Equivalent	-	13,907
Evaporative Power (Lbs. of water from and at 212°F. per lb. of coal).	12.45	14.21

Calculation of Theoretical Amount of Sulphur Dioxide in Drier Air.

Assuming 0.75 per cent combustible sulphur in the coal used, and a coal consumption of 10 per cent on beets with a drier capacity of 5 tons beets per hour; also that all the sulphur enters the drier as SO_2 and that the air passing through the drier is 4000 lbs. per minute:-

The coal burned per hour will be 1120 lbs., and the sulphur burned per hour, $\frac{0.75 \times 1120}{100} = 8.40$ lbs.

Then lbs. SO_2 per minute, ($S : SO_2 = 1 : 2$), $= \frac{8.40}{60} = 0.28$ lb.

and per cent SO_2 in the drier air $= \frac{0.28 \times 100}{4000} = 0.007$.

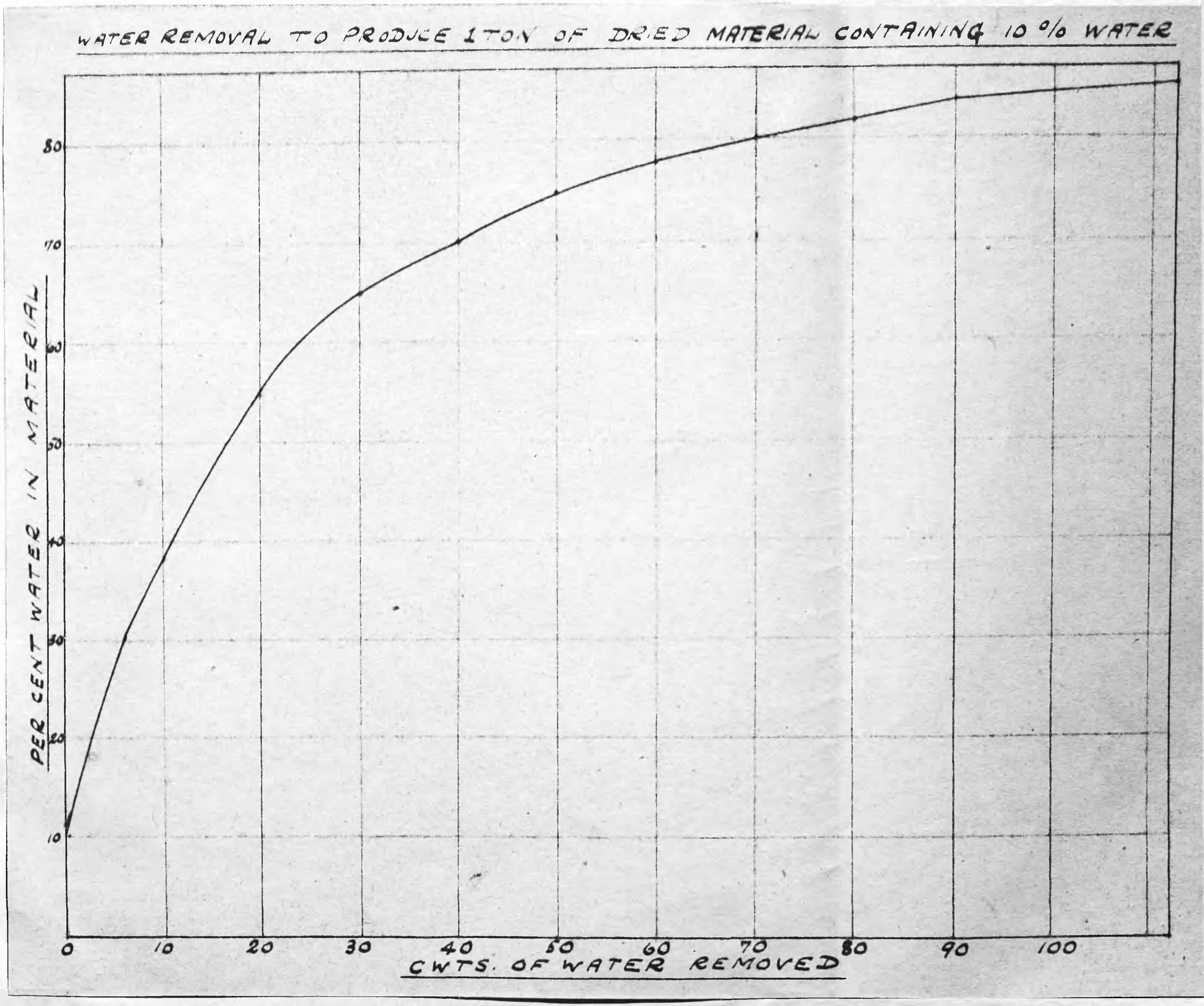

WATER REMOVAL TO PRODUCE 1 TON OF DRIED MATERIAL CONTAINING 10 % WATER
PER CENT WATER IN MATERIAL
CWTS. OF WATER REMOVED
10
20
30
40
50
60
70
80
0
10
20
30
40
50
60
70
80
90
100

Figure 4d

DRYING FACTORS.

The drying factor represents the weight of wet material required to produce one part of dried material at the given moisture contents - that is, it is the ratio $\frac{(\text{Solids in Dried material})}{(\text{Solids in wet material})}$.

Per cent Moisture in Wet material	Per cent Moisture in Dried material						
	4	5	6	7	8	9	10
70	3.20	3.17	3.13	3.10	3.07	3.03	3.00
72	3.43	3.39	3.36	3.32	3.28	3.25	3.22
74	3.69	3.65	3.62	3.58	3.54	3.50	3.46
75	3.84	3.80	3.76	3.72	3.68	3.64	3.60
76	4.00	3.95	3.92	3.88	3.83	3.79	3.75
78	4.36	4.31	4.27	4.22	4.18	4.14	4.09
80	4.80	4.75	4.70	4.65	4.60	4.55	4.50

It is seen in the above table that in the drying of sugar beets with average moisture content of the fresh beet at 76.5 per cent, and dried cossettes at 7.5 per cent moisture the drying factor will be $\frac{92.5}{23.5}$ or 3.94. For most purposes the factor 4.0 is satisfactory.

Typical Results in the Drying of Beet Cossettes.

The amount of water to be removed in drying a substance will naturally vary with the water content of the substance and the curve shown in Figure 4d shows the amount of water in cwts. that must be removed to produce 1 ton of finished material of 10 per cent water content from any state of wetness.

The heat required to evaporate 1 lb. of water at a temperature of 100°F. is 1093 B.Th. Us. made up of 1033 B.Th.Us. as latent heat of vaporisation and 60 B.Th.Us. for heating the moisture from say 40°F. to 100°F. This figure does not include the heat absorbed in heating the dry matter of the material. In general in manufacturing processes 1,500 to 1,900 B.Th.Us. per lb. of water are required. Any leakage of air and the exit of air not completely saturated will decrease the efficiency of drying. Coal or coke may be regarded as the cheapest form of fuel for direct utilisation in Chain Grate Stoker furnaces. Gas Producers or Oil-burning furnaces may also be used. In these direct systems the gases from the main source of heat are mixed with the air and high thermal efficiency is thus obtained. Any external sources of waste heat such as exhaust steam, boiler flue gases, or the exhaust products from Gas or Oil engines should also be incorporated in the heating system. Assuming 1,700 B.Th.Us. per lb. required per lb. of water removed, and taking coal at 13,500 B.Th.Us. per lb. each lb. of coal will evaporate approximately 8 lbs. of water.

Some typical figures for a 5 ton per hour Drier with coal furnace, exhaust steam heaters, and arrangements for utilisation of Boiler flue gases are here shown :-

Drying Results over three months drying of Beet Cossettes.

The fuel used was coal nuts of 13,500 B.Th.Us. per lb. Calorific Value.

Average Moisture Content of Fresh Beet Cossettes = 77.64 per cent
Average Capacity of the Drier for Fresh Beet = 5.03 Tons/ Hour.
Average Moisture Content of Dried Beet = 8.20 per cent
Average Hourly Evaporation of Water = 8,530 lbs.
Average Coal Consumption, per cent on Fresh Beet = 6.38 per cent
Equal to 143 lbs. fuel per ton of Fresh Beet.
Lowest Coal Consumption in any 24 hours = 6.10 per cent
Equal to 137 lbs. fuel per ton of Fresh Beet.
Average Power Consumption per ton of Fresh Beet = 15 k.w.

The complete utilisation of Boiler flue gases brought this fuel consumption down to 5.0 per cent on the weight of Fresh Beet.

In this 5 ton Drier the first and second stages are divided underneath the conveyor band into a number of separate cells by steel partitions with air locks. This offsets the variable resistance encountered by the drying air from one end of each of these stages to the other due to the varying moisture content of the material in its 7-8 inches thick layer. Without this cellular control the greater part of the air entering these stages would take the line of least resistance, thus reducing the effective area of the drying band. The material in the third stage is nearly dry, so that resistance to the air is fairly even all over this stage and cellular control is not necessary. The three stages are separated by air locks, and the divisions or cells below stages 1 and 2 have separate controls for admission of air.

Analyses of Cossettes from the three stages of a multi-stage Drier.

The samples were taken by inserting a wire mesh basket 12 inches square and 10 inches deep in the bed of cossettes at the feed end of the drier. Three such baskets were used across the width of the drying belt, one being removed at the end of each stage.

1. Test on first drying Stage.

Hour	Fresh Beet Entering Drier			Cossettes from End of first Stage			Cossettes from Discharge End of Drier		
	% Sugar	% Red. Sugar	% Water	% Sugar	% Red. Sugar	% water	% Sugar	% Red. Sugar	% Water
1st.	16.6	0.15	75.4	18.25	0.31	70.8	63.6	0.88	9.0
2nd.	15.9	0.15	75.4	17.30	0.24	74.4	62.8	0.88	9.0
3rd.	14.5	0.27	75.4	17.10	0.36	70.3	61.0	1.40	9.0
4th.	14.8	0.27	75.4	17.30	0.34	70.7	59.2	1.40	9.0
		2.	Test on Second Drying Stage.						
1st.	15.3	0.19	76.2	37.90	0.60	24.9	64.6	0.71	10.6
2nd.	15.8	0.20	76.2	39.90	0.63	23.4	63.9	0.82	10.6
3rd.	17.8	0.16	76.2	41.2	0.65	23.2	64.0	0.77	10.6
4th.	15.3	0.20	76.2	38.6	0.63	24.2	62.4	0.88	11.4

Dried cossettes sampled from discharge end of Driers :-

	% Sugar	% Reducing Sugars	% Water
Top of Belt	64.2	0.45	6.8
Bottom of Belt	65.0	0.64	4.1

See Figure 4e.

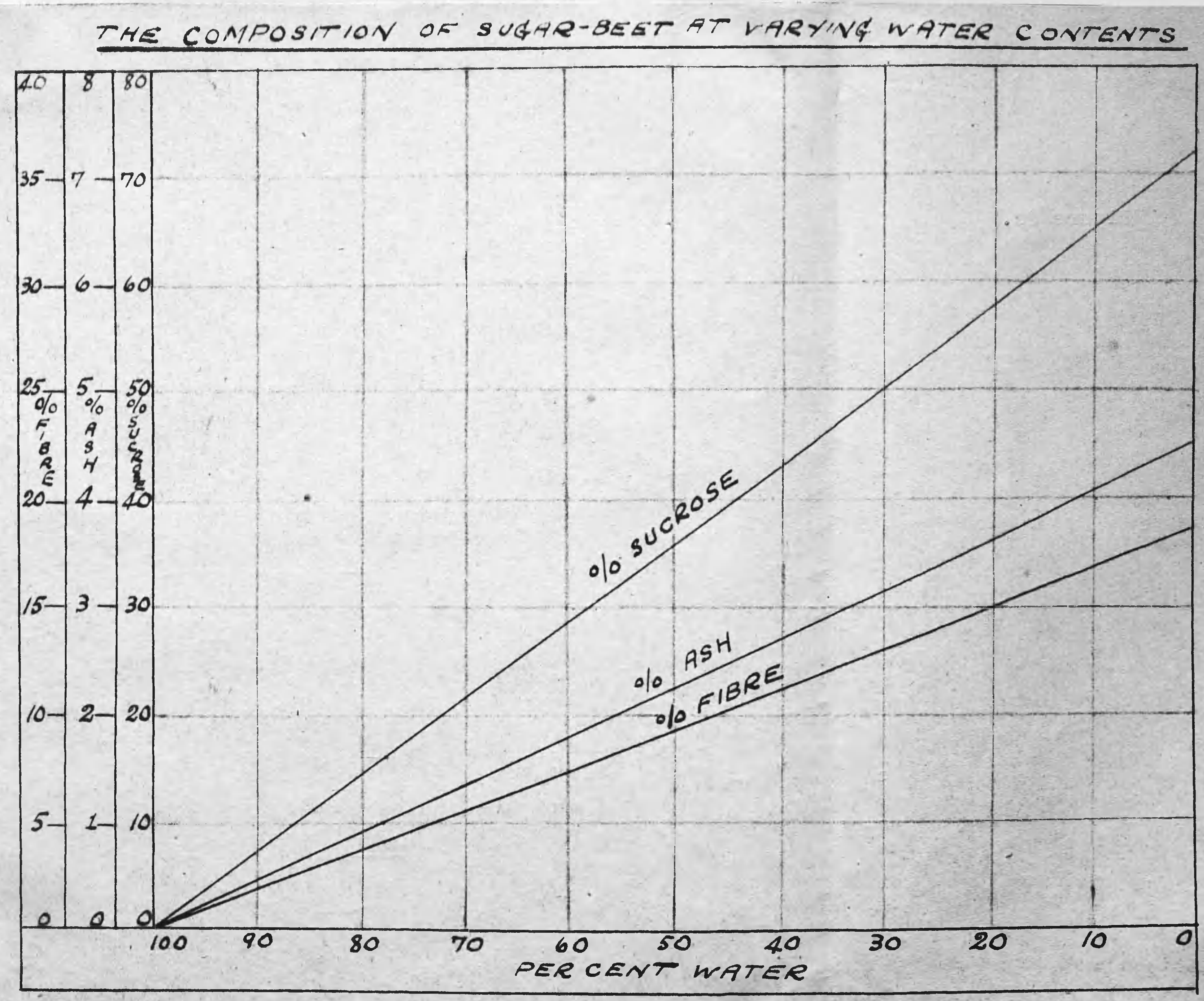

THE COMPOSITION OF SUGAR-BEET AT VARYING WATER CONTENTS
% FIBRE
% ASH
% SUCROSE
40
35
30
25
20
15
10
5
0
8
7
6
5
4
3
2
1
0
80
70
60
50
40
30
20
10
0
% SUCROSE
% ASH
% FIBRE
100
90
80
70
60
50
40
30
20
10
0
PER CENT WATER

Figure 4e

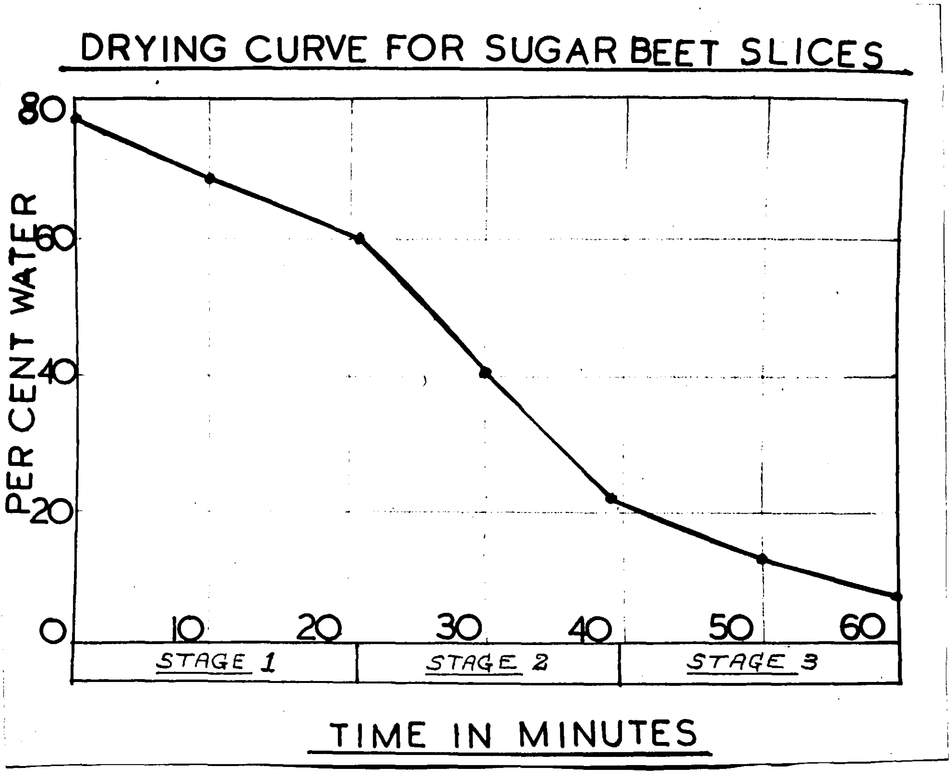
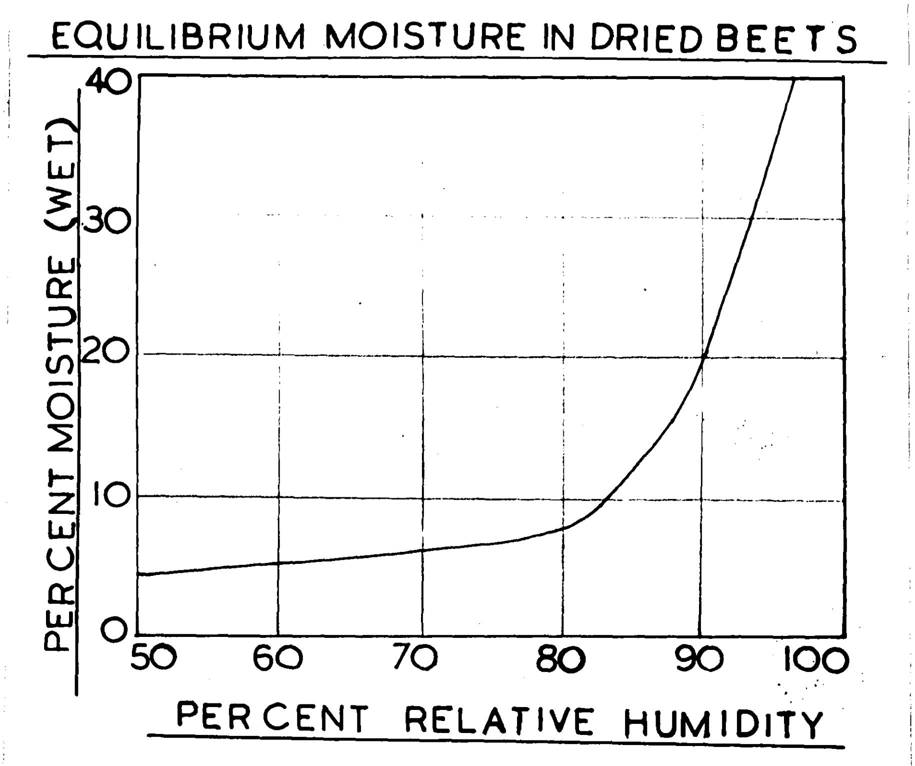


Figure 4ea.

The moisture content of dried beet slices during drying when measured as a function of time gave a curve of the type shown in Figure 4ea. It appears that the moisture content diminishes as a linear function of time in each of three stages.The curves have been constructed on the basis of the experiments with sample baskets passing through the 5 tons per hour driers.

It is probable that in the beginning evaporation takes place at the surface, and saturated sugar solution gradually deposits crystals which may wholly or partially close the pores through which the solution has been reaching the external surface. In the final stages the drying from the interior may take place by diffusion of water vapour through the crystal film.



Figure

4eb.

EQUILIBRIUM MOISTURE IN DRIED BEETS.

This figure is of obvious importance in the storage of dried beets. Some data obtained by the author using air currents of known humidities are shown in the graph, Figure 4eb.

A critical point occurs at about 83 per cent relative humidity when there is a very sharp rise in the amount of water absorbed by the dried cossettes as the air humidity increases.

The time required for attainment of the equilibrium exceeded 24 hours at the humidities used in the experiments.

The temperature of the material ranged from 15 to 18°C. at a barometric pressure of 758 mm.

THE CHEMICAL CONDITIONING OF DRIED BEET COSSETTES

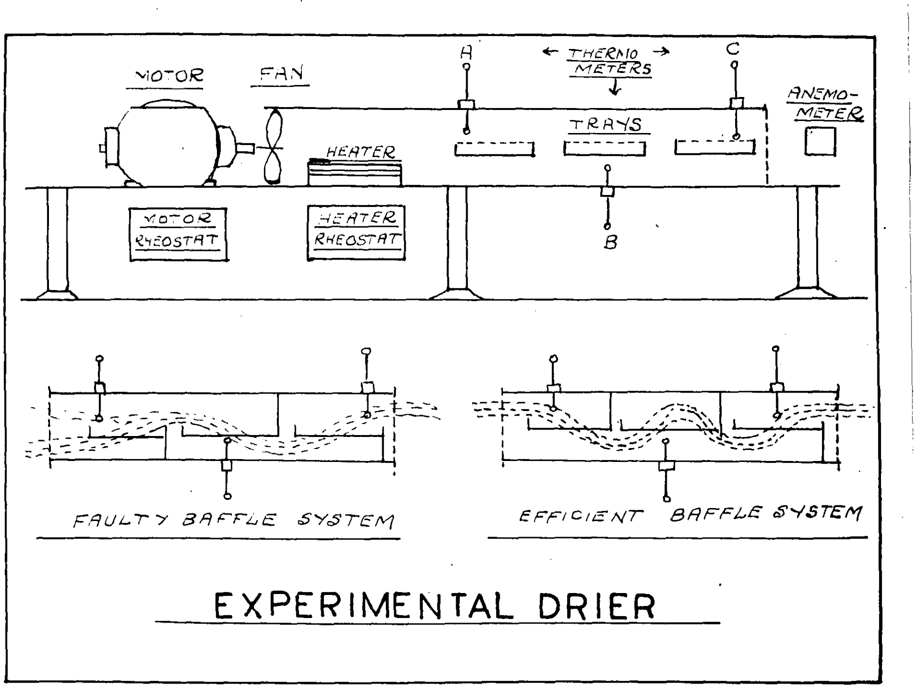
One of the main problems arising in the extraction of dried beet cossettes is the loss caused by inversion of sucrose during diffusion. In the ordinary wet beet process this loss is negligible due to the greater speed of working, and to the fact that fresh beet slices are only faintly acid, having a pH value of 6.4 to 6.6.

The cause of this inversion is the higher acidity of dried beet cossettes, the pH value of which ranges from 4.5 to 5.5, and this acidity is reflected in the low pH value of the diffusion juice, at about 4.5 pH.

It was at first thought that this increase in acidity was due to concentration of acidity during drying with possibly decomposition of some of the salts present. It was soon realised, however, that the acid gases present in the furnace air were much more likely to be the cause. The sulphur dioxide formed during combustion of the coal will probably be transformed to sulphurous acid in contact with the wet cossettes, and may even be partially oxidised to sulphuric acid which has a high inverting power.

Experiments were made using hot air without furnace gases present, and the beet thus dried was found to undergo practically no fall in pH value. This appeared to show that the greater part of the acidity developed during drying with furnace gases was due to the sulphur dioxide in these gases.

The next step was the attempted production of neutral dried cossettes by treatment of the fresh beet slices with a suitable reagent.



EXPERIMENTAL DRIER

Figure

4ec.

EXPERIMENTAL BEET DRIER.

The trays used were made of stout wire gauze and were 9 inches long by 3½" wide by 1" deep. The fan was cut from tin plate and had 16 vanes. It was coupled directly to the motor.

It was found that without baffles in the drier the hot air rose to the top of the drier giving uneven temperatures in the trays. The first arrangement of baffles shown above as "faulty" gave dry slices in trays 1 and 3, but damp slices in tray 2.

The second baffle system shown was satisfactory. Each tray was loaded with 100 gms. of fresh slices.

The average drying conditions maintained in the drier after some preliminary adjustments were :- Temperatures - A, 132°C., B, 83°C., C, 73°C., and air velocity 380 feet per minute.

The results of trials made with various reagents are summarised below :-

1. Ordinary drying oven with no air circulation

Treatment	pH After Treatment	Inversion % on sugar Untreated	Treated	Remarks
Ammonium Carbonate	4.0	0.77	0.73	
Lime 0.75%	7.7	0.03	0.86	Results very variable.
Lime 1.0%	7.4	0.86	0.92	
Lime + SO_2	2.0	--	--	Very high inversion loss

2. Small experimental fan drier

Treatment	pH After Treatment	Inversion % on sugar Untreated	Treated	Remarks
Nil	6.2	0.05	--	pH of fresh beet = 6.4
1. Lime 0.2%	7.4	0.13	0.11	Tendency here to destroy reducing sugars.
2. Lime 0.5% * CO_2 and SO_2	7.2	0.29	0.26	
3. Caustic soda 0.025%	6.9	0.28	0.13	Slightly greenish Cossettes after Soda
4. Trisodium phosphate 0.5%	7.0	0.06	0.01	
5. Powdered chalk 2%	6.8	0.02	0.05	
6. Sodium carbonate 0.2%	7.0	0.16	nil	

2. Small Experimental fan drier (continued):-

Treatment	pH After Treatment	Inversion % on Sugar		Remarks
		Untreated	Treated	
7. Bleaching Powder 0.4%	7.0	0.23	0.03	
8. Ammonia Solution, 2N	6.7	0.10	0.01	Cossettes very hygroscopic.
9. Borax 0.4%	7.4	0.40	0.64	
10. Ammonium Chloride 1%	5.9	nil	0.13	

CONCLUSIONS :- Pure air was used in all these tests so that the inversion occurring without treatment is a measure of the effect of heat and internal changes in lowering the pH value. These results can therefore be taken as giving a true reflex of the influence of the various reagents on inversion. There would seem to be a wide choice of reagents with which the fresh cossettes can be treated so that a neutral dried cossette results. This might have the effect of yielding a diffusion juice which was almost neutral, and in this way the diffusion battery inversion loss might be kept to a minimum.

A similar result might on the other hand, be achieved by the neutralisation of the furnace gases before they reach the slices.

THE CHEMICAL CONDITIONING OF BEET SLICES IN THE DRYING PROCESS.

EXPERIMENTAL RESULTS - DRYING IN A STILL OVEN.

Reagent used for treatment	Amount % on F.beet	F. beet	Invert ratio		pH		Increase in Invert Ratio	
			Untr. D.C.	Treated D.C.	F.B.	Treated D.C.	Untr. D.C	Treated D.C.
Ammonium Carbonate	0.28	0.81	1.20	1.49	6.4	4.5	0.39	0.68
"	0.28	0.68	1.47	1.49	6.4	4.0	0.79	0.81
"	0.28	0.85	1.96	1.56	6.4	3.5	1.11	0.71
Lime Water	0.022 g.lime	0.66	1.17	1.20	6.4	6.6	0.51	0.54
"	0.030 g.lime	1.20	2.15	1.73	6.4	6.5	0.95	0.53
Milk of Lime 15°Brix	1.12 g.lime	1.10	1.10	0.39	6.7	7.6	0.00	-0.71
"	0.75	0.99	1.85	0.96	6.3	7.7	0.86	-0.03
Dry lime Drying to 62% Sugar	1.0	0.99	1.85	1.91	6.3	7.4	0.86	0.92
Dry lime Drying to 68% Sugar	1.0	1.57	1.40	1.06	6.6	7.4	-0.17	-0.51
Dry lime Drying to 68% Sugar	0.5	1.57	1.40	0.46	6.6	7.3	-0.17	-1.11
Dry lime Drying to 68% Sugar	0.3	1.63	1.72	1.20	6.4	7.3	-0.09	-0.43
To 65% Sugar	0.15	1.63	1.72	1.05	6.4	7.1	-0.09	-0.58

CHEMICAL CONDITIONING - DRYING IN AN AIR CURRENT.

Reagent used for treatment	Amount % on F. beet	Invert Ratio			pH		Increase in Invert Ratio	
		F. Beet	Untr. D.C.	Treated D.C.	F.B.	Treated D.C.	Untr. D.C.	Treated D.C.
Lime powder	0.5	0.80	0.37	0.40	6.6	7.6	-0.43	-0.40
" "	0.25	0.80	0.37	0.39	6.6	7.4	-0.43	-0.41
" "	0.125	0.67	0.29	0.50	6.4	7.4	-0.38	-0.17
" "	0.0625	0.67	0.29	0.40	6.4	7.2	-0.38	-0.27
Ditto, drying to 57% Sugar	0.20	0.67	0.57	0.68	6.4	7.5	-0.10	0.01
Ditto, drying to 56% Sugar	0.10	0.67	0.57	0.70	6.4	7.3	-0.10	0.03
Lime powder	0.20	0.67	0.78	0.80	6.4	7.4	0.11	0.13
" "	0.25	0.60	0.86	0.88	6.4	6.6	0.26	0.28
" "	0.50	0.60	0.86	0.89	6.4	7.2	0.26	0.29
Caustic soda Soln. 0.2%	0.008	0.60	0.74	0.70	6.4	6.6	0.14	0.10
"	0.016	0.60	0.74	0.68	6.4	6.8	0.14	0.08
"	0.018	0.71	0.70	0.72	6.4	6.7	-0.01	-0.01
"	0.024	0.71	0.70	0.74	6.4	6.7	-0.01	0.03
NaOH 0.5%	0.025	0.60	0.73	0.88	6.4	6.9	0.13	0.28
"	0.015	0.60	0.73	0.79	6.4	6.8	0.13	0.19
$Na_3(PO_4).12H_2O$ 2%	0.20	0.73	0.92	0.91	6.5	6.4	0.19	0.18
" (Solution)	0.12	0.73	0.92	0.93	6.5	6.6	0.19	0.20
$Na_3(PO_4).12H_2O$ (Solid)	0.5	0.73	0.67	0.74	6.5	7.0	-0.06	0.01
	1.0	0.73	0.67	0.72	6.5	7.1	-0.06	-0.01
"	0.5	0.73	0.66	0.99	6.5	6.8	-0.07	0.26
"	0.25	0.73	0.66	0.88	6.5	6.5	-0.07	0.15
$CaCO_3$ powder	1.00	0.62	0.80	0.88	6.5	6.7	0.18	0.26
"	0.30	0.60	0.80	0.92	6.5	6.7	0.18	0.30
"	2.00	0.62	0.60	0.57	6.5	6.8	-0.02	-0.05
"	0.50	0.62	0.60	0.60	6.5	6.6	-0.02	-0.02
$Na_2CO_3.10H_2O$	0.20	0.59	0.75	0.59	6.4	7.0	0.16	0.00
"	0.10	0.59	0.75	0.59	6.4	6.8	0.16	0.00
Bleaching Powder	0.70	0.59	0.82	0.90	6.4	6.9	0.23	0.31
	0.40	0.59	0.82	0.62	6.4	7.0	0.23	0.03
Ammonia Soln.	0.21	0.72	0.82	0.81	6.6	6.7	0.10	0.09
Borax (solid)	0.40	0.70	1.10	1.34	6.6	7.4	0.40	0.64
NH_4Cl (")	1.00	0.83	0.83	0.97	6.7	5.9	0.00	0.13

SECTION 3.

THE DESIGN AND OPERATION OF A DIFFUSION BATTERY FOR THE EXTRACTION OF SUCROSE FROM DRIED SUGAR BEETS.

PART 1 : GENERAL :

1. The Diffusion Process :
2. General Principles of Design for Diffusion Apparatus :
3. The Control of the Working of a Diffusion Battery :
4. Factors in the Diffusion Process :
5. Trials with an Experimental Diffusion Battery.

THE EXTRACTION OF SUGAR FROM THE SUGAR BEET

The first method used (c. 1796) for the extraction of sugar from the sugar beet was hydraulic pressing of the rasped roots in one or more stages. In 1831 de Dombasle (French Patent 7981, 1831) introduced the process of slicing the beet and treating the slices with liquors of gradually decreasing sugar content. He used wooden vats open at the top, in the first of which the slices were heated with live steam. In the remaining four vats the leaching proper took place. A sixth vessel contained the cold water supply.Pumps were provided to circulate the liquors, and the leaching vats were fitted with false bottoms of perforated wood.

From his experiments de Dombasle concluded that cold water would only leach out a small quantity of sugar from the cossettes no matter how small the slices were. Boiling temperature should be avoided however, and only enough heat used to destroy the vegetable principle and prevent decomposition of the sugar by bacterial action.

Duquesne (F.P. 697, 1845) was responsible for the introduction of closed diffusion cells made of sheet iron, but it was not until 1864, and after many years of work that Robert et Cie made warm leaching successful on the plant scale (F.P 65,607,1864: see Brit.P. 594, 1866).

The work of Fremy (Sitzber. K. Akad.Wiss.Wien,50,442,1864) on pectose had led to an observation by Wiesner that 80°C. was too high a temperature for extraction. He advised 50°C., whic h was low enough tp prevent swelling of the pectose in the cell walls. This swelling greatly hindered diffusion. There was also risk at

80°C. of partial solution of the pectose with resulting impure juices which were more difficult to purify.

To-day the optimum temperature at the head of the battery is considered to lie between 72° and 80°C., since it has been found that coagulation of albuminoid substances is aided between these temperatures. The speed of diffusion is also much greater so long as actual destruction of the cell walls is avoided. At lower temperatures bacterial action is promoted and the enzymes diastase (60 -68°C.) and peptase (38 - 49°C.) are active.

In the early diffusion cycles the time taken was often very prolonged. Thus Donald (T.I. Chem.E.,15,86,1937) states that the average cycle time was 8 hours in 1874, which had been reduced to 48 minutes, and even as low as 18 minutes by 1880. At present many factories work 2.5 to 3.0 cells per hour, although as many as 7.0 cells per hour are filled in certain factories.

The velocity of the circulating liquids has been the subject of several studies. Thus Bouchon (Bull. assoc. chim. suc.,11,32, 1893) investigated the effect of the height to diameter ratio of a diffusion cell, and found that with the height small there was more rapid circulation since the slices did not pack so tightly. It is clearly of advantage,however, from the factory output point of view, to pack as much beet as possible into each cell.

Szyfer (Deut. Zuckerind.,18, 539, 1894) found that good results were obtained with a juice velocity of 18 cms. per minute, and the poorest results at 40 cms. per minute.

Lizeray (Alcool et Sucre,2, 75 & 105, 1894) showed that with

4 mm. cossettes, the resistance of the cossettes was about equal to that of the battery, while with 3.0 - 3.5 mm. cossettes, the resistance became two and a half times that of the battery.

Donald (loc. cit.) has reviewed the diffusion process in beet sugar manufacture, and has given an extensive bibliography.

THEORETICAL CONSIDERATIONS.

In the fresh beet the plant cells are full of liquor holding the soluble matter in solution. After drying these cell walls collapse, and the water removal leaves the precipitated soluble matter inside the cells.

In diffusion of such material, the speed of solution will depend on the extent of rupture of the cell walls. If the walls remained unbroken, the solvent will have to diffuse into the cell, dissolve the soluble material, and then pass out again with this material in solution. There is thus diffusion through the cellulose membraneas well as through the film at the liquid / solid interface. With ruptured cells there is only normally diffusion through the filter at the liquid / solid interface.

It has been shown by Gayley (J. Amer. Leather Chem. Assoc.,15, 344, 1920) that tannins from chestnutwood tend to diffuse preferentially along the fibres of the wood instead of across them, this being in accordance with expectation from a consideration of the structure of the wood. By analogy, it is probable that sugar will diffuse more readily from beet slices along the grain than across it.

THE DIFFUSION PROCESS.

The diffusion process of extraction of sugar from beetroots consists in heating the sliced beet cossettes with hot juice and slowly lixiviating the mass with water in a systematic manner.

The liquor is displaced forward through a series of diffusion vessels filled with cossettes by additions of water to the first vessel until the extracted juice has a concentration of about 15°Brix.

During this process three different actions are taking place simultaneously-

1. The washing out of the cell contents from broken cells,
2. The diffusion by dialysis of the soluble matter contained in the dead but otherwise uninjured vegetable cells,
3. The gradual solution of the difficultly soluble constituents of the beets.

The last of these is undesirable and must be restricted, since increase in the extraction of such impurities gives a lower purity juice which causes trouble in later stages of manufacture.

If diffusion could be carried out with beet reduced to the thickness of thread, an almost ideal extraction would result, but the diffusion battery would soon choke with this fine material, which in any case would be difficult to prepare.

The time for complete diffusion is regulated by the dimensions of the largest cossettes, but it must be remembered that the smaller chips are already over-exhausted when this time has elapsed, and considerable amounts of non-sugars may thus have passed into the juice. It is thus apparent that uniform smooth slices are especially desirable, and that the smaller and more nearly perfect are the cossettes, the better is the diffusion work, and the better are the operating conditions in the succeeding parts of the process.

The diffusion process can be regarded as consisting of FOUR operations :-

1. Size reduction of the solid :
2. Contact with a solvent for diffusion to take place :
3. Separation of the liquid and solid phases :
4. Recovery of the solvent (if necessary).

Theoretically this process may be represented by a modified Noyes-Whitney equation in which are included as constants all the resistances to mass transfer :- the interface reaction ; the solid ; the cell wall ; the stagnant film ; and the bulk of the solvent.

The theoretical calculation is best based on the number of equilibriums occurring rather than on the number of cells filled.

If simple decantation is practised, the number of cells M, required will equal the number of contacts. In diffusion work such as that used for sugar beets, the number of cells Mb will bear the relation(2Mb - 1) to the number of contacts, i.e. :-

Decantation - say 19 cells required, then Number of contacts is 19 :
Diffusion - " 10 " " , " " " " "
(20 - 1), or 19

General principles of design for diffusion apparatus.

The general plan will include :-

A. The diffusion cells : B. The calorisators : C. Accessories, and the design problem will be concerned with :-

E. Type of apparatus chosen : F. Its general design : G. Structural details.

A diffusion battery may be regarded as a chemical engineering unit process system : the particular example selected is the extraction of sugar from dried beet cossettes by water in a ten-cell diffusion unit. Many of the factors involved are common to design problems for other unit processes, and are given in detail.

This system aptly illustrates two well-known axioms in chemical engineering - that what goes in must come out, and that the ideal effluent from an industrial plant is distilled water or pure air.

A basic problem here was the difference of behaviour of the dried material from that of ordinary fresh beet slices, while a subsidiary difficulty was the familiar one of translating a qualitative laboratory performance to the necessarily quantitative extraction required for economic work in a large size unit.

Earlier work on a large scale had shown that a diffusion battery of standard pattern did not work efficiently on dried beet cossettes. The main troubles were channelling and short-circuiting of the juice giving uneven extraction, production of excessive amounts of foam, and choking of the pipes by accumulations of fine cossette dust.

Losses of sugar were very heavy, the extraction seldom reaching 85 per cent.

It was therefore decided to conduct experiments to determine the following :-

1. A design of diffusion battery suitable for this material
2. The percentage extraction obtainable with such a battery
3. The behaviour of the constituents of the dried beet cossettes during extraction.
4. The effect of conditioning the cossettes before or after drying to influence their subsequent extraction.

Six diffusion batteries in all were operated : these were :-

1. A large scale battery of standard wet beet design, giving not above 85 per cent extraction with dried beet cossettes
2. A seven cell pilot plant experimental battery, capacity 25 lbs. of dried cossettes per cell.
3. A ten cell pilot plant battery of special design, capacity 28 lbs. dried cossettes per cell
4. A laboratory battery with 14 cells, capacity 200 gms. per cell
5. A continuous diffusion battery of large pilot plant scale, total capacity, 80 lbs. dried cossettes, per hour.
6. A large scale battery, designed on the performance of No. 3 battery above : cell capacity 896 lbs. dried cossettes (8 cts.)

Of these systems, Nos. 3,4, and 6, were successful : the designs for these were evolved from the less successful work with the remainder.

The Control of the Working of a Diffusion Battery.

A reliable method for determining the conditions existing in a diffusion battery is not easily obtained. The only method which gives even an approximation is that of taking samples from different parts of each vessel simultaneously and analysing them. When the analytical results are plotted on a graph a curve is obtained which should have a determined shape when based on rational rules. Irregylar working of the battery will be revealed by an irregular curve. This method of testing the performance of a battery was proposed by Battut (La Sucrerie Indigene,27,414,1886) : some of the Battut Diagrams are shown in Figures 8,9,10,and11. Similar curves due to Stammer and Saillard are shown in Figures 3, 4, and 5, and a curve illustrating American practice (private communication) is given in Figure 7.

Curves obtained in the work on Dried Beet Cossettes are shown in Figures 18 to 25. In these curves the decrease in pH value as the juice density increases is well evident. The Brix° "ex cell" represents the density of a random sample taken from the cell while the battery was in operation : the final Brix° is that of the mixed contents of the cell when run off at the end of each test. When working with dried beet cossettes it was found that the absolute temperature maximum permissible was 90°C. : this is the maximum generally taken for fresh beet diffusion also.

Battut concluded from his graphical results that the maximum exhaustion of cossettes takes place at 65°C., and not 75°C., as had been commonly supposed. The coagulation of albumen is more complete at the higher temperature,however,and the juices purer.

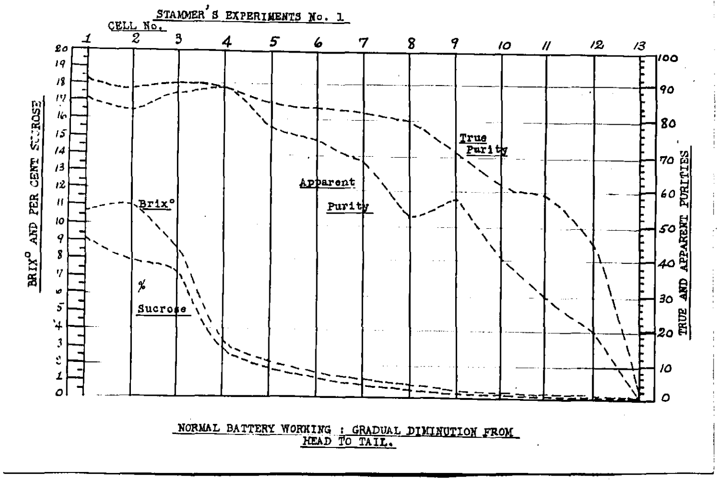


Fig.4f

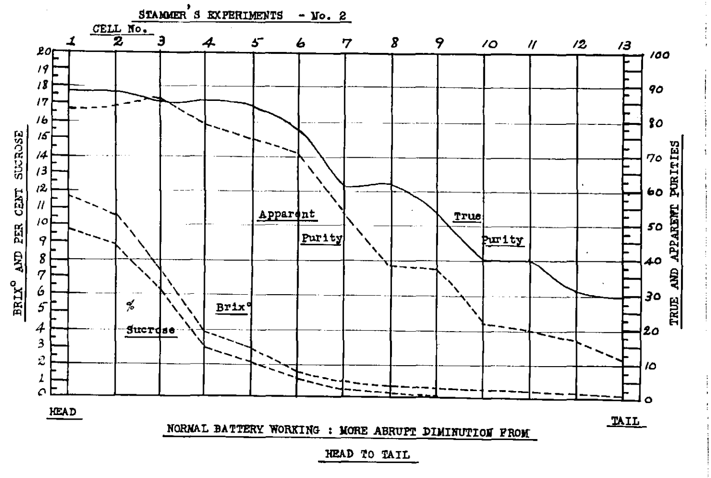


Fig.4g

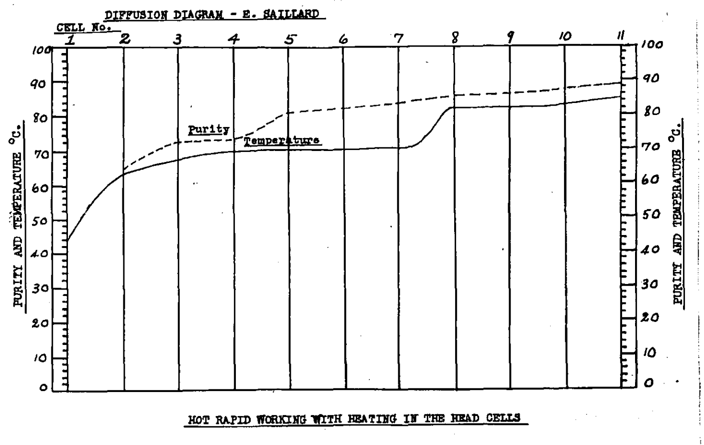


Fig.5

The diffusion Process in Beet Sugar manufacture :-

The factors influencing the extraction of sugar from the beet by the diffusion process may be conveniently classified as follows:-

1. Design and construction of the system,
2. Materials entering, circulating, and issuing,
3. Operation and Control, including Economics.

This general scheme may be expanded under each of the above headings :-

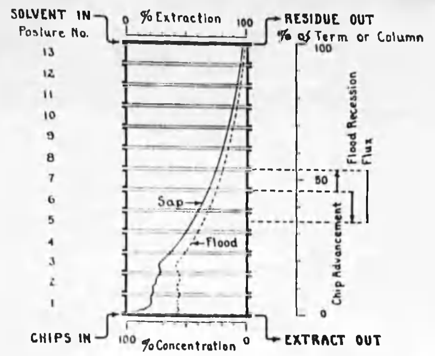
1. Design and Construction of the system- General Plan
    - (a) Type
    - (b) General design
    - (c) Structural details

Under these headings will be included, the number, shape, and size of the vessels, their capacity for beets, the ratio of height to diameter of the cells, the screening area provided in the vessels with its ratio of screening surface to total surface, and its efficiency. The arrangement of the cells-e.g. in two lines or in a circle, and the total length of the diffusion column will also be considered here.

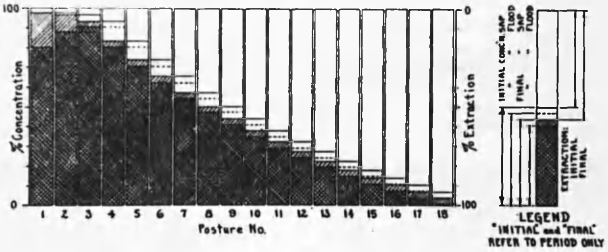
Structural details :- These include the actual materials of construction, the types of valves and their positioning, the pipes and their dimensions, length and gauge of chains used for supporting the beet slices, the calorisators and their heating capacity , the steam traps, and the gaskets for cell closure. Other important points in general design are the position of the pipelines, the ease of access to the cells and calorisators, and the overall water-tightness of the system.

Graphical Representation of the Diffusion Process.

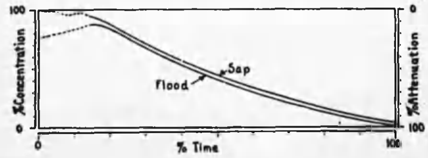
(M.J.Proffitt).



(a) COLUMN CONCEPT



(b) BATTERY CONCEPT



(c) TYPICAL ATTENUATION CURVES WITH CONTINUOUS FLUX (EITHER INTEGRAL OR PARTIAL)

Fig.6

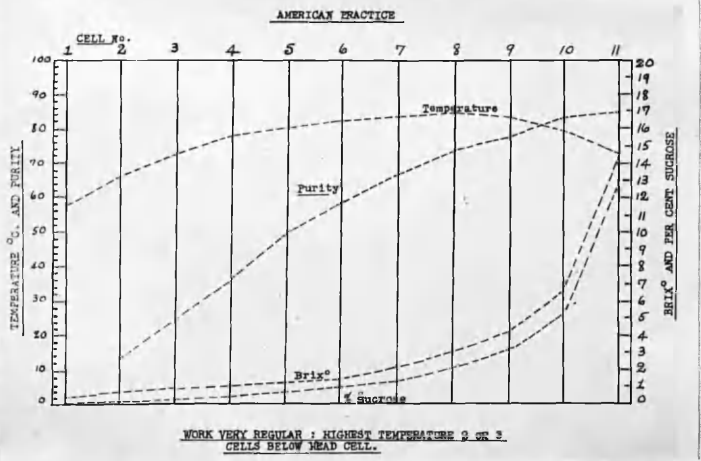


Fig.7

DIFFUSION APPARATUS - CELLS

STRUCTURAL DETAILS :-

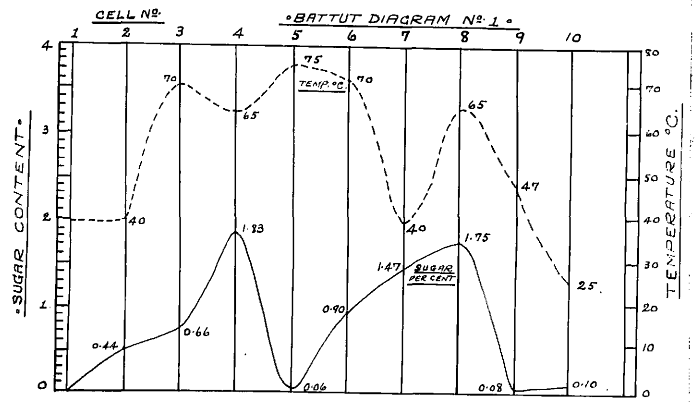
Materials of Construction :- Cast iron is preferable for the cell bodies, and can be recommended for all piping except vertical pipes, which should be of forged iron. Copper is expensive, and is liable to attack by the juices.

Pipes :- The pipe joints should not be cast with the vessel. All piping should be of adequate diameter for the flow of liquid, and should be as short in length as possible, thus avoiding dilution of the juice. Bends are preferable to elbows, which impede the juice flow. The internal dimensions of the pipes should bear a ratio to the cell diameter of about 1 to 12 for efficient circulation.

Valves :- These should be flat-seating and independent. They should be easy of access, and by preference situated at the working front of the vessels. The valve seatings should be of soft rubber which lasts longer than fibre if carefully handled. (Hard fibre leaks if the valve stem position moves).

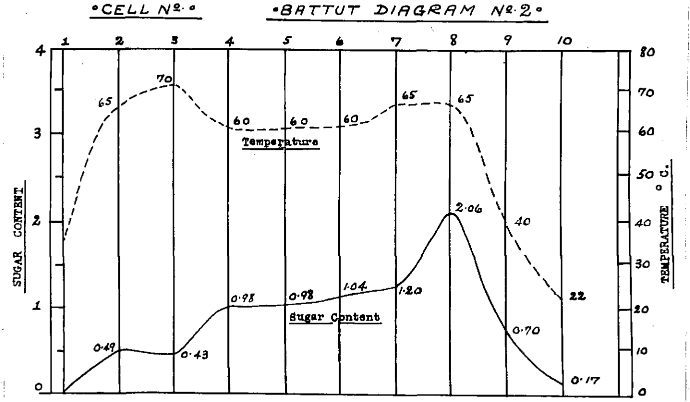
Bye-passing arrangements :- This is very convenient in case of serious mishap such as a cracked cell, or for severe choking of a cell. The pipes used should be short with valves very close to the cell walls. Alternatively two standard pipes may be provided which can be joined up.

Mechanical tightness :- It is clearly essential that the system should be as free as possible from leaks or potential sources of leaks.



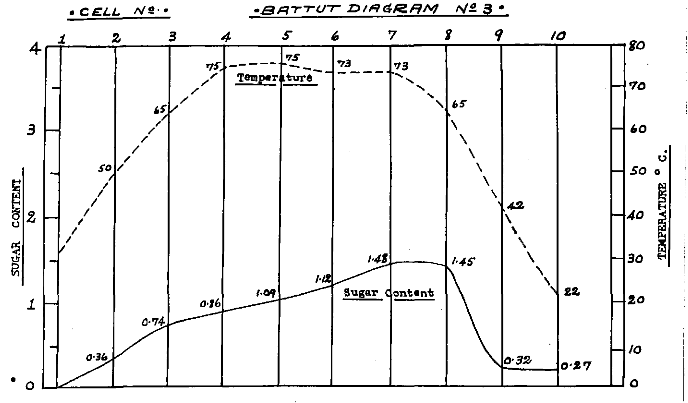
IRREGULAR WORK-POOR EXHAUSTION, ALTHOUGH CONSIDERABLE INCREASE OF SUGAR PERCENTAGE BETWEEN CERTAIN CELLS.

Fig.8



MORE REGULAR WORK : CONSIDERABLE INCREASE IN SUGAR CONTENT BETWEEN CELLS 7 AND 8.

Fig.9



TEMPERATURES VERY REGULAR AND EXTRACTION REGULAR , BUT VERY SLIGHT SUGAR INCREASE FROM CELL TO CELL (DUE TO COSSETTES BEING TOO LARGE).

Fig.10

CALORISATORS :-

STRUCTURAL DETAILS :- These should have adequate heating power, and should have heating tubes of dimensions such that the battery circulation is never slowed down in them. Access to the calorisators should be easy for cleaning, or in case interior choking occurs. Each calorisator should be provided with a steam-trap, and these should in turn lead to a main steam-trap.

Gaskets :- Cell closure should be preferably by pressure joints, water inflated.

Ammonia pipes and gas ejection :- There should be a gas blow-off cock on the top of each vessel, and also on both the juice and steam sides of each calorisator at the top.

Control devices :- 1. Thermometers :- There should be a thermometer attached to each vessel, placed in a position where the bulb is in direct contact with the flux. These instruments should be of mercury type, with bold figures, and should be placed where they can be easily read. Central thermometers of the recording type may be provided for average daily returns of head and tail temperatures. Since temperature is such an important factor in battery operation, every care should be taken to maintain regular temperatures, and to record them properly.

2. Pressure gauges :- These should be of automatic type.

3. Juice measurement :- Wherever possible the juice should be weighed on automatic recording scales - i.e. in a weigh-tank.

2. Materials entering, circulating, and issuing :-

(a) Entering :- Factors to be considered are the size and quality of the slices, their packing in the cells, and their freedom from small particles and large uncut fingers. The filling apparatus and its operation are likewise important.

(b) Circulating :- The water entering will be considered under the heading solvent. The flux or circulating liquids in the cells must be controlled for velocity and temperature, and the draw-off juice for volume, density (Brix°), and purity.

(c) Issuing :- The draw-off juice has been mentioned above. The other materials issuing are the waste water and the exhausted or waste pulp. The arrangements for discharge of these will require attention, and the discharge temperature and sugar content of both products are of vital importance.

Gaseous interference and foaming :- There should be a minimum of air trapped while filling the cells, and arrangemant must be made for release of gases evolved during extraction,e.g. by ammonia pipes.

3. Operation, Control, and Economics :- There must be adequate sampling and chemical control of the various products, including testing of condensates for sugar traces. The labour should be well-trained assuring efficiency in actual manipulation of the flow. There is also variation possible in the actual formation of the cells worked, that is, in the cycle of filling, extracting, and emptying the cells. The steam consumption and the balance of materials in and out of the system should be worked out for average working conditions.

The Raw Material :- In considering the diffusion of wet or dried beet cossettes the properties which are significant include :- The porosity : the relative ease of diffusion : The percentage of broken cells present : the quality of the beets- whether sound, bolted, or frosted roots: the dimensions of the slices- length, breadth, thickness, and surface area : the general physical properties of the slices : the sugar content and other analytical data for the cossettes (careful selection of analytical methods is important here) : the percentage of small particles, dust and large,badly sliced pieces present : Freedom from dirt- i.e. the washing efficienc the mechanical strength of the slices : and in the case of dried beet slices, the reducing sugars content, the per cent water present, the ash percentage, and the content of harmful nitrogen.

General arrangement of the battery :- The operating platform should be placed high up on the cells. The pipe-lines must be placed at least parallel to the bottoms of the cells to ensure proper drainage when emptying the cells. The calorisators should be placed similarly. Care must be taken that there is no excessive resistance to the flow of juice through the calorisator tubes. The calorisator bodies should be insulated. Throughout the system there should be a total absence of juice and water pockets. The clamping valve-doors at the cell tops should be of the single action wheel type. The best arrangement of the battery for say twelve cells is in two rows of six, so that the return line from no. 12 to no. 1 is not abnormally long. The screen holes should be made so that there is maximum screening area per unit of total area.

Section 3. SOLVENT USED:-

In most cases the solvent used will be water, although certain advantages are claimed for the use of alcohol. The alcohol process was largely developed by the French , and was used about 1860 for the removal of gums from sorghum juice. It was later elaborated to give nearly complete precipitation of the sugar, so eliminating several stages in the water extraction process. This process is feasible, but has proved to be either too expensive or too much restricted by Government legislation.

The factors requiring consideration for the solvent may be grouped as below :-
1. Supply : 2. Quantity used : 3. Quality of supply : 4.Temperature at entrance,5.Pressure available, 6. Economy of use, 7. Treatment of waste solvent : 8. Possible re-circulation of used solvent,
9. Corrosion factors.

Volume of water entering :- This determines the juice density, the rate of extraction, and the evaporator economy. The supply of fresh water should be adequate and continuous, and it should be of suitable quality. A hard water may not necessarily be a disadvantage, since diffusion juice is always acid. The pressure used on the battery is a key factor in circulation : it is normally kept within the limits 7-15 lbs. per square inch. A meter should be provided to measure the total amount of water used, and careful control should be made of the water amount used for washing out the cells after emptying.

Corrosion problems are also directly affected by the quality of the water supply.

General points on battery operation :- The timing of the cycle must be controlled- i.e., for filling the cell, going through the flow-cycle, and discharging. The battery working must not be hindered by allowing the waste pulp sump to become too full : similarly the pumping away of waste water must be co-ordinated with the treatment given to this water in the effluent plant. A comprehensive reporting system is necessary for the proper control of the battery working.

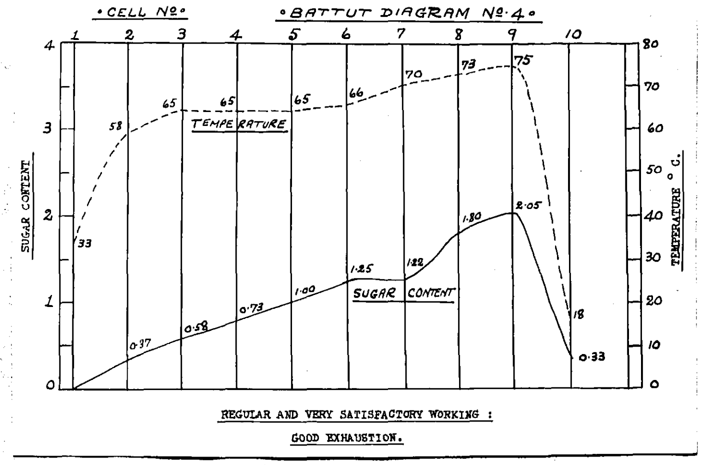
The lagging of the cells may be practised for heat economy : for the same reason the battery should be kept as free as possible from cold air currents. The size of the pulp discharge door should be arranged to give gravity emptying of the waste pulp, although this is seldom complete where chains are used in the cells.

Ecohomics of the system :- This can be stated to include :-
1. the Capital cost : Fuel and Steam costs : Labour costs : Overhead costs : Running costs, and Depreciation.

Type of Apparatus :- The type of apparatus used is a primary consideration, involving the following general factors :-

1. The daily amounts of material to be treated,
2. Whether operation is to be by batch or in a continuous system,
3. Whether the material is to be treated while static or is to be stirred or otherwise moved during extraction.

Location of apparatus :- The placing of the battery in the factory will have regard to:- 1. Access to raw materials, steam, power, and water : 2. Waste disposal, 3. Adequate control, 4. Minimum labour, 5. Relation to the other stages of the process, 6. Proper working conditions for the operators.



REGULAR AND VERY SATISFACTORY WORKING :

GOOD EXHAUSTION.

Fig.11

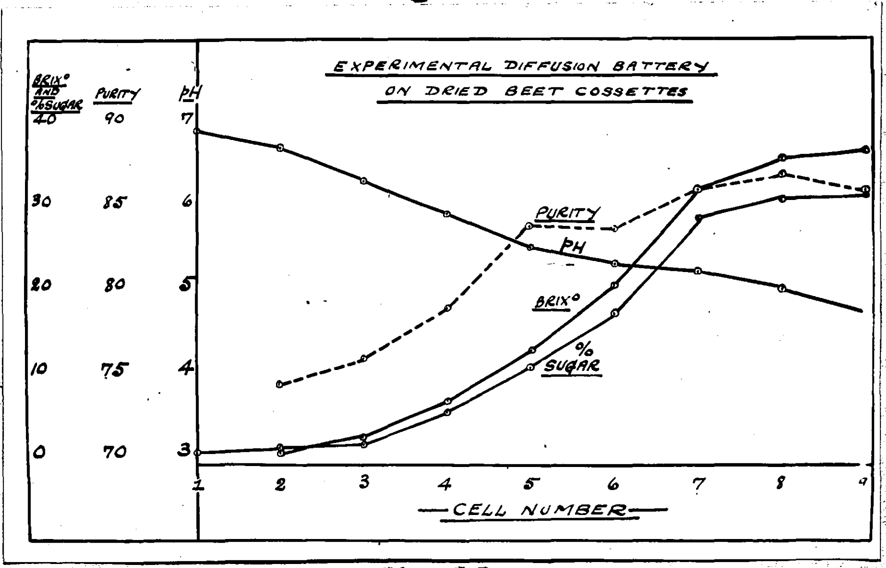


Fig.12

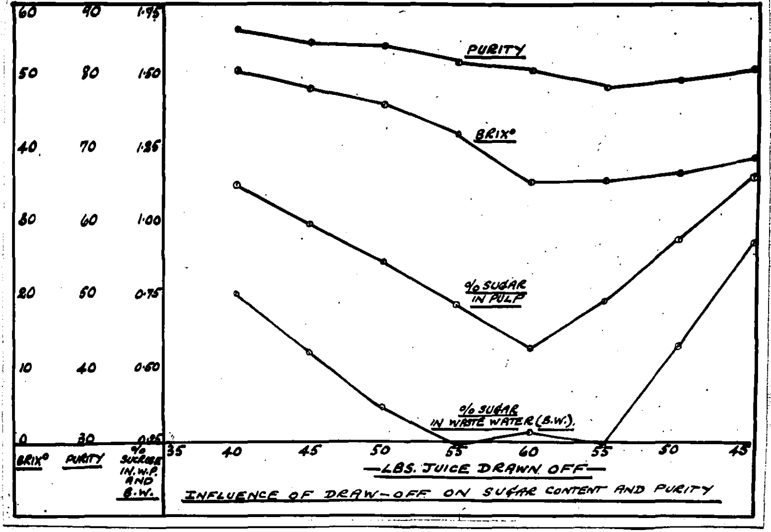


Fig.13

Experimantal Diffusion Battery.

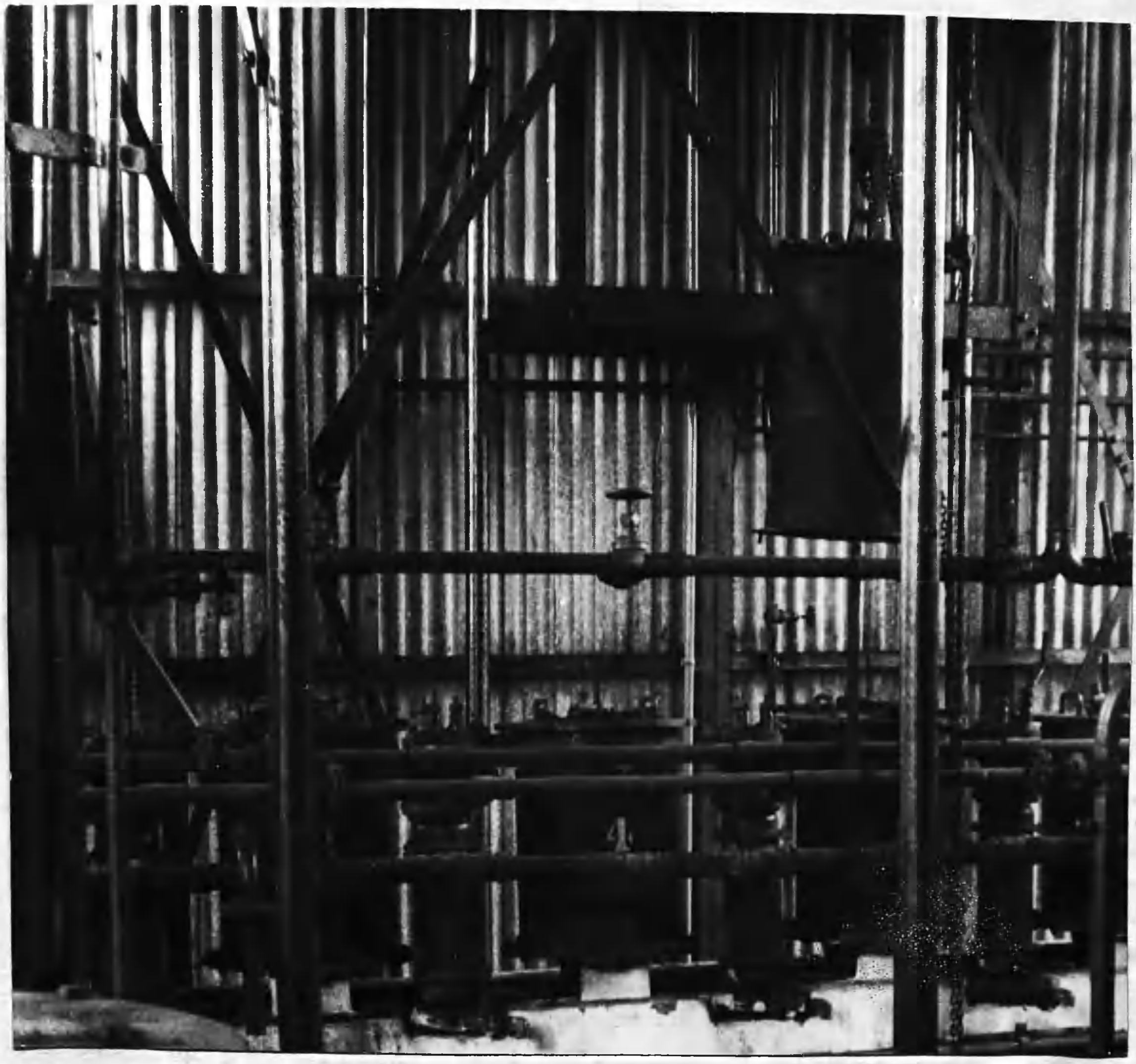


Fig.14

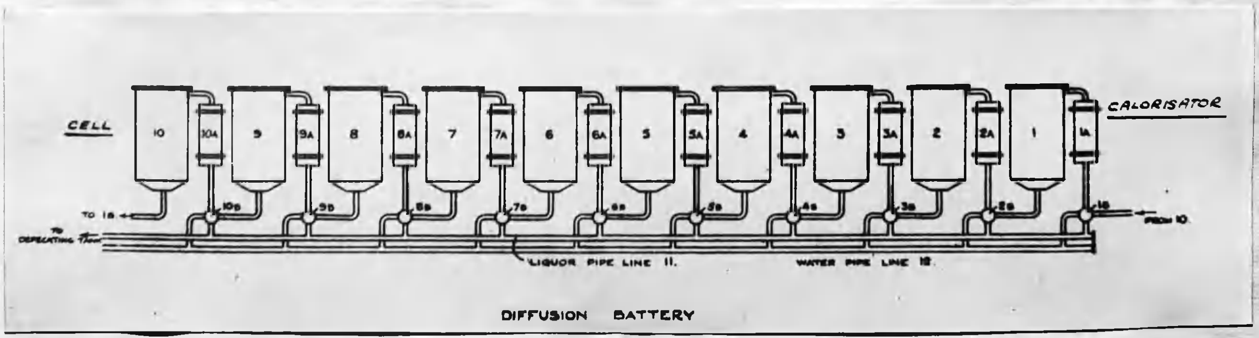


Fig.15

Trials with Improved Experimental Diffusion Battery.

Test No. :-	1.	2.	3.
Duration of test, hours	24	24	24
No. of vessels in battery	10	10	10
Wt. Cossettes per cell, lbs.	28	28	28
% Dust in Cossettes	9.5	6.4	6.8
Juice Draw-off, lbs.	45	45	38-42
Draw-off, % on cossettes	160	160	136-150
Theoretical Draw-off, lbs.	42.6	43.0	41.1
Theoretical Draw-off,% on Cossettes	152	153	147
ANALYSES			
Cossettes, Sugar%	61.28	61.63	61.12
Juice, Brix°	48.06	46.71	47.78
Sugar%	38.90	37.96	39.17
Purity	80.94	81.27	82.00
Waste Pulp Sugar%	0.33	0.16	0.32
Waste Water Sugar%	0.20	0.08	0.12
Lbs. Sugar Entering	821.29	770.90	822.00
Extraction, % on Sugar	97.07	97.65	95.54
Waste Pulp, % on Sugar	1.67	0.74	1.62
Waste Water, % on Sugar	0.74	0.29	0.50
Inversion, % on Sugar	2.25	0.51	0.58
Circulating pipe, % on Sugar	--	0.63	1.44
Total Extraction, (including Circulating pipe,)% on Sugar	--	98.28	96.98
Unknown Loss, % on Sugar	--	0.18	0.32
% Waste Pulp on Cossettes	314	311	315
% Waste Water on Cossettes	233	248	246
Cells drawn off	45	44	50
Cells Filled	55	50	56
Cells Emptied	47	42	48
Average Cells per hour	1.87	2.08	2.33

The analytical figures represent the average results of the analyses made for each cell.

TRIALS WITH EXPERIMENTAL DIFFUSION BATTERY:

Test No. :-	1	2	3	4	5	Presoaking
Duration of test Hours	24	27	18	12	24	15
No. of vessels in Battery	7	7	10	10	10	7
Wt. Cossettes per Cell, lbs.	28.5	28	28	28	28	28
Per cent Dust in Cossettes	5.7	4.25	5.1	8.05	5.4	2.9
Draw-off Juice lbs.	32.4	49	50	40	45	27.3
Draw-off per cent on Cossettes	114	175	178	143	160	98
Theoretical draw-off, lbs.	40.5	41.7	45.1	43.1	--	--
ditto, % on Coss.	142	149	161	154	--	--
ANALYSES						
Cossettes, Sugar%	62.37	63.39	60.38	62.34	62.14	61.91
Juice Brix°	49.89	42.18	38.61	46.82	46.30	--
Sugar%	41.63	34.51	31.20	39.05	38.20	39.18
Purity	83.45	81.82	80.81	83.41	82.50	--
Waste Pulp Sugar%	2.02	1.18	0.39	0.73	0.38	1.30
Waste water Sugar%	0.95	0.49	0.13	0.24	0.19	1.07
Lbs. Sugar entering	904.0	1195.47	770.5	593.6	929.89	337.8
All % on Sugar						
Extraction %	86.1	90.63	94.4	81.73	96.06	76.08
Waste Pulp %	10.34	5.83	2.02	3.61	1.94	8.34
Waste water%	3.51	1.71	0.50	0.93	0.68	5.08
Inversion %	1.33	1.17	1.75	1.57	1.09	1.20
Unknown Loss %	--	0.66	1.35	12.16	0.23	9.30
Cells filled	61	74	53	42	61	30
Cells drawn-off	56	64	46	31	53	24
Cells emptied	56	67	44	33	52	24
Cells filled per hour	2.54	2.74	2.94	3.50	2.54	2.00

DISCUSSION OF RESULTS.

TRIAL 1 : 7 CELLS :- The holes in the screens used in this test were ⅛" in diameter and this caused poor circulation and, in one case complete choking. Prior to Trial 2 these holes were increased to 5/16 -inch diameter and no further difficulty in circulation was encountered.

TRIAL 2 : 7 CELLS :- A draw-off varying from 143 per cent to 213 per cent on Dried Cossettes was taken during this trial, and it was found that the sugar content of the waste pulp and water, and the concentration of the juice were in direct relation to the draw-off. It was also evident that 7 cells were not enough and that a battery of at least 10 cells would be necessary for extracting dried beet.

TRIAL 3 :- Three cells were added to the seven of the previous tests and a uniform draw-off of 178 per cent on Dried Cossettes was maintained. This trial gave much improved extraction.

UNIFORMITY OF EXTRACTION :- The following analyses, made during this trial, indicated fairly uniform extraction conditions :-

SAMPLE FROM	PER CENT SUGAR		
	I.	II.	III.
Top of Vessel	0.79	0.54	0.40
Middle of Vessel	0.96	0.76	0.49
Bottom of Vessel	1.69	1.50	0.45
Average	1.15	0.93	0.45
Actual average content by analysis	1.09	0.77	0.40

TRIAL 4 : LOWER DRAW-OFF :- The draw off in this trial was kept constant at 143 per cent on Dried Cossettes, and a corresponding rise in the sugar content of the waste pulp and water was observed. The abnormally low extraction recorded was found to be due to the juice remaining in the return circulation pipe containing 16 per cent of sugar. Allowing for this, the extraction becomes 93.5 per cent.

TRIAL 5 :- A draw - off of 160 per cent on Dried Cossettes was taken in this test with satisfactory results. With allowance for certain known leaks, it was considered possible to obtain a 98 per cent extraction with this battery.

TRIALS WITH IMPROVED BATTERY :- The battery designed as a result of the above trials had a ratio of height to diameter of unity with increased screening area and minimum lengths of piping. Ten cells were used and a draw-off of 160 per cent od Dried Cossettes was taken. The three trials made gave satisfactory results. In the third test, the influence of the lower draw-off on the extraction is clearly seen.

This experimental battery was used as the basis for the design of a large scale battery to deal with 25 tons of Dried Cossettes per day (equivalent to 100 tons of fresh beets).

DIMENSIONS :- Diameter 4' 5" by 4' 5" high : area of bottom 15.3 sq. ft. with a circumferential screen 6 inches deep. Total screen area per cell 22.2 sq. ft. Screen perforations ¼" at ⅜" pitch equal to 35.4 per cent of total area : circular holes. Screening area equivalent to ¼ sq. ft. per cu. ft. of cell volume.

Cells filling 825 lbs. of Dried Cossettes per vessel, or 12.5 lbs. per cu. ft. Recommended draw-off 150 per cent on Dried Cossettes, giving 1237 lbs. juice per cell at 48°Brix, or 315 gallons juice per hour.

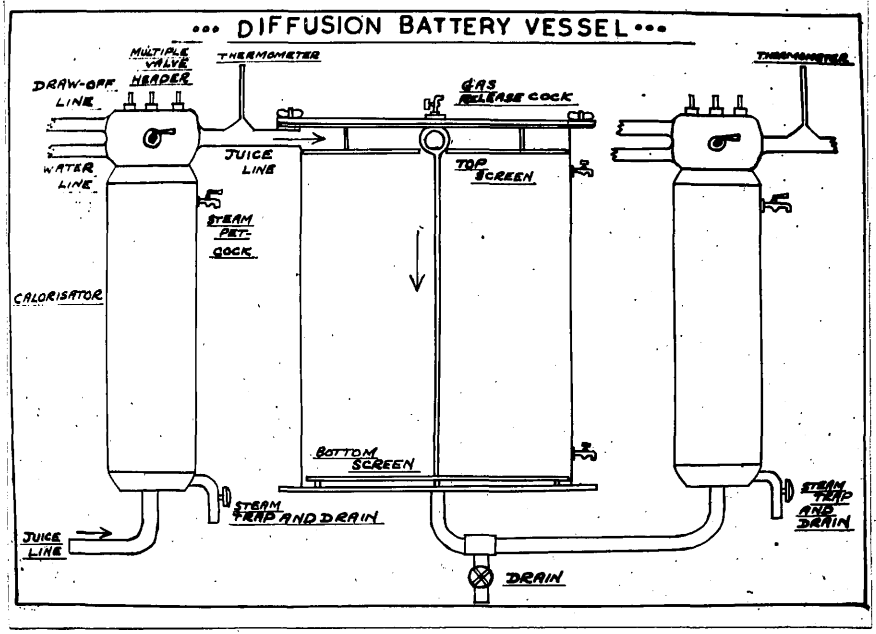

DIFFUSION BATTERY VESSEL
MULTIPLE VALVE HEADER
THERMOMETER
DRAW-OFF LINE
GAS RELEASE COCK
THERMOMETER
WATER LINE
JUICE LINE
TOP SCREEN
STEAM PET-COCK
CALORISATOR
BOTTOM SCREEN
STEAM TRAP AND DRAIN
STEAM TRAP AND DRAIN
JUICE LINE
DRAIN

Fig.16

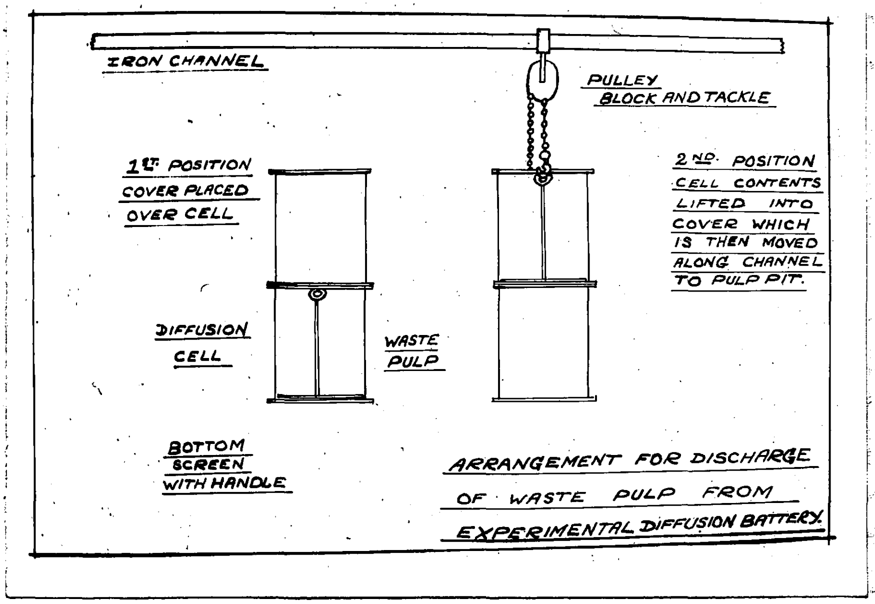

IRON CHANNEL
PULLEY BLOCK AND TACKLE
1ST POSITION COVER PLACED OVER CELL
2ND POSITION CELL CONTENTS LIFTED INTO COVER WHICH IS THEN MOVED ALONG CHANNEL TO PULP PIT.
DIFFUSION CELL
WASTE PULP
BOTTOM SCREEN WITH HANDLE
ARRANGEMENT FOR DISCHARGE OF WASTE PULP FROM EXPERIMENTAL DIFFUSION BATTERY.

Fig.17

THEORETICAL DRAW - OFF ON IMPROVED EXPERIMENTAL DIFFUSION BATTERY

Purity :-	Juice at 46°Brix						Juice at 48°Brix					
%Sucrose in Dried Cossettes	80 Gallons	lbs.	84 Gallons	lbs.	88 Gallons	lbs.	80 Gallons	lbs.	84 Gallons	lbs.	88 Gallons	lbs.
58	3.5	42.4	3.33	40.3	3.18	38.5	3.28	40.2	3.15	38.2	3.00	36.7
60	3.61	43.7	3.45	41.8	3.28	39.7	3.43	41.9	3.27	40.0	3.13	38.2
62	3.74	45.3	3.56	43.1	3.40	41.2	3.54	43.3	3.37	41.2	3.22	39.4

Purity :-	Juice at 50°Brix						Juice at 52°Brix					
%Sucrose in Dried Cossettes	80 Gallons	lbs.	84 Gallons	lbs.	88 Gallons	lbs.	80 Gallons	lbs.	84 Gallons	lbs	88 Gallons	lbs.
58	3.15	38.8	3.00	37.0	2.87	35.4	3.00	37.3	2.87	35.7	2.74	34.0
60	3.27	40.3	3.11	38.3	2.99	36.8	3.11	38.7	2.96	36.8	2.83	35.2
62	3.38	41.6	3.25	40.0	3.07	37.8	3.21	39.9	3.00	37.3	2.92	36.3

Calculation :-

$$\text{Lbs. draw-off} = \left[\frac{\text{Dried Cossettes filled} \times \%\text{S. in D.C.} \times \%\ \text{Extraction} \times 100}{\%\ \text{Sugar in juice} \times 100} \right] = X$$

$$\text{Gallons draw-off} = \left[\frac{X}{\text{lbs. wt per gallon}} \right]$$

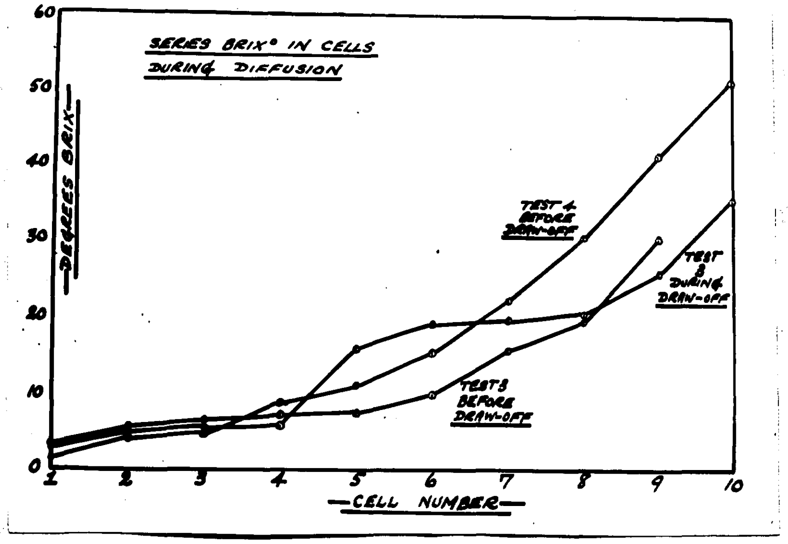

SERIES BRIX° IN CELLS
DURING DIFFUSION
—DEGREES BRIX—
0
10
20
30
40
50
60
TEST 4
BEFORE
DRAW-OFF
TEST
3
DURING
DRAW-OFF
TEST 3
BEFORE
DRAW-OFF
1
2
3
4
5
6
7
8
9
10
—CELL NUMBER—

Fig.18

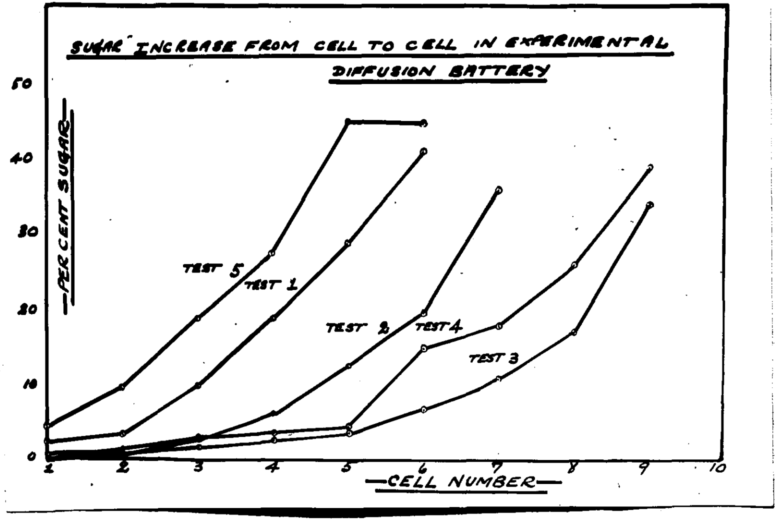

SUGAR INCREASE FROM CELL TO CELL IN EXPERIMENTAL
DIFFUSION BATTERY
—PER CENT SUGAR—
0
10
20
30
40
50
TEST 5
TEST 1
TEST 2
TEST 4
TEST 3
1
2
3
4
5
6
7
8
9
10
—CELL NUMBER—

Fig.19

APPROXIMATE STEAM REQUIREMENTS PER HOUR FOR AN EXPERIMENTAL DIFFUSION BATTERY.

BASIS :- 100 lbs. Dried Cossettes per hour containing 60 per cent Sucrose. Per cent Draft)=189 lbs. Raw Juice at 35°Brix per hour.
189%   )

Assuming 97 per cent Extraction of sugar
313 per cent Wet Pulp on weight Dried Cossettes
242 per cent Waste Water on " " "

Specific Heats :- Dried Cossettes, Wet Pulp and Waste Water taken as approximately equal to 1 : Raw Juice at 35°Brix = 0.806.

Radiation Loss assumed to be approximately 15 per cent of total heat supplied.

Heat Supplied per hour :-

(a) Heat in Dried Cossettes (100 lbs. at 59°F.):-

$$= 100 \times (59-32) \times 1 = 2{,}700 \text{ B.Th.Us.}$$

(b) Heat in Battery Supply Water (68 gallons at 113°F.) :-

$$=680 \times (113-32) \times 1 = 55{,}080 \text{ B.Th.Us.}$$

(c) Heat in steam to Battery Calorisators :- "X"

Heat Leaving per Hour :-

(d(Heat in Raw Juice :-(189 lbs. per hour at 122°F. :-

$$= 189 \times 0.806 \times (122-32) = 13{,}710 \text{ B.Th.Us.}$$

(e) Heat in wet Waste Pulp : 313 lbs. at 90% water and 131°F. :-

$$= 313 \times 1 \times (131-32) = 30{,}987 \text{ B.Th.Us.}$$

(f) Heat in Battery Waste Water : 242 lbs. at 131°F. :-

$$= 242 \times (131-32) \times 1 = 23{,}958 \text{ B.Th.Us.}$$

$$(d) + (e) + (f) = 68.655 \text{ B.Th.Us.}$$

(g) Radiation Loss (15 %) = $\frac{(d) + (e) + (f) \times 15}{85} = \frac{68{,}655 \times 15}{85}$

$$= 12{,}116 \text{ B.Th.Us.}$$

The $a + b + c = d + e + f + g$, or $57{,}780 + x = 80{,}771$

and $x = 22{,}991$ B.Th.Us. per hour to Calorisators

Approximate lbs. steam required per hour for Calorisators :-

Steam Pressure = 20 lbs./sq.inch

Temperature of Condensate $= \dfrac{\text{Temp. Head Calorisator} + \text{Temp. Tail Calr.}}{2}$

$$= \frac{176 + 113}{2} = 145^{\circ}\text{F.}$$

B.Th.Us. per lb. steam at 20 lbs./sq.inch pressure condensing at

$$145^{\circ}\text{F.} = L + \frac{145-32}{212-32} \times h = 942 + \frac{113}{180} \times 227 = 1078$$

Lbs. steam required per hour at 20 lbs./sq.inch pressure :-

$$= \frac{22{,}991}{1078} = 21.33 \text{ lbs.}$$

Taking Conductivity Efficiency of Calorisators at 80 per cent :-

Lbs. Steam per Hour to Battery Calorisators = 26.67 at 20 lbs./sq".
= say 27 lbs.

Lbs. Steam per Hour to Battery Feed Water :-

B.Th.Us. Required per Hour,(b), = 55,080

Using steam at 60 lbs./sq.inch and condensing to 113°F.

B.Th.Us. per lb. steam = 1180 : so lbs. steam per hour $= \dfrac{55{,}080}{1180}$

= 46.68 or say 47 lbs. steam per hour at 60 lbs./ sq. inch pressure.

CONTINUOUS DIFFUSION.

Several British beetsugar factories employ a modification of the diffusion battery - the continuous diffuser. This consists of a long cylinder about 9 feet in diameter and 82 feet in length, inclined at an angle of 4° to the horizontal. The cylinder is partitioned into 22 chambers in each of which paddles are fitted. The paddles lift the cossettes by stages from the lower to the higher end of the diffuser. A flow of hot water from the higher end gives continuous extraction, the raw diffusion juice leaving at the lower end. The water from the pulp presses is returned to the diffuser to recover the sugar which it contains.

Sugar losses in this type of diffusion apparatus are somewhat higher than in the cell diffusion battery.

This Raabe-Paschen diffuser is made by the Maschinen und Werkzeugfabrik A.G. vorm A. Paschen : it is shown in various stages of development in Figure 19a (due to M.B.Donald, T.I.Chem. E., 15, 94, 1937).

The first design provided separate weirs and overfalls (German patent 267,133, 1912 : U.S. patent 1,077,296). It was found that sand and other foreign matter collected in the non-perforated part. To prevent this the weir was enclosed by a perforated cover and the liquors were caused to converge to keep the exit clear (German patent 331,129,1919). In later designs circular screens allow the liquor to flow through them, the cossettes being advanced by a side spiral (German patent 612,092, 1932), or by a bucket-shaped device in the circular screen itself (German patent 616,054,1933).

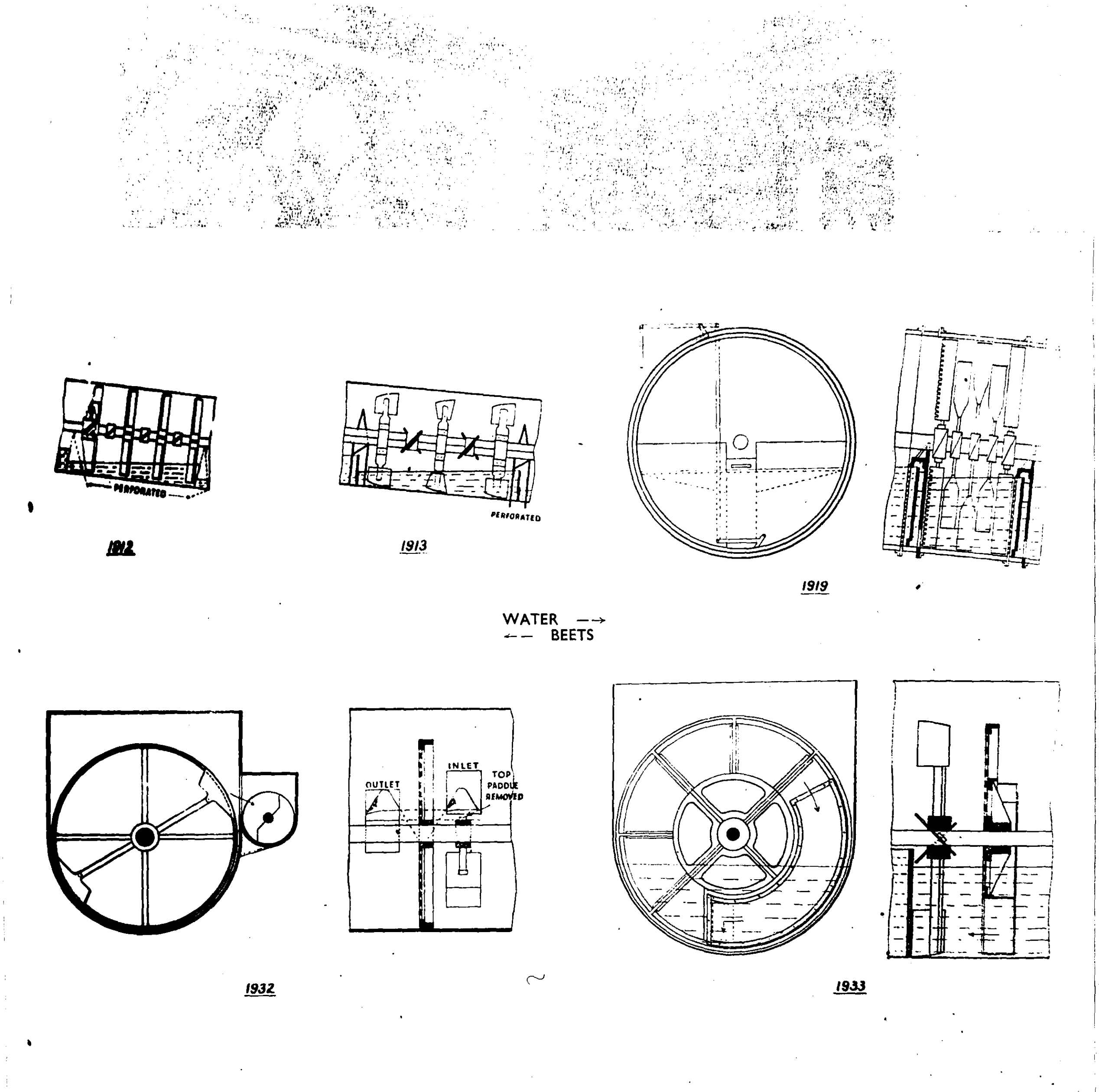


Figure 19a...The Raabe-Paschen Continuous Diffuser...
Evolution : (M.B.Donald,T.I.Chem.E.,15,94, 1937.)

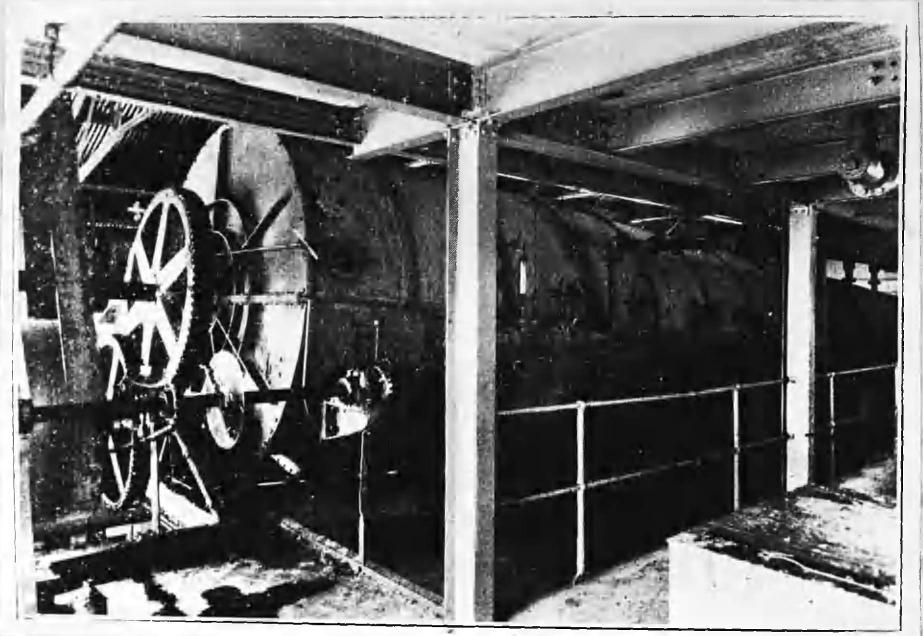


Figure 19b... The Raabe-Paschen Continuous Diffuser.

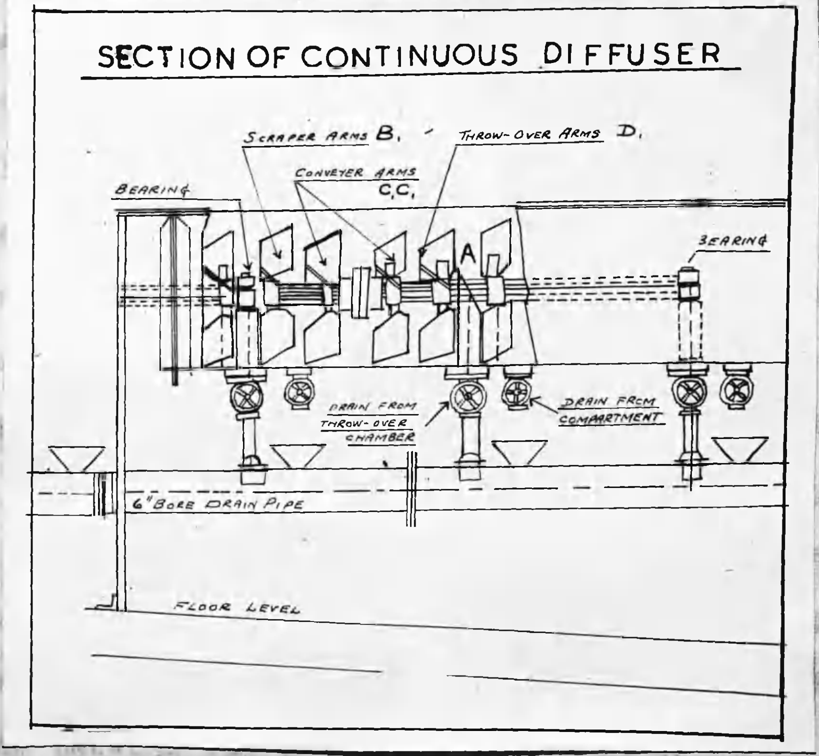


Figure 19c... Section of Experimental Continuous Diffuser.

AN EXPERIMENTAL CONTINUOUS DIFFUSER.

The continuous diffusion battery operated by the author was specially constructed for experimental work with dried beet slices.

The cylinder was 22 inches in diameter by 48 feet long, the lower half of the body being cast iron, and the upper half mild steel plate.

As shown in Figure 19b the lower part was divided into 17 chambers by partitions extending up to near the centre line. A shaft in two parts passed through the centre, each part being driven separately from the end of the diffuser (lower part 10 r.p.m., and higher part 8 r.p.m.). In each chamber there were four sets of arms. Scraping arms B kept the strainer A of the throw-over chamber free of pulp, and conveying arms C,C, propelled the pulp towards the comb-shaped arms D which lifted the pulp into the succeeding chamber.

The dried beet cossettes entered at the lower end of the diffuser, where they mixed with the liquid, and were thrown over into each succeeding chamber, passing from the top chamber to a conveyor carrying them to the pulp press. Fresh water entered at chamber F or G, while the water returned from the pulp press entered about half-way along the diffuser. Thus the fresh hot water met exhausted cossettes, passed through the strainer plate in the top chambers, over the weir lip of the partitions A, and then down between the partition plates to the next chamber, so meeting richer cossettes in succession until it left as concentrated juice at the lower end of the diffuser.

The dried cossettes were heated in a small pre-soaking tank and mixed with some previously obtained diffusion juice before entering the continuous diffuser.

The total fresh water required in such a diffuser even for fresh beets is less than half that necessary for the battery diffusion process. On fresh beets the cycle time is approximately 30 minutes, and fresh slices are normally only steamed at the slicing machines to raise their temperature to a point suitable for diffusion.

EXPERIMENTAL RESULTS.

Preliminary tests :- The pre-soaking tank as originally constructed would not discharge cossettes, and the discharge chute was lowered 3 inches and a baffle plate inserted with satisfactory results. In the first test the cossettes were exhausted to 0.46 per cent sugar, but a high density juice was not obtained.

In the second test juice of 27°Brix was obtained with pulp at 1.8 per cent sugar, but the juice purity was very low due to the prolonged soaking of the cossettes in the pre-soaking tank with consequent softening of the slices and choking of the diffuser screens. Considerable difficulty was found in maintaining sufficient heat for correct diffusion. Little water is necessary to produce a juice of 35-50°Brix, and since the quantity of slices treated was small in relation to the length of the diffuser, the heat loss was excessive, and it was necessary to carry high temperatures at bothe ends, with adverse effect on the juice purity.

The diffuser required a good deal of attention mechanically. The fine dust in the pulp was not carried forward through the diffuser and tended to accumulate in the chambers and either choke the screens or emerge with the juice. The advantage claimed that the pulp press water could be returned to the diffuser is not obtained with dried cossettes owing to the lowering of the juice purity due to the pulp press water.

Although the temperature could not be raised to the desired level, the third test gave an extraction of 86.5 per cent with waste pulp containing 2.1 per cent of sugar and juice at 48°Brix.

Results

Duration of test, hours	10.5
Wt. cossettes entering per hour, lbs	80
Per cent dust in dried cossettes	5.1
Juice drawn off, lbs. per hour	161
Draw-off, per cent on cossettes per hour	200
Theoretical draw-off per cent	133

Analyses	Dried cossettes	Raw Juice	Waste Pulp
Brix°	--	44.71	--
Sugar, per cent	64.0	36.05	2.11
Purity	--	80.63	--

Balance

Lbs. sugar entering in dried cossettes 840 lbs. at 64.0 per cent sugar	537.60
Lbs. sugar entering in Stock juice	114.20
Total	651.80
Lbs. sugar in battery at end	190.70
Lbs. sugar entering, total	461.10

Extraction, per cent on sugar	86.56
Known loss, including 1.3 per cent inversion loss	11.82
Unknown loss per cent on sugar	1.62
	100.00

Lbs. juice drawn off	1173
Lbs. waste pulp	2558

BOILING OF TREATED JUICE FROM THE CONTINUOUS DIFFUSER.

The juice was very dirty and contained a large amount of suspended pulp particles. A double clarification was given, the juice being passed through a high speed Sharples clarifier to remove the pulp and then limed to pH 7.2 and re-clarified. The clear juice was boiled to grain in a vacuum pan.

ANALYSES :-	BRIX°	PER CENT SUGAR	PURITY	pH VALUE
Raw Juice	44.71	36.05	80.63	4.5
Double Clarified Juice	46.30	38.70	83.5'	7.2
Massecuite	90.92	75.40	82.93	7.0
Green Syrup	79.90	60.20	75.36	6.9
Unwashed sugar	-	95.10	-	-

Per cent yield of crystals from massecuite............36.4

CONCLUSIONS.

The continuous diffuser would require to be provided with an efficient heating and screening system specially designed for use with dried cossettes.

It is apparent that there is greater room for losses to occur in a diffuser where both the slices and the juice are in motion. The average purity of the juice obtained and the average loss in the pulp are both less favourable then results easily maintained in a cell diffusion battery.

The maintaining of a continuous diffuser in good working order was found to be much more difficult than the maintenance of a cell battery, even in the short working periods of these tests.

SECTION 3.

PART 2 : THE DIFFUSION OF DRIED COSSETTES : - THE INVERSION PROBLEM :

1. Analyses of Diffusion Juices from Dried Cossettes :
2. Inversion - Diffusion Trials :
3. Summary of Trials.
4. The Formation of Invert Sugar during Beet Drying.

THE PROBLEM OF INVERSION IN THE DIFFUSION OF DRIED BEET COSSETTES

The main factors controlling the extent of inversion of sugar in the diffusion process are the temperature, the time of contact, the pH value of the cossettes and the juice, the density of the final raw juice drawn off, and the percentage extraction which is required. Subsidiary factors are the size of the beet slices, their chemical composition, and their compression in the battery.

Catalytic action due to the iron vessels or to the occluded gases of the battery may also be significant. The method of heating the circulating flux of the system will undoubtedly be most vital in determining the extent of inversion, or even destruction of sugar. Incidental factors such as spasmodic working or local overheating must be ignored in a general survey of the causes of this inversion.

The increase in the reducing sugars / sucrose ratio which is observed in diffusion may be occasioned in part by the formation of other reducing substances during extraction, to general errors in the methods of analysis, to the under-extraction of sucrose with complete extraction of reducing sugars, or to the influence of other bodies present in the dried cossettes on the determination of either sucrose or reducing sugars, but it is probable that the bulk of the rise is caused by inversion of sucrose.

Two problems which are of interest may be answered by the experimental work which was carried out on extraction with special reference to the behaviour of the reducing sugars. These are :-

1. Is the invert ratio increase greater when the initial amount of

reducing sugars present in the cossettes is high- in other words does invert-sugar catalyse the formation of more invert-sugar?
2. Does the invert ratio rise as the percentage extraction of sucrose is increased?

EXPERIMENTAL WORK :-

1. The diffusion battery :- This consisted of twelve iron vessels each holding approximately 200 gms. of dried cossettes. Each vessel was provided with copper screens top and bottom, and the connecting pipes were of copper. The outsides of the vessels and pipes were lagged, and the cells were arranged one above the other for convenience in working.

The trials were made (a) on ordinary 'acid-dried' cossettes- i.e. dried with furnace gases ; (b) on 'neutral' cossettes dried with pure air; and (c) on 'acid-dried' cossettes with chemical treatment in the battery. Sixteen tests were made in all.

Dimensions of the battery :-

Each cell was 6.1 inches long by 3.6 inches diameter : the effective length between screens being 5.6 inches. This gave a screen of 10.18 square inches, and a capacity of 57 cubic inches which was equivalent to 0.934 litre. The 200 gms. fill of dried cossettes per cell therefore amounted to 214 gms per litre or 21.4 Kgs. per Hectolitre.

Reagents used :- From the tests made on addition of reagents during beet drying, it was decided to try the effect of conditioning the water used for the battery with 1. Sodium hydroxide, 2. sodium carbonate, 3. Ammonium Carbonate, and 4. Lime.

ANALYSES OF DIFFUSION JUICES FROM DRIED COSSETTES

DESCRIPTION	FROM D.C. DRIED WITH FURNACE GASES		FROM D.C. DRIED WITH PURE AIR		FROM BEST DRIED COSSETTES (SELECTED)	
	ON WET %	ON DRY %	ON WET %	ON DRY %	ON WET %	ON DRY %
WATER	63.78	--	66.19	--	42.30	--
SUCROSE	31.40	86.70	29.10	86.07	50.20	86.90
Reducing SUGARS	0.82	2.86	0.67	1.98	1.05	1.82
ASH	0.73	2.02	0.93	2.75	1.21	2.16
OTHER ORGanIC MATTER (By Difference)	3.27	9.03	3.11	9.20	5.30	9.18
BRIX°	36.22	--	33.81	--	57.70	--
TOTAL NITROGEN	0.28	0.77	0.20	0.59	0.36	0.63
AMMONIACAL NITROGEN	0.07	0.20	0.05	0.15	0.10	0.18
PROTOPECTIN	0.50	1.38	0.56	1.66	0.42	0.73
SOLUBLE PECTIN	0.04	0.11	0.05	0.11	0.07	0.12
PENTOSAN	0.14	0.39	0.26	0.77	0.32	0.55
INVERT RATIO	--	2.61	--	2.30	--	2.09
pH VALUE	4.70	--	6.30	--	5.10	--
PURITY	86.70	--	86.07	--	86.90	--
ALBUMINOID NITROGEN	1.75	3.56	1.25	2.75	2.25	2.81

The albuminoid nitrogen was taken as 6.25 times(total nitrogen less ammoniacal nitrogen.).

ANALYSES OF DIFFUSION JUICES FROM DRIED COSSETTES

ASH CONSTITUENTS.

DESCRIPTION	FROM D.C. DRIED WITH FURNACE GASES		FROM D.C. DRIED WITH PURE AIR		FROM D.C. DRIED COSSETTES (SELECTED)	
	ON WET D.J.	ON DRY ASH	ON WET D.J.	ON DRY ASH	ON WET D.J.	ON DRY ASH
INSOLUBLE MATTER	0.34	16.73	0.41	14.96	0.22	10.36
SULPHATE SO_4''	0.18	8.91	0.57	20.80	0.33	15.73
SO_3''	--	7.43	--	--	--	--
CHLORIDE Cl'	0.04	2.10	0.03	1.26	0.04	1.82
P_2O_5	0.06	2.96	0.10	3.74	0.10	4.65
Al_2O_3 + Fe_2O_3	0.22	10.71	0.17	6.07	0.11	5.37
CaO	0.16	7.92	0.05	1.87	0.03	1.50
MgO	0.09	4.60	0.08	3.05	0.09	4.12
ALKALIS BY DIFFERENCE	0.93	46.07	1.34	48.25	1.18	56.45
SO_3	0.004	--	0.0005	--	--	--
LIME SALTS (AS CaO)	0.16	--	--	--	--	--

INVERSION-DIFFUSION TRIALS.

1. Diffusion at 15°C.;acid-dried cossettes ; 15 mins. contact.

2. " " 15°C.;pure-air-dried cossettes ; 15 mins. contact.

3. " " 15°C.;pure-air-dried cossettes ; water made alkaline.

4. Repeat of No. 1 Trial, using different dried cossettes.

5. Cold diffusion of pure-air-dried cossettes ; 15 mins. contact.

6. As in No. 5 Trial, with only 5 minutes contact time.

7. Cold diffusion of acid-dried cossettes with 5 mins. contact time.

8. Hot Diffusion (60°C.) of pure-air-dried cossettes : 5 mins.contact.

9. Hot Diffusion (60°C.) of acid-dried cossettes with only 5 mins. contact-time.

10. Hot Diffusion (75°C.) of pure-air-dried cossettes with 5 minutes contact-time.

11. Hot Diffusion (75°C.) of acid-dried cossettes with 5 minutes contact-time.

12. Hot Diffusion (78°C.) of pure-air-dried cossettes with 5 minutes contact-time.

13. Hot Diffusion (78°C.) of acid-dried cossettes : 5 mins. contact.

14. Hot Diffusion (78°C.) of pure-air-dried cossettes treated with Ammonium Carbonate to pH 7.1 ; 5 minutes contact time.

15. As in No. 14 Trial, using acid-dried cossettes.

16. As in No. 14 Trial, but cossettes treated with 0.5 per cent lime.

INVERSION DIFFUSION TRIALS

No. 1: Diffusion at 15°C.

Conditions :- Fill=200 gms. 'acid-dried' cossettes of analysis - % Water, 8.50 : % Sugar, 62.40 : % Invert sugar, 1.14 : % Invert Sugar on dry, 1.25 : Invert Ratio, 1.83.

Fifteen minutes contact in each cell - 12 cells filled

Cell No.	Mins Con tact	Bx° ex cell	Bx° at end	% Sug ar	% Inv.	Inv- ert Ratio	% Inv. on dry	pH	Gms. Jce.	Gms. Pulp	Purity
1.	15	--	1.19	1.10	0.23	20.9	19.33	7.5	210	610	92.45
2.	30	8.8	1.44	1.30	0.11	8.46	7.64	7.4	225	605	90.26
3.	45	16.3	2.64	2.30	0.23	10.00	8.71	7.3	180	650	87.12
4.	60	25.4	3.69	3.50	0.29	8.29	7.86	7.1	205	640	94.86
5.	75	27.8	5.59	5.10	0.21	4.12	3.76	7.0	205	640	91.24
6.	90	31.9	7.39	7.00	0.22	3.14	2.98	6.9	210	635	94.73
7.	105	32.5	9.59	8.60	0.29	3.37	3.02	6.7	215	630	89.69
8.	120	33.1	12.74	12.00	0.45	3.75	3.53	6.5	230	610	94.19
9.	135	37.2	16.88	16.00	0.65	4.06	3.85	6.3	315	590	94.77
10.	150	38.9	22.88	20.50	0.81	3.95	3.54	5.9	355	595	89.62
11.	165	41.9	31.36	28.50	0.76	2.67	2.39	5.6	325	615	90.88
12.	180	43.5	42.84	38.50	0.48	1.25	1.12	5.3	385	605	89.89

% Sugar in Pulps :- Cell 1 = 2.4 : cell 2 = 3.0 : cell 3 = 4.6

Remarks :- The most noteworthy feature in this test is the high purity of juice obtained by cold extraction. There is also a steady drop in the pH value of the juice as it concentrates from cell to cell. See Figures 20 and 21.

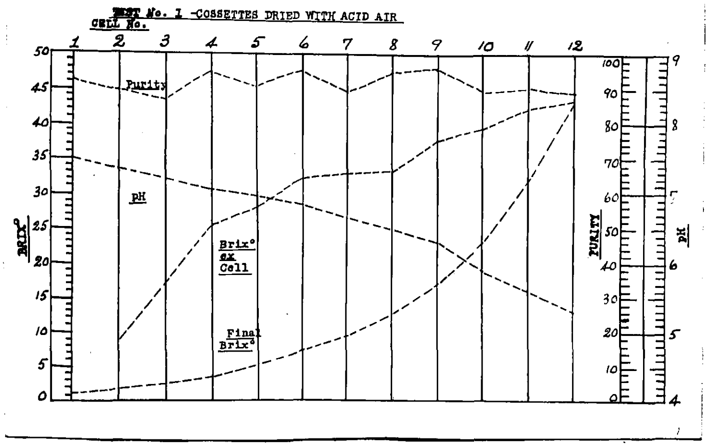

TEST No. 1 -COSSETTES DRIED WITH ACID AIR
CELL No.
1 2 3 4 5 6 7 8 9 10 11 12
BRIX°
0 5 10 15 20 25 30 35 40 45 50
Purity
pH
Brix° ex Cell
Final Brix°
PURITY
0 10 20 30 40 50 60 70 80 90 100
pH
4 5 6 7 8 9

Fig.20

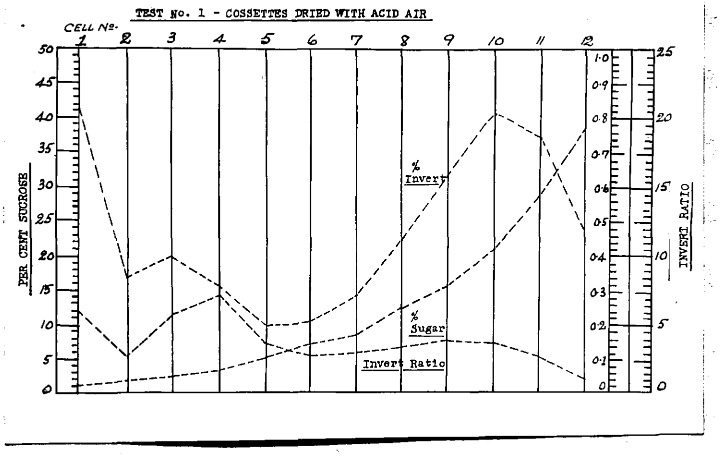

TEST No. 1 - COSSETTES DRIED WITH ACID AIR
CELL No.
1 2 3 4 5 6 7 8 9 10 11 12
PER CENT SUCROSE
0 5 10 15 20 25 30 35 40 45 50
% Invert
% Sugar
Invert Ratio
0 0·1 0·2 0·3 0·4 0·5 0·6 0·7 0·8 0·9 1·0
INVERT RATIO
0 5 10 15 20 25

Fig.21

INVERSION DIFFUSION TRIALS

No. 2 Diffusion at 15°C. using cossettes dried with 'pure' air.

Conditions :- Fill = 100 gms. Cossettes analysis - % Water, 12.0 : % Sugar, 60.8 : % Invert Sugar, 0.71 : % Invert Sugar on dry, 0.80 : Invert Ratio, 1.16. 15 minutes contact ineach of 12 cells filled.

Cell No.	Mins Contact	Bx° ex cell	Bx° at end	% Sugar	% Invert	Invert Ratio	% Invert on dry	pH	Gms. Jce.	Gms. Pulp	Purity
1.	15	--	0.40	0.20	0.45	225.0	112.5	6.9	520	370	50.0
2.	30	7.53	0.45	0.30	0.62	207.0	137.8	6.8	525	360	66.67
3.	45	9.13	0.60	0.50	0.33	66.0	55.0	6.8	530	370	83.33
4.	60	11.33	1.15	1.00	0.12	12.1	10.52	6.6	545	350	86.96
5.	75	13.23	2.05	1.80	0.22	12.22	10.73	6.4	540	370	87.80
6.	90	14.48	3.35	2.90	0.32	11.03	9.55	6.3	510	380	86.58
7.	105	16.14	4.05	3.60	0.18	5.08	4.52	6.2	520	405	88.88
8.	120	16.29	5.40	4.80	0.21	4.29	3.81	6.1	530	355	88.88
9.	135	19.89	7.73	7.00	0.16	2.33	2.11	6.0	530	350	90.55
10.	150	20.49	11.33	10.1	0.23	2.28	2.03	6.0	520	360	89.15
11.	165	21.19	15.34	14.o	0.15	1.04	0.95	5.9	595	270	91.26
12.	180	23.14	20.84	19.2	0.21	1.07	0.99	6.3	715	210	92.12

Total water used :- 9 litres. % Sugar in pulp in last vessel =0.6

Remarks :- It is clear from the above results that the drying with pure air has had a marked effect on the invert ratio during extraction. In the last few cells worked there has been little or no increase in this figure. See Figures 22 and 23.

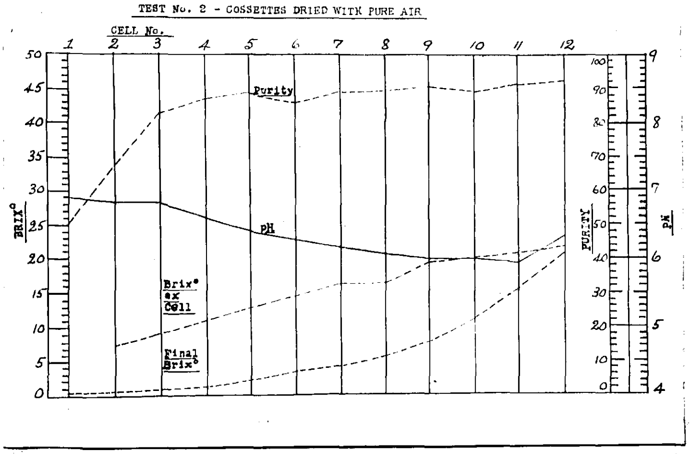

TEST No. 2 - COSSETTES DRIED WITH PURE AIR
CELL No.
1
2
3
4
5
6
7
8
9
10
11
12
BRIX°
50
45
40
35
30
25
20
15
10
5
0
Purity
pH
Brix° ex Cell
Final Brix°
PURITY
100
90
80
70
60
50
40
30
20
10
0
PH
9
8
7
6
5
4

Fig.22

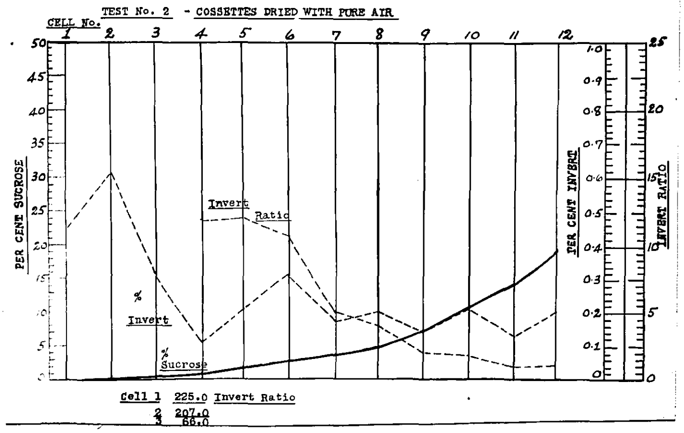

TEST No. 2 - COSSETTES DRIED WITH PURE AIR
CELL No.
1
2
3
4
5
6
7
8
9
10
11
12
PER CENT SUCROSE
50
45
40
35
30
25
20
15
10
5
0
Invert Ratio
% Invert
% Sucrose
PER CENT INVERT
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
INVERT RATIO
25
20
15
10
5
0
Cell 1 225.0 Invert Ratio
2 207.0
3 66.0

Fig.23

INVERSION DIFFUSION TRIALS

No. 3 Diffusion at 15°C. -Water made alkaline with NaOH

Conditions :- Fill = 100 gms./~~air~~ pure-dried cossettes, analysis - %Water, 8.5 : % Sugar, 62.8, : % Invert Sugar, 0.6 : % invert Sugar on dry, 0.66 : Invert Ratio, 0.96 : 15 mins. contact in each cell. Twelve cells filled, and then 13 : samples taken after 25 cells.

Cell No.	Mins Contact	Bx° ex cell	% Cell Sugar	% Invert	Invert Ratio	% Invert on dry	pH	Gms. Joe.	Gms. Pulp	Purity
1.	210	See below	0.80	0.12	14.38	12.23	9.0	360	450	--
2.	225		2.70	0.16	6.08	5.74	8.95	365	460	--
3.	240		3.70	0.27	7.30	6.68	8.50	450	410	--
4.	255		5.49	0.19	3.56	3.50	8.05	320	420	--
5.	270		7.90	0.21	2.61	2.57	7.7	365	410	--
6.	285		8.50	0.25	2.94	2.88	7.5	380	390	--
7.	300		13.60	0.22	1.62	1.51	7.3	410	365	93.46
8.	315		15.16	0.25	1.66	1.57	7.1	460	360	94.66
9.	330		17.70	0.29	1.61	1.49	7.0	540	355	92.68
10.	345		22.40	0.28	1.23	1.15	6.8	585	370	93.33
11.	360		30.20	0.22	0.73	0.69	6.6	585	365	94.14
12.	375		38.90	0.48	1.23	1.13	6.4	590	360	91.68

Remarks :- The sodium hydroxide was added to the battery water supply to give 0.084 per cent in solution. It is seen that the invert ratio has not greatly increased in these conditions, but that a slight amount of inversion is still occurring. See Figures 24 and 25.

INVERSION DIFFUSION TRIALS

No. 3 Brix° of each cell after 15 minutes contact:-

Cell No.	Brix°	Brix° at end	Minutes Contact
1	--	--	15
2	4.95	--	30
3	8.93	--	45
4	11.33	--	60
5	12.58	--	75
6	12.88	--	90
7	15.49	--	105
8	17.99	--	120
9	19.19	--	135
10	21.64	--	150
11	22.39	--	165
12	24.04	--	180
13	27.36	--	195
14	27.48	0.94	210
15	29.26	2.84	225
16	30.81	4.04	240
17	31.91	5.49	255
18	34.84	8.02	270
19	36.59	8.69	285
20	38.44	14.55	300
21	38.94	15.95	315
22	39.92	19.10	330
23	40.32	24.00	345
24	42.06	32.08	360
25	45.52	42.42	375

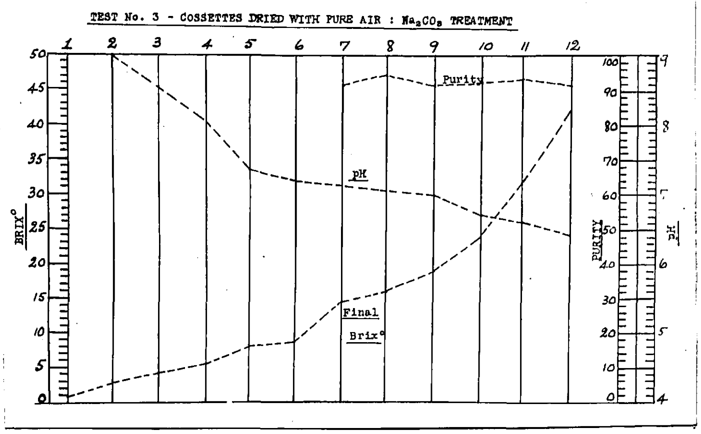

TEST No. 3 - COSSETTES DRIED WITH PURE AIR : Na_2CO_3 TREATMENT
1 2 3 4 5 6 7 8 9 10 11 12
BRIX°
0 5 10 15 20 25 30 35 40 45 50
Purity
pH
Final
Brix°
PURITY
0 10 20 30 40 50 60 70 80 90 100
pH
4 5 6 7 8 9

Fig.24

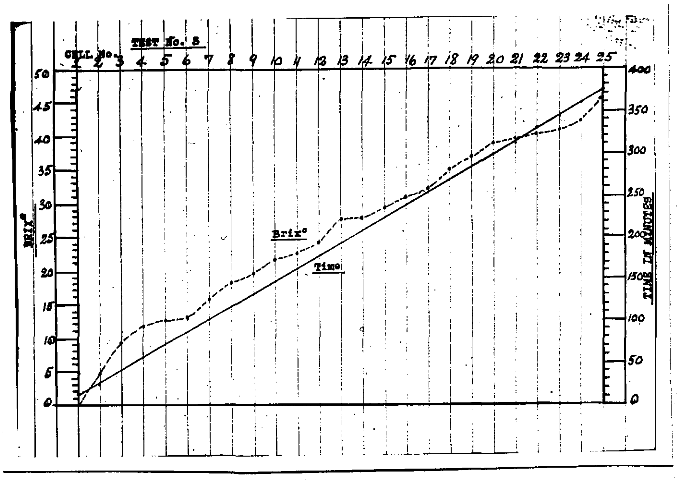

CELL No.
TEST No. 3
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
BRIX°
0 5 10 15 20 25 30 35 40 45 50
Brix°
Time
TIME IN MINUTES
0 50 100 150 200 250 300 350 400

Fig.25

INVERSION DIFFUSION TRIALS

No. 4 - Repeat of No. 1 trial - Diffusion of 'acid-dried' cossettes at 15°C.

Conditions :- Filling 200 gms. cossettes of analysis Water, 9.3 % : % Sugar, 62.4 % : Invert-Sugar, 0.6 % ; Invert Ratio, 0.96 : 15 mins. contact in each cell: 12 cells filled.

Cell No.	Mins. Contact	Bx.° ex cell	Bx.°	% Sugar	% Invert	Invert Ratio	% Invert on dry	pH	Gms. Jce.	Gms. Pulp	Purity
1	15	7.38	0.44	0.30	0.26	85.0	58.0	6.9	330	575	--
2	30	12.73	0.59	0.50	0.18	36.5	31.0	6.7	310	590	--
3	45	16.99	1.39	1.10	0.18	16.6	13.2	6.5	290	580	--
4	60	22.99	2.54	2.20	0.32	14.6	12.6	6.3	360	550	--
5	75	26.86	4.29	3.70	0.29	7.7	6.6	6.2	230	625	--
6	90	29.56	5.79	5.20	0.22	4.23	3.8	6.1	330	590	--
7	105	30.71	7.84	7.30	0.25	3.42	3.2	5.9	300	600	--
8	120	33.99	11.27	10.30	0.29	2.77	2.5	5.7	285	630	91.41
9	135	36.44	14.27	12.90	0.34	2.64	2.4	5.5	360	580	90.42
10	150	38.79	19.93	18.00	0.50	2.78	2.5	5.3	440	540	90.33
11	165	39.84	27.31	24.20	0.60	2.48	2.2	5.0	550	475	88.59
12	180	41.84	38.54	33.90	0.90	2.65	2.3	4.7	690	420	87.94

Waste pulps :- % Sugar :- Cell 1 = 1.3 : cell 2 = 1.9 : cell 3 = 2.5: 9.2 litres of water used in test.

Remarks :- Comparing this trial with No. 1, it is seen at once that there is considerable divergence in the results : the initial invert sugar content may be the cause of this.

INVERSION DIFFUSION TRIALS

No. 5 - Cold diffusion of pure-air dried cossettes:)-

Conditions :-

Filling 200 gms. cossettes of analysis :- Water, 9.2 % : Sugar, 62.8 % : Invert-Sugar, 0.6 % : Invert Ratio, 0.96 : 15 mins. contact in each cell : 12 cells filled.

Cell No.	Mins. Con-tact	Bx.° ex cell	Rx.°	% Sug-ar	% Inv-ert	Inv-ert Ratio	% Inv-ert on dry	pH	Gms. Jce.	Gms. Pulp	Pur-ity
1	15	6.55	1.14	1.10	0.16	16.3	--	6.9	260	635	--
2	30	7.20							250	640	
3	45	13.19							265	635	
4	60	16.99	5.09	4.90	0.14	2.9	--	6.8	260	640	--
5	75	19.79							270	630	
6	90	22.84							290	620	
7	105	26.36	11.27	10.7	0.19	1.79	--	6.4	270	610	94.97
8	120	28.56							290	620	
9	135	31.11							320	580	
10	150	34.89	19.68	18.8	0.25	1.33	--	6.0	430	520	95.52
11	165	35.09	26.31	24.4	0.43	1.76	--	5.9	470	470	92.72
12	180	36.14	35.29	33.20	0.45	1.36 6	--	6.3	640	340	94.08

Waste pulp fro, cell No. 1 :- % Sugar = 1.6 : total water used = 8.9 litre

Remarks :- This test again showed that even with pure-air dried cossettes of low acidity and with cold diffusion, the invert ratio rises, but is much less then with acid-dried cossettes.

INVERSION DIFFUSION TRIALS

No. 6 :- Cold diffusion of pure air-dried cossettes with shorter contact time :-

Conditions :- Filling 200 gms. per cell of cossettes of analysis :- Water, 10.3 % : Sugar, 59.2 % : Invert-sugar, 0.61 % : Invert Ratio, 1.03 : 5 minutes contact inneach cell : 12 cells filled.

Cell No.	Mins. Com-tact	Bx° ex cell	Bx°	% Sug-ar	% Inv-ert	Inv-ert Ratio	% Inv-ert on dry	pH	Gms. Jce.	Gms. Pulp	Pur ity
1	5	5.93	2.25	2.1	0.21	9.8	--	6.9	250	620	--
2	10	10.18							260	630	
3	15	11.33							280	620	
4	20	12.03	5.35	5.1	0.18	3.49	--	6.6	270	640	--
5	25	13.23							280	640	
6	30	15.04							290	635	
7	35	16.84	9.53	9.00	0.18	2.03	--	6.3	300	630	--
8	40	19.29							370	580	
9	45	20.49							350	555	
10	50	21.09	14.74	13.40	0.27	2.01	--	6.2	400	490	90.89
11	55	22.24	18.54	17.30	0.16	0.94	--	5.7	560	430	93.30
12	60	24.09	22.99	21.60	0.26	1.18	--	5.9	620	390	93.97

Cell No. 1 :- % Sugar in waste Pulp = 4.7

Remarks :- There appears to be a slight reduction in the invert ratio by the speeding up of the contact time.

INVERSION DIFFUSION TRIALS

No. 7 :- Cold diffusion of 'acid-dried' cossettes with shorter contact time :-

Conditions :- Filling 200 gms. per cell of cossettes, of analysis :- Water, 8.6 % : Sugar, 60.0 % : Invert-sugar, 0.88 % : Invert Ratio, 1.47 : 5 minutes contact in each cell : 12 cells filled.

Cell No.	Mins. Contact	Bx.° ex cell	Bx°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	7.4	3.25	2.90	0.14	4.9	6.5	220	625	--
2	10	12.1						220	630	
3	15	16.24						200	635	
4	20	20.64	6.75	6.2	0.19	3.1	6.1	200	640	--
5	25	24.64						210	645	
6	30	25.96						220	650	
7	35	29.11	14.0	12.7	0.29	2.26	5.7	230	650	90.72
8	40	30.11						290	640	
9	45	32.06						250	695	
10	50	33.46	23.44	20.6	0.57	2.77	5.4	380	580	87.72
11	55	35.60	29.71	26.4	0.80	3.01	5.3	400	630	88.86
12	60	35.85	38.70	34.3	1.10	3.21	4.8	510	570	88.63

Cell No. 1 :- % Sugar in Waste Pulp :- 4.3 %

Remarks :- There has again been a large increase in the invert ratio and acidity with the use of cossettes dried with furnace gases.

INVERSION DIFFUSION TRIALS

No. 8 :- Hot diffusion at 60°C. of pure-air dried cossettes with shorter contact time :-

Conditions :- Filling 200 gms. per cell of cossettes ,of analysis :- Water, 11.8 % : Sugar, 63.2 % : Invert-Sugar, 0.58 % : Invert Ratio, 0.92 : 5 minutes contact in each cell : 12 cells filled.

Cell No.	Mins. Contact	Bx.° ex cell	Bx°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	8.05	1.75	1.40	0.15	10.6	6.6	270	570	--
2	10	12.23						260	590	
3	15	15.24						300	605	
4	20	15.99	6.95	6.20	0.27	4.27	6.5	300	610	--
5	25	17.34						320	600	
6	30	17.89						240	640	
7	35	18.19	15.29	14.10	0.27	1.88	6.2	240	645	92.21
8	40	22.99						230	640	
9	45	24.04						310	600	
10	50	28.56	23.09	21.60	0.31	1.41	5.9	310	610	93.56
11	55	29.11	29.86	28.00	0.66	2.36	5.6	370	640	93.78
12	60	31.31	34.01	32.00	0.62	1.94	5.9	520	570	93.97

Cell No. 1 :- % Sugar in Waste Pulp :- 1.6

Remarks :- This test shows very clearly the increase in inversion caused by even a moderate increase in temperature.

INVERSION DIFFUSION TRIALS

No. 9 :- Hot diffusion at 60°C. of 'acid-dried' cossettes with shorter contact time :-

Conditions :- Filling 200 gms. per cell of cossettes of analysis :- Water, 9.9 % : Sugar, 61.6 % : Invert-Sugar, 0.61 % : Invert Ratio, 0.99 : 5 minutes contact in each cell : 12 cells filled.

Cell No.	Mins. Contact	Bx.° ex cell	Bx.°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	11.32	1.15	1.00	0.16	16.0	6.4	215	540	--
2	10	13.65						210	560	
3	15							200	590	
4	20	20.60	5.45	5.10	0.25	4.9	6.1	205	645	--
5	25	23.48						210	630	
6	30	24.98						250	640	
7	35	25.73	12.58	11.60	0.29	2.46	5.5	245	665	92.23
8	40	26.43						250	655	
9	45	28.68						350	640	
10	50	33.93	21.59	19.60	0.46	2.35	5.3	420	600	90.59
11	55	36.72	28.46	25.90	0.79	3.03	4.7	540	520	91.01
12	60	37.67	39.75	34.40	0.74	2.15	4.8	600	470	88.08

Cell No. 1 :- % Sugar in Waste Pulp :- 1.8

Remarks :- Using 'acid-dried' cossettes, the purity of the juice obtained is seen to be appreciably lower than with the pur-air dried cossettes.

INVERSION DIFFUSION TRIALS

No. 10 :- Hot diffusion at 75°C. of pure-air dried cossettes with short contact time :-

Conditions :- Filling 200 gms. per cell of cossettes, of analysis :- Water, 10.0 % : Sugar, 62.0 % : Invert-Sugar, 0.58 % : Invert-Ratio, 1.04 : 5 minutes contact in each cell : 12 cells filled.

Cell No.	Mins. Contact	Bx.° ex Cell	Bx.°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1.	5	6.98						290	630	
2	10	9.38	1.95	1.50	0.15	10.2	6.5	275	635	--
3	15	11.33						290	625	
4	20	13.33						285	640	
5	25	14.59	5.55	5.00	0.23	4.6	6.3	290	645	--
6	30	17.49						290	640	
7	35	20.49	12.53	11.60	0.37	3.15	6.1	300	630	92.60
8	40	24.61						310	635	
9	45	28.06						320	630	
10	50	31.31	22.84	21.50	0.44	2.05	5.9	325	650	94.14
11.	55	32.66	29.56	27.80	0.45	1.62	5.5	400	620	93.04
12	60	36.90	36.10	33.20	0.51	1.54	5.7	590	530	91.96

Cell No. 1 :- % Sugar in Waste Pulp :- 1.8

Remarks :- As far as was possible, the temperature in the head cell of the battery was kept at 75°C. There has been little variation in the invert ratio from the results at 60°C.

INVERSION DIFFUSION TRIALS

No. 11 :- Hot diffusion at 75°C. of 'acid-dried' cossettes with short contact time :-

Conditions :- Filling 200 gms. per cell of cossettes, of analysis :- Water, 11.0 % : Sugar, 61.6 % : Invert-Sugar, 0.64 : Invert Ratio, 1.04 : 5 minutes contact in each cell : 12 cells filled.

Cell No.	Mins. Contact	Bx.° ex cell	Bx.°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	10.83						265	625	
2	10	12.73	1.60	1.10	0.16	14.8	6.5	260	630	--
3	15	16.79						275	615	
4	20	20.49						265	640	
5	25	22.84	6.20	5.70	0.25	4.39	6.2	270	620	--
6	30	25.16						275	610	
7	35	29.06	15.34	14.10	0.28	1.95	6.0	280	610	91.91
8	40	33.21						300	580	
9	45	33.46						335	565	
10	50	35.60	25.91	23.60	0.47	1.99	5.5	320	560	91.07
11	55	36.65	33.01	29.90	0.58	1.92	5.3	490	580	90.59
12	60	38.30	41.60	36.80	1.01	2.74	4.7	530	630	88.45

Cell No. 1 :- % Sugar in Waste Pulp :- 1.4

Remarks :- The rise in invert-sugar content in the last cell (No. 12), seems abnormal, and may be due to local over-heating.

INVERSION DIFFUSION TRIALS

No. 12 :- Hot diffusion at 78°C. of pure-air dried cossettes treated with Na_2CO_3 to pH 7.1 : short contact time.

Conditions :- 200 gms. cossettes per cell. Analysis :- Water, 11.8 %: Sugar, 60.4 % : Invert-Sugar, 0.53 % : Invert Ratio, 0.88 : 5 mins. contact per cell : 12 cells filled: Na_2CO_3 used-0.2 % on D.C. weight.

Cell No.	Mins. Contact	Bx.° ex cell	Bx.°	% Sug-ar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	8.03						280	635	
2	10	8.38	1.90	1.70	0.16	9.59	7.1	285	640	--
3	15	13.09						275	625	
4	20	13.24						280	630	
5	25	13.24	7.75	7.00	0.27	3.79	6.6	290	620	--
6	30	14.29						295	605	
7	35	18.09	15.24	14.10	0.24	1.70	6.7	300	625	92.53
8	40	20.79						305	630	
9	45	21.34						330	615	
10	50	24.64	22.84	21.30	0.23	1.08	6.8	340	620	93.26
11	55	27.01	28.01	26.10	0.19	0.74	6.9	410	600	93.15
12	60	30.31	33.61	30.40	0.38	1.25	7.2	580	520	92.58

Cell No. 1 :- % Sugar in Waste Pulp :- 2.0

Remarks :- It is evident that inversion still occurs despite the treatment with alkali, but is considerably lessened.

INVERSION DIFFUSION TRIALS

No. 13 :- Hot diffusion at 78°C. of 'acid-dried' cossettes treated with Na_2CO_3 to pH 7.1 : short contact time.

Conditions :- 200 gms. cossettes per cell. Analysis :- Water, 10.6 %: Sugar, 59.2 % : Invert-sugar, 0.94 % : Invert Ratio, 1.59 : 5 mins. contact per cell : 12 cells filled : Na_2CO_3 used-0.2 % on D.C. weight

Cell No.	Mins. Contact	Bx.° ex cell	Bx.°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	8.73	1.85	1.70	0.14	7.9	7.1	260	635	--
2	10	13.94						270	620	
3	15	20.19						275	610	
4	20	21.54	9.38	8.30	0.31	3.7	6.5	260	625	--
5	25	25.16						280	610	
6	30	26.81						275	620	
7	35	27.41	20.29	17.80	0.33	1.85	6.4	290	600	87.72
8	40	29.26						305	585	
9	45	32.36						340	565	
10	50	33.41	29.94	26.80	0.50	1.87	6.3	345	545	89.50
11	55	35.05	37.70	33.00	0.64	1.94	6.0	330	560	87.54
12	60	39.40	42.35	37.40	0.995	2.66	6.4	495	590	88.35

Cell No. 1 :- % Sugar in Waste Pulp :- 1.6

Remarks :- These acid-dried cossettes would require a larger dose of sodium carbonate to ensure that the diffusion went on at 6.9-7.1 pH.

INVERSION DIFFUSION TRIALS

No. 14 :- Hot diffusion at 78°C. of pure-air dried cossettes treated with $(NH_4)_2CO_3$ to pH 7.1 : short contact time.

Conditions :- 200 gms. cossettes per cell : Analysis :- Water, 9.0 %: Sugar, 61.2 % : Invert-Sugar, 0.51 : Invert Ratio, 0.83 : 5 mins. contact per cell : 12 cells filled : $(NH_4)_2CO_3$ - 0.4 % on D.C. wt.

Cell No.	Mins. Contact	Bx.° ex Cell	Bx.°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	7.03	3.25	2.50	0.15	5.92	7.1	280	635	--
2	10	12.19						270	630	
3	15							285	625	
4	20	14.44	8.83	7.60	0.18	2.34	6.7	295	635	--
5	25	14.89						280	640	
6	30	15.79						295	620	
7	35	19.44	17.34	16.10	0.19	1.92	6.9	300	615	92.85
8	40	19.79						315	625	
9	45	20.49						330	640	
10	50	22.24	24.04	22.10	0.19	0.87	7.3	390	600	91.94
11	55	22.99	26.66	23.80	0.18	0.75	7.5	410	590	89.28
12	60	25.71	29.66	26.80	0.30	1.12	7.7	565	635	90.33

Cell No. 1 :- % Sugar in Waste Pulp :- 1.6

Remarks :- The waste pulp was greener than with soda treatment, and the juice was slightly darker than usual.

INVERSION DIFFUSION TRIALS

No. 15 :- Hot diffusion at 78°C. of 'acid-dried' cossettes treated with $(NH_4)_2CO_3$ to pH 7.1 : short contact time.

Conditions :- 200 gms. cossettes per cell : Analysis :- Water, 11.2 per cent : Sugar, 58.4 % : Invert-Sugar, 1.32 % : Invert Ratio, 2.26: 5 minutes contact per cell : $(NH_4)_2CO_3$:- 0.4 % on D.C. weight.

Cell No.	Mins. Contact	Bx.° ex Cell	Bx.°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	4.04	2.74	2.00	0.16	8.2	7.0	270	620	--
2	10	10.77						260	625	
3	15	15.45						280	610	
4.	20	18.90	8.91	7.60	0.17	2.24	6.6	270	630	--
5	25	20.60						265	620	
6	30	21.90						285	610	
7	35	24.15	16.35	15.10	0.27	1.75	6.3	305	590	92.37
8	40	26.53						330	560	
9	45	30.33						325	555	
10	50	30.43	25.98	23.30	0.16	0.70	6.2	495	570	89.69
11	55	31.03	33.33	29.80	0.81	2.70	6.1	490	560	89.41
12	60	37.27	38.37	33.70	0.94	2.79	6.1	510	620	87.82

Cell No. 1 :- % Sugar in Waste Pulp :- 1.9

Remarks :- The juice here was dark, and the pH was too far on the acid side to keep inversion down. As a whole, however, this test and No.14 gave the best results obtained in inversion-reduction.

INVERSION DIFFUSION TRIALS

No. 16 :- Hot diffusion at 78°C. of pure-air dried cossettes treated with 0.5 % Lime : short contact time.

Conditions :- 200 gms. cossettes per cell : Analysis :- Water,10.9%; Sugar, 58.4 % : Invert-Sugar,0.48 % : Invert Ratio,0.82: 5 minutes contact per cell : 12 cells filled.

Cell No.	Mins. Contact	Bx° ex Cell	Bx°	% Sugar	% Invert	Invert Ratio	pH	Gms. Jce.	Gms. Pulp	Purity
1	5	3.35						280	620	
2	10	6.75	3.65	2.9	0.15	5.0	7.3	285	630	--
3	15	10.03						290	625	
4	20	10.18						295	620	
5	25	12.38	8.03	7.4	0.15	2.1	6.9	280	640	--
6	30	12.88						300	625	
7	35	15.64						310	620	
8	40	16.24	14.59	13.4	0.32	2.35	7.0	315	640	91.85
9	45	17.34						325	605	
10	50	18.09	19.89	18.4	0.58	3.13	7.1	325	610	92.51
11	55	26.34	23.14	21.8	0.44	2.02	7.5	390	595	94.23
12	60	26.36	26.31	24.7	0.58	2.35	7.7	540	565	93.87

Cell No. 1 :- % Sugar in Waste Pulp :- 2.6

Remarks :- The lime was made into a cream with water and well mixed with the total bulk of cossettes before the test. The above results show a considerable increase in the invert ratio with conditions almost completely alkaline throughout the system.

SUMMARY OF INVERSION DIFFUSION TRIALS

CONDITIONS	TRIAL No.							
	1	2	3	4	5	6	7	8
Gms. Fill	200	100	100	200	200	200	200	200
Contact time mins.per cell	15	15	15	15	15	5	5	5
Temp. °C. at Head	15	15	15	15	15	15	15	60
Cossettes	Acid	Neut.	Neut.	Acid	Neut.	Neut.	Acid	Neut.
Invert Ratio Cossettes	1.83	1.16	0.96	0.96	0.96	1.03	1.47	0.92
Invert Ratio 3rd, Head Vessel	3.95	2.28	1.23	2.78	1.33	2.01	2.77	1.41
Invert Ratio 2nd. Head Vessel	2.71	1.04	0.73	2.48	1.76	0.94	3.01	2.36
Invert Ratio Head Vessel	1.25	1.07	1.23	2.65	1.36	1.18	3.21	1.94
Tail Pulp % Sugar	2.4	0.6	3.7	1.3	1.6	4.7	4.3	1.6
Highest Brix°	42.8	20.8	42.4	38.5	35.3	23.0	38.7	34.0
Purity at Head	89.9	92.1	91.7	87.9	94.1	94.0	88.6	94.0
pH Value at Head	5.3	6.3	6.4	4.7	6.3	5.9	4.8	5.9
Treatment	--	--	soda water	--	--	--	--	--

SUMMARY OF INVERSION DIFFUSION TRIALS
(CONTINUED)

CONDITIONS	TRIAL No.							
	9	10	11	12	13	14	15	16
Gms. Fill	200	200	200	200	200	200	200	200
Contact Time Mins. per cell	5	5	5	5	5	5	5	5
Temp. °C. at Head	60	75	75	78	78	78	78	78
Cossettes	Acid	Neut.	Acid	Neut.	Acid	Neut.	Acid	Neut.
Invert Ratio Cossettes	0.99	0.94	1.04	0.88	1.59	0.83	2.26	0.82
Invert Ratio 3rd. Head Vessel	2.35	2.05	1.99	1.08	1.87	0.87	0.70	3.13
Invert Ratio 2nd. Head Vessel	3.03	1.62	1.92	0.74	1.94	0.75	2.70	2.35
Invert Ratio Head Vessel	2.15	1.54	2.74	1.25	2.66	1.12	2.79	2.35
Tail Pulp % Sugar	1.8	1.8	1.4	2.0	1.6	1.6	1.9	2.60
Highest Brix°	39.8	36.1	41.6	33.6	42.4	29.7	38.4	26.3
Purity at Head	88.1	92.0	88.5	92.6	88.4	90.4	87.8	93.9
pH Value at Head	4.8	5.7	4.7	7.2	6.4	7.7	6.1	7.7
Treatment	--	--	--	Soda Ash	Soda Ash	Amm. Carb,	Amm. Carb.	CaO
% Reagent on Cossettes	--	--	--	0.2	0.2	0.4	0.4	0.5

CONSIDERATIONS REGARDING THE FORMATION OF INVERT- SUGAR DURING THE DRYING OF SUGAR BEET.

The invert ratio = $\dfrac{\%\ \text{Invert-Sugar} \times 100}{\%\ \text{Sucrose}}$

Let FI = % Invert-Sugar in fresh beet : FS = % Sucrose in fresh beet.

Let DI = % Invert-Sugar in Dried cossettes, and

Let DS = % Sucrose in dried cossettes

Then Increase in Invert Ratio $= \left(\dfrac{100DI}{DS} - \dfrac{100FI}{FS} \right)$

Example :- FI = 0.127 : FS = 17.05 : DI = 0.858 : DS = 64.53

so increase in Invert Ratio $= \left(\dfrac{100 \times 0.858}{64.53} - \dfrac{100 \times 0.127}{17.05} \right)$

which equals 0.585.

The increase of invert- sugar only represents 342/360 parts of sucrose, i.e. 0.95 of sucrose . So for the above example the formula becomes :- $\left(\dfrac{85.8 \times 0.95}{64.53} - \dfrac{12.7}{17.05} \right) = 0.518$

Formula on tonnage :-

FI : FS : DI : DS, as before : TD = tons dried cossettes and TF = tons fresh beet. The per cent Inversion on beets during drying is given by :-

$$\left(\frac{\dfrac{TD \times DI \times 0.95}{100} - \dfrac{TF \times FI}{100}}{TF} \right) = \text{say, } \frac{A}{TF}$$

Then Loss of Sucrose due to Inversion expressed as a per cent on Sucrose present in the original beet :-

$$= \left(\frac{A}{\dfrac{TF \times FS}{100}} \right)$$

An example is given to show the application of this formula during a day's run :- TD = 52.7161 tons : TF = 201.419 tons (in 24 hours).
So formula becomes :-

$$\left(\frac{\frac{52.7161 \times 0.858 \times 0.95}{100} - \frac{201.419 \times 0.127}{100}}{201.419} \right)$$

Which works out to 0.086 per cent loss of sucrose by inversion on weight of fresh beet entering.

$$\text{Per cent on Sugar entering} = \left(\frac{0.173 \times 100}{\frac{201.419 \times 17.05}{100}} \right) = 0.504$$

The final difference between the increase in the Invert Ratio and the per cent Loss on sugar due to inversion represents the inaccuracy in the actual analyses and in the weighing and sampling.

In order to obtain an accurate figure for the amount of sugar as sucrose lost by formation of invert-sugar during drying it is necessary to have :-

1. Accurate weighings, and no "mechanical" losses,
2. No alteration of the polarisation during drying except that due to inversion.
3. No formation of dextro-rotatary matter capable of concealing loss of sugar and polarisation.
4. Assurance that the original invert-sugar, as also that formed by inversion is not destroyed during the drying process.

It is at once apparent that there is no guarantee that any of the points mentioned can be assumed ; on the contrary it is certain that most of these errors occur.

If we consider that destruction of sucrose is small enough, we can assume that the Polarisation of the dried cossettes is equal to 'n' times the Polarisation of the fresh beet where 'n' is the Drying Ratio. On this basis the Invert Ratio of the dried material instead of being $\left(\frac{DI \times 100}{DS}\right)$ is $\left(\frac{DI \times 100}{nFS}\right)$.

It will be seen that the increase in Invert Ratio or the destruction of sucrose during drying, calculated in this way, will be :-

$= FS \left\{\frac{DI}{DS} - \frac{FI}{FS}\right\}$. Taking the figures of the previous example this will give:-

Increase in Invert Ratio $= 17.05 \left(\frac{0.858}{64.53} - \frac{0.127}{17.05}\right) =$

$= 17.05 \times 0.00585 = 0.0997$. This does not allow for the 0.95 factor for conversion of sucrose to invert-sugar, so allowing for th this the calculation becomes more complicated.

The essence of the calculation is that DI -the invert-sugar found in the dried cossettes consists of the original invert in fresh beet multiplied by the drying Ratio plus the invert formed by inversion again multiplied by the drying Ratio; i.e. say there is 0.1 % invert in fresh beet and a drying Ratio of 4, this will be 0.4 % invert in the dried cossettes. Thus if we find 0.6 % invert in the dried cossettes the difference 0.2 will be due to sucrose inverted if no other change has taken place, and this amount of sucrose inverted will be (0.2 x 0.95) or 0.19 per cent. If we take fresh beet at 15.0 polarisation and dried cossettes at 60.0 polarisation the F.B. invert Ratio will be 0.67, and the D.C. invert ratio will be 1.00, and the increase in invert ratio 0.33.

However taking (DI - nFI) x 0.95 as the true increase in invert-sugar the amount is (0.6 - 0.4) x 0.95 = 0.19 per cent increase in invert, and therefore the true increase in invert ratio will be :-

$$\frac{(0.19 \times 100)}{60} = 0.317 \text{ (instead of 0.33).}$$

Drying Ratio :- This may be variously defined as :-

1. The proportion of dry material to wet material by (a) weight : (b) volume.
2. The proportion of wet material required to produce one unit of dried material.

The percentages of moisture, polarisation, fibre, and ash should agree for the wet and dry materials after correction by this factor.

This drying ratio is clearly important, and if a true average figure is known it would be possible to obtain a correct balance of the sucrose and weight of cossettes produced by multiplying the % sucrose in the fresh beet by this drying ratio.

The following excerpt shows campaign averages over 50 days :-

Tons fresh beet sliced = 9538.8910

% Polarisation = 18.21

% Water = 73.47 : so % Solids = 26.53

% Water in Dried Cossettes = 8.16 : % Solids = 91.84

The Drying Ratio = $\frac{91.84}{26.53}$ = 3.4617

The theoretical % Polarisation in Dried Cossettes = 63.04

Actual percentage in D.C. from lab. average = 65.44

Tons Dried Cossettes recorded = 2636.1642

If % polarisation is 65.44 and the theoretical weight of Dried Cossettes produced is 2755.551 tons (9538.8910/3.4617) the loss will be given by $\frac{2755.551 \times 63.04}{65.44}$ = 2654.49 tons D.C., the difference from the recorded weight (2636.1642) being 18.33 tons. The loss from the recorded weights and analyses is shown below :-

Tons sucrose (polarisation) in fresh beet = 1737.032
Tons sucrose (polarisation) in dried coss.= 1725.118
Tons Loss of sucrose (polarisation) = 11.914

Summarising :-

Tons sucrose in fresh beet = 9538.9910 x 0.1821 = 1737.032(Actual)
Tons sucrose in dried coss.= 2755.5510 x 63.04 = 1737.099(Theory)
Tons sucrose in dried coss.= 2636.1642 x 65.44 = 1725.118(Actual)

It is clear that the theoretical sucrose in the dried cossettes takes no account of inversion or destruction losses.

The key figure in these analyses is the per cent polarisation in the fresh beet. In drying control this is estimated by a hot digestion method, and such methods are known to give almost always a slightly higher polarisation (0.1-0.2) than the cold digestion practised in the tare house, and it may therefore be possible that the loss in drying as recorded may be due in part to errors in the method of analysis and to differences in the sampling.

A balance such as that above is only a check on the overall accuracy of the chemical control of the drying process.

SECTION 4.

THE PURIFICATION OF RAW BEET DIFFUSION JUICES OF HIGH DENSITY FROM DRIED BEETS :

PART 1 : GENERAL :

1. Sugar Manufacture :
2. Definitions of Technical Terms used :
3. The Purification of Sugar Juices :
4. The Composition of Raw Juices from the Cane and Beet :
5. The Composition of Products in Beet Sugar Manufacture:
6. Colloids in Beet Sugar Juices and their removal :
7. The Determination of Colloids in Sugars and Sugar Products.

SUGAR MANUFACTURE

The process of sugar manufacture can be divided into three parts-

1. Extraction of the sugar from the plant yielding a raw juice,
2. Purification of the raw juice
3. Crystallisation of sugar

On the efficiency of the extraction depend the quantity and purity of the raw juice, and on the purification process depend the quality and yield of the final sugar. These two processes are more important than the crystallisation process, which, while relatively skilled, is essentially mechanical.

Beet Sugar Manufacture :- Synopsis

The washed beets which have been 'topped' and 'tailed' are cut into slices called cossettes, of inverted V-section.

The cossettes are packed into the cells of a diffusion battery where the sugar, with soluble impurities, is extracted by water at carefully regulated temperature. The raw juice thus obtained is purified by chemical treatment, and the precipitated impurities are removed by filtration.

The sugar is recovered from the purified juice by evaporation and fractional crystallisation. When the mother-liquor can no longer be profitably treated it is discarded (as molasses).

Premises fundamental in other industries are equally applicable to the sugar industry, i.e., the impurities should be removed and the final product obtained in the minimum time and at the minimum cost, and there should be maximum yield of the final product.

DEFINITIONS OF TECHNICAL TERMS USED :

Brix°	The Brix hydrometer gives directly the percentage of sucrose in pure sucrose solutions. When impurities are present in a solution the Brix° shown is higher than the true sucrose content.
Direct Polarisation	This is the sum of the readings due to all sugars present in a given sugar solution. In raw sugars containing only about 1 per cent of reducing sugars the direct polarisation is very close to the true percentage of sucrose.
Purity	The approximate amount of sucrose as shown by the direct polarisation, when multiplied by 100 and divided by the Brix° of a solution is known as the apparent purity : it is also known as the purity coefficient or quotient.
Massecuite.	This term, (literally a "cooked mass"), refers to the mixture of crystals and mother-liquor resulting from the boiling and crystallisation of sugar liquors in a vacuum pan.
Molasses	This term is applied to the syrup spun off from a massecuite in centrifugals. The final molasses is the syrup from the lowest purity massecuite, and the impurities in this syrup are sufficiently great in amount to make it uneconomical to recover further sucrose from it by ordinary means.
Cossettes	These are the slices into which the sugar beets are cut by revolving knives. They are about three inches long, a quarter of an inch wide, and an eighth of an inch thick.

THE PURIFICATION OF SUGAR JUICES: INTRODUCTION

The raw juice extracted from the sugar cane or from the sugar beet is a complex mixture of organic and inorganic substances, some in suspension, some in colloidal solution, and some in true solution.

Many of these compounds exert a harmful effect on the crystallization of sugar from the juices, causing slow working in the evaporation and boiling pans, and in the subsequent separation of the crystals. If allowed to remain in the juice they will increase the amount of molasses formed.

The amount of sugar produced will depend on how efficiently these impurities can be removed.

Over twelve centuries ago in Egypt the use of lime and heat was practised for making raw sugar, and this is largely the process used to-day, when it is probable that about 90 per cent of the world's cane sugar is made with lime as the sole chemical employed.

This is undoubtedly due to the small difference of profit to be expected by changing existing methods, since there are many suitable reagents available for purification. Thus Von Lippmann, (Deut. Zuckerind.,34, 9, 1909) listed 622 proposed processes for sugar manufacture, and many others have been described since then.

Few of these have persisted, mainly because of the low price of sugar, and the small margin of profit in its manufacture.

Recent work on purification of sugar juices by ion exchange using synthetic resins has so far proved uneconomic owing to the high cost of the resins and their regenerating chemicals, and to the need to keep temperatures below 20°C., which is difficult in the tropics.

The Purification of Sugar Juices.

In beet sugar manufacture and in the making of cane plantation white sugars, lime and sulphurous acid, or lime, sulphurous acid, and carbonic acid are used, and these three agents are those mainly used in current processes. Sodium carbonate finds occasional use in eliminating lime-salts. Animal charcoal is used only in sugar refineries, and decolorising carbons are used to a limited extent in the direct manufacture of white sugars.

The purification by lime and heat appears to be largely an inorganic reaction in which the flocculent precipitate traps the coarse suspensions of the juice, occludes the finer suspensions, and adsorbs some of the colloids : few ,if any, of these reactions can be quantitative. The colloids removed aremainly irreversible- i.e. they do not re-disperse when taken up again with water. Reversible colloids appear to pass through the process almost without change. Paine, Keane, and McCal~~lep~~ip (I.E.C.,p.262,1928), showed that an excess of lime over the optimum amount required for defecation probably converts irreversible colloids into the reversible type, and may enter into direct chemical combination with these reversible colloids : it also appears to have a peptising effect on the pectinous substances in the juice. We thus have a scientific basis for the avoidance of excess lime, which has long been known to cause poor after-working, and to produce dark sticky sugars.

Many workers have shown that the phosphate content of cane juice is a vital factor in efficient purification. Walker (I.E.C., 164, 1923), found that 0.02 gm. P_2O_5 per ml. of juice was the minimum requirement for good clarification. R.H.King, (The Planter,287, 1927), found that the ferric, aluminium, and silicate ions of the juice formed a very gelatinous precipitate when lime was added, and that much organic matter was occluded in this precipitate and thus removed from the juice : he agreed that phosphate ion had a major influence in proper clarification.

Paine and his co-workers showed that colloid elimination was directly proportional to the amount of lime added and the amount of P_2O_5 present at a controlled pH value. They found that added phosphate had the same effect as that naturally present in the juice. Noel Deerr ("Cane Sugar", London, 1920) found that filtration through asbestos would remove 75 per cent of the total non-sugars eliminated by a lime and heat treatment.

COMPOSITION OF CANE AND BEET RAW JUICES.

The sugar cane and the sugar beet vary greatly in composition depending on the country of origin, the climate, the locality, and the particular year. The character of the soil, the age of the plant and its variety, the manner of fertilisation and the mode of cultivation have also considerable effect on its composition. This variation is naturally reflected in the composition of the raw juices extracted, but the non-sugars of these juices can be classified qualitatively as follows :-

1. Mineral Matter:- this generally consists of salts of sodium, potassium, calcium, magnesium, aluminium, iron and ammonium which have been acquired from the soil during the growth of the plants. These bases are combined with acids as chlorides, sulphates,

nitrates, phosphates, and etc.

2. Organic Salts:- composed of the same mineral elements combined with organic acids such as acetic, oxalic, citric, tartaric, malic and succinic acids.

3. Nitrogenous organic compounds:- such as albuminoids. These bodies occur more abundantly in beet juice, which contains among others, asparagine, betaine, glutamine, legumine, leucine, trimethylamine, and tyrosine, with compounds derived from these.

4. Non-nitrogenous organic compounds :- These include glucose and levulose, Raffinose (in beet), waxes, aromatic substances, pectin and related bodies, mannite, dextran, cellulose, gums, essential oils, arabimose, vanillin, and colouring matter.

5. Enzymes :- These include soluble ferments, acting for the most part by hydrolysis as colloid catalysers. Diastase, invertase, maltase, lactase are the chief sugar-splitting enzymes known to be present. Emulsin, which attacks glucosides is present, and there are several proteo-splitting enzymes, and also oxidase, reductase, and catalase, which effect biological oxidations and reductions.

Cane-wax, a complex mixture of alcohols or esters of high-boiling point, has been found to be mainly responsible for the objectionable colloidal properties of cane juices, particularly that part of the wax soluble in acetone. Much of the wax is removed in defecation, but part may re-enter the juice during the washing and steaming of the filter-press cake.(Bardorf,I.E.C.,20,258,1928. :21,366,1929).

SILICA :- In organic combination, silica appears to affect the milling qualities and the ease of clarification of the cane. The milling would seem to be mainly influenced by the "encrusting" silica, usually abundant in the peripheral tissues of grasses, (Hardy, I.S.J.,120, 1945). Phosphate and silica in the soil are mutually replaceable in certain chemical combinations (Branchley, Maskell, and Warington, Ann Appl. Biol.,45,1927),so that the silicate status of soil may be closely connected with its status as regards phosphate, and Hardy suggests that suitable soil treatments may reduce clarification trouble in the factory due to colloidal inorganic compounds, particularly silica.

OTHER ORGANIC MATTER :- It is beyond doubt that pentosans, gums, pectins, and various products of carbohydrate oxidation may interfere with purification and filtration processes. Phosphate seems to be concerned in this oxidation (Dickens, Nature,1057, 1936). Preliminary studies of uronic acid and methoxyl content of cane juices have been made (Browne and Phillips, I.S.J.,430,1939).

PROTEINS :- Proteins are thought to aid clarification, presumably because they form stable flocs when the juice is heated and limed. Theymay possibly hydrolyse into peptones and amino-acids during these processes.

ASH :- It has been suggested that juice quality may in some cases be due to the presence of traces of manganese in the plant. It is known that sulphates and chlorides are often harmful, and that the calcium intake of the plant is uniform, regardless of the lime status of the soil.

The Composition of Products in Beet Sugar Manufacture.

The ordinary process of Beet Sugar Manufacture by the Double Carbonatation Process generally gives a purity rise of 3 to 3.5 degrees. The figures shown diagrammatically in Figure 26 portray clearly the gradual increase in purity as defecation prodeeds, and the decrease in density due to the various filtrations.

The pressed juice sample is one obtained by hydraulic pressure in the laboratory, when more impurities are extracted than by diffusion. The fluctuation of density is important from the heat economy standpoint : excessive dilution must be avoided for obvious reasons. The Melter Solution consists of Second Product Sugar dissolved in thin juice and returned to process.

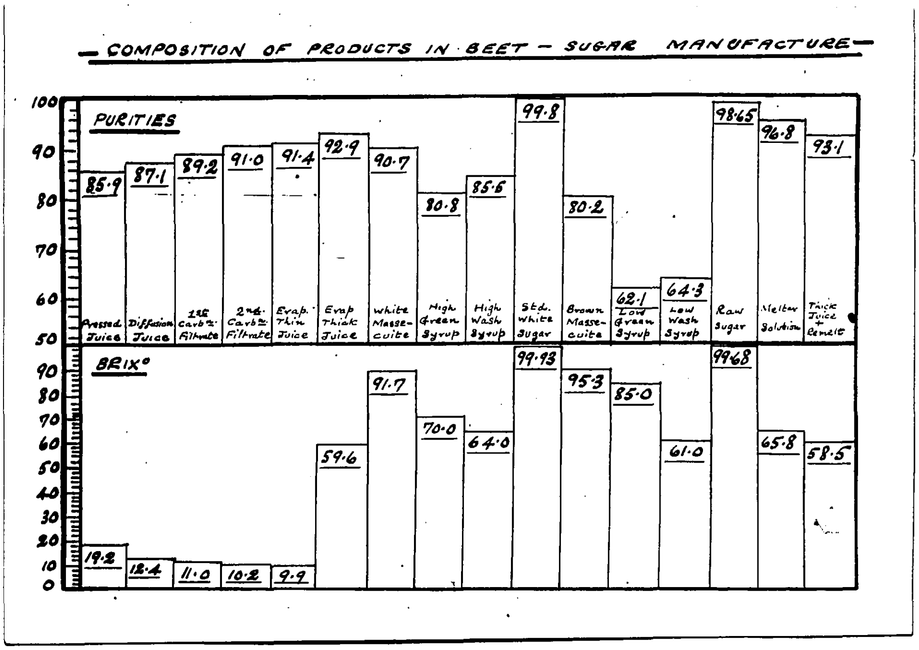


Figure 26

COLLOIDS IN BEET SUGAR MANUFACTURE AND THEIR REMOVAL.

Colloid chemistry is important in beet sugar technology as has been emphasised by Kruyt (Arch. Suikerind.,29,1102,1921) and by Berge (Bull.Soc.Chim.Belg.,38,31,1929). The organic matter associated with the sugar in beets is largely of colloidal character : with diffusion processes there is a purer juice than where extraction is made by pressure. The colloids flocculate in diffusion juic at pH 4.5 and pH 10.5, and at these values hot water diffusion is not possible because of inversion loss in the acid range or very slow diffusion in the alkaline range.

The raw diffusion juice is usually purified by double carbonatation, this consisting of the addition of lime (2 Kgs. per 100 Kgs. beets) and passage of CO_2 at 75°C. After filtering, this operation is repeated at 90°C.,using 0.25 to 0.50 Kgs. lime per 100 Kgs. beet. The filtered juice should now be brilliant and free from colloids. Heat coagulates the colloids, and their flocculation is total at 10.5 - 11.5 pH (Aten,Rec. Trav.Chem.,45,792,1926),corresponding to the addition of 0.1 gm. CaO per 100 Kgs. beets. The excess carbonate acts as an adsorbent and as a filter-aid : this may be shown by use of a Sharples Centrifugal which shows two layers,one of almost pure $CaCO_3$,and one One of $CaCO_3$ plus organic matter of a bluish tint. Baissac (Planter and Sugar Manufacturer,76,540,1926) found that the most desirable swelling of cane juice colloids occurs at circa 7.0 pH, and that further liming causes greater swelling and much reduced filtration rates.

Concentration of the purified juice causes the appearance of colloids escaping removal in the previous process : these are mainly of emulsoid type (Paine and Balch, I.E.Chem.,16,1255,1924). This colloidal matter strongly retards sugar crystallisation : thus Berge (loc.cit.) reports tests with three sugar solutions :- 1.Blank, 2. Containing added colloids from molasses, and 3. Treated with 0.25 per cent Norit and filtered. All were seeded with sucrose and evaporated under identical time/temperature conditions : the yields of sugar were 33.8 , 4.8, and 34.2 gms. respectively.

BEHAVIOUR OF JUICES WITH LIME.AND HEAT.

Addition of lime to hot juice yields a precipitate which becomes optimum in quantity and properties with correct lime control. The precipitate sweeps down colloidal impurities and remove the colloidal matter both by adsorption and mechanical action.

The exact pH value necessary for maximum defecation has been hotly disputed . Paine and Balch (loc.cit.) state that maximum clarification and minimum inversion loss occurs when cane juices are limed (hot or cold) at pH 8-9, the pH varying with individual juices. Roxas (I.S.J.,26,486,1924) mentions that liming cold and then heating to boiling point gave two points of maximum clarity, at pH 5.22 - 6.50 and pH 11-12. Honig and Khainovsky (Arch. Suikerind.,35,639, 1937) obtained maximum defecation when the pH of the treated juice was 7.2-7.6. Britton has studied pH limits in defecation ("Hydrogen Ions," London,p. 397 seq.,1929). He found that sucrose acted as a buffer against decrease in pH value in the reaction between calcium hydroxide and aqueous solutions of phosphoric acid. At 20°C. precipitation of calcium is delayed until pH 6.7 is reached and 1.5 equivalents of calcium hydroxide are added.

The determination of Colloids in sugars and sugar products.

The removal of colloids is one of the principal aims in the clarification of impure sugar juices. Colloids increase the viscosity of the products and hinder crystallisation ; they are adsorbed on sugar crystals during their growth and cause the production of dull off-coloured sugars.

Methods proposed for the determination of colloids in sugar products include direct methods such as dialysis, ultra-filtration, and and centrifuging, and other methods such as the determination of the'Gold number'or of the'Dye number'.

Dialysis is tedious,and difficult to control and standardise, and has not been much used. Centrifuging requires very high speeds and expensive equipment and for these reasons has not been widely adopted. Ultra-filtration, however, has been used with considerable success by Paine, Gertler, and Lothrop (I.E.C.,26,73,1934), who used a method due to Dawson. Paine, Badollet, and Keane (I.E.C., 16, 1252, 1924) made determinations of the Gold numbers of granulated sugars and of beet molasses. The Dye number method was devised by Badollet and Paine,(I.S.J.,vol.28, 28, 97, 137, 497,(1926) : Louisiana Planter,79, 121, (1927), and has been fairly extensively used in the cane-sugar industry.

The Dye Number :- This method is based on the fact that the colloid substances in cane and beet juices carry a negative charge,and that this charge can be neutralised by the addition of a known amount of a positively charged colloid causing complete flocculation of the colloid complex when the isoelectric point is reached.

The dye Night Blue has been found satisfactory as the positive colloid, giving rapid flocculation and settling of the precipitate. It is used as a 0.1 per cent solution, not more than a week old.

The pH value of the product to be tested must be adjusted to a uniform figure, choosing a fairly low value as standard : values of 5.2pH and 6.0 pH have been used in work with cane products.

The adjustment of pH value is made with 0.05 N HCl and 0.05 NaOH.

For approximate measurements, portions of 25 ccs. each of the product, containing about 100 mgms. solids, are placed in tall tubes, and varying amounts of Night Blue solution (made up to 25 ccs.) are added. After shaking and allowing to settle for a few minutes the tubes are examined in transmitted light ; those showing the largest flocs and the most rapid settling indicate the range of the isoelectric point.

<u>Cataphoresis apparatus :-</u> In order to determine the exact isoelectric point the migration of the colloidal particles under the influence of an electric current is observed by means of an ultramicroscope. Particles with negative charge travel to the positive electrode, and vice versa. Addition of a colloid of opposite charge reduces the migration velocity of the particles, and at the isoelectric point migration stops. Excess of the oppositely charged colloid then reverses the direction of the migration. **See Figures 27 and 28.**

<u>Example :-</u> Five gms. of a raw sugar was made up to 100 ccs. after filtering and adjusting the pH value to 6.0. It required 20 ccs. of

Night Blue solution, equal to 20 mgms. of dye.

Hence $\frac{20}{5} \times 100 = 400$, is the Dye Number of the sugar.

Where the water content of the sugar is over 2 per cent, the Dye Number should be based on the sugar solids. If possible a dilution is chosen such that the quantity of dye solution required for 100 ccs. lies between 15 and 25 ccs. The procedure should be closely standardised as regards the time consumed in mixing and reading, to obtain comparable results.

The Dye method was applied to the raw diffusion juice and to the clarified juices at various stages of the lime/aluminium sulphate process. A typical determination of isoelectric point is shown below :-

Diffusion Battery Supply water - pH at isoelectric point

Milligrams of Dye.	Order of Magnitude of flocculation.	Migration of Colloidal Particles	pH at Isoelectric Point.
4.0	X	Negative	-
4.5	XX	Negative	-
5.0	XXX	Negative	-
5.5	XXXX	Slowly Negative	-
5.7	XXXX	Positive and Negative	4.93
5.9	XXXX	Slowly Positive	-
6.5	XXX	Positive	-
7.0	XX	Positive	-
7.5	X	Positive	-

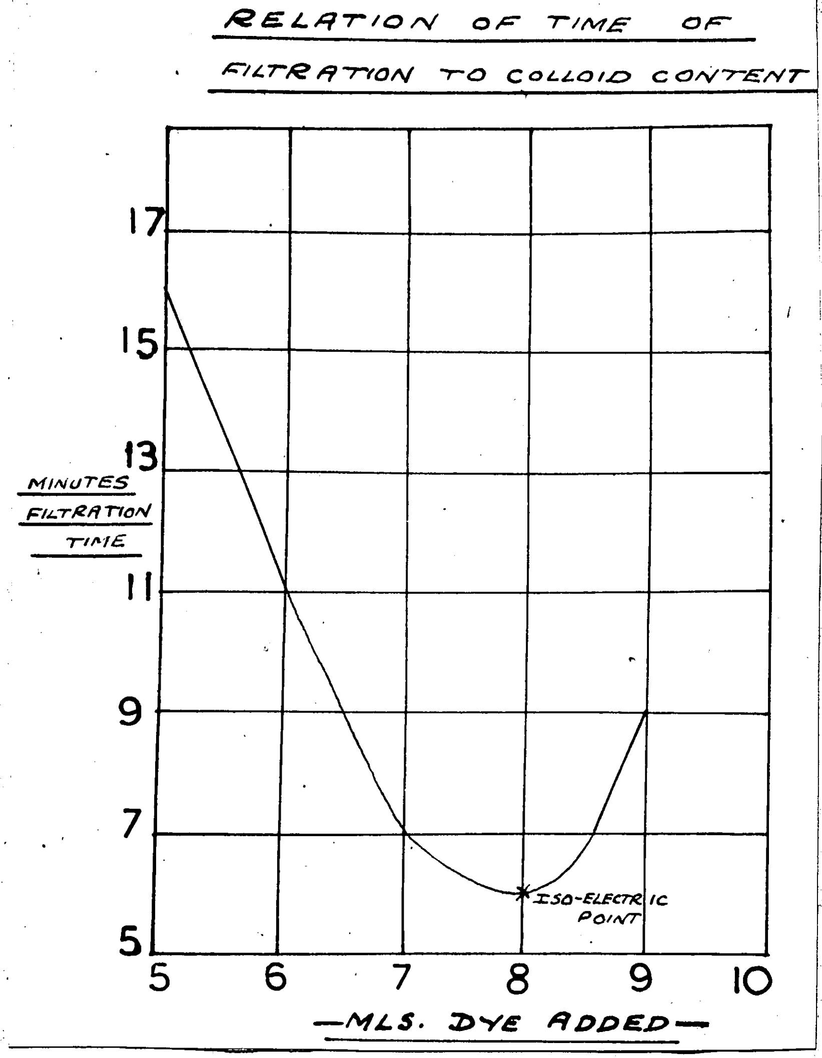

RELATION OF TIME OF
FILTRATION TO COLLOID CONTENT
17
15
13
11
9
7
5
MINUTES
FILTRATION
TIME
ISO-ELECTRIC
POINT
5
6
7
8
9
10
—MLS. DYE ADDED—

Figure 26a.

The work of Badollet and Paine has been criticised by Mattson (J.Phys.Chem., 32, 1532, 1928), who states that since the presence of different electrolytes and a difference in reaction modifies the electrical neutralising power of colloidal material, an exact proportion between the amount of dye required and the colloid content should not be expected. This does not detract from the value of the method for comparative purposes.

Mattson appears to have been the first to apply a dye (methylene blue) to indicate the proportion of colloidal matter present in raw sugars and molasses.

Control of pH :- It has been pointed out that to obtain comparable results all the products in a series must be adjusted to the same pH value, and since the use of alkali is liable to cause partial flocculation of the colloids, it is best to select a pH value below 7.0 as standard. A figure of 5.2 pH has been found satisfactory for cane sugar products, but 6.0 pH has also been used, particularly for refinery products.

Direct determination of Colloids :- Dumanski and Charin have devised a method of precipitation for estimation of colloidal matter in sugar products.(See Gundermann, I.S.J., p.276, 1933). As applied to diffusion juice 25 g. of the juice are treated with 7 ccs. of N/10 oxalic acid, 30 ccs. of ether, and 240 ccs. of 96% alcohol under reflux in a water-bath for 30 minutes in a conical flask. The residue is filtered, washed with 96% alcohol, and dried to constant weight at 100°C. Gundermann found from 3.454 to 4.736 g. per 100 polarisation of colloids in beet diffusion juice.

THE ELIMINATION OF COLLOIDS IN THE ALUMINIUM SULPHATE PROCESS OF PURIFYING DIFFUSION JUICE FROM DRIED BEET COSSETTES.

	PRODUCT	DYE VALUE
1.	Raw Diffusion Juice	1890
2.	Filtered Limed Juice (0.5per cent on beets).	303
3.	Filtered Juice after Lime and Al2$(SO_4)_3$	112
4.	" " " " " " and SO_2	86
5.	" " " " " " " CO_2	46
6.	First Massecuite	52
7.	First Sugar	17
8.	First Syrup	77
9.	First Syrup after 0.2 per cent Suchar carbon	30
10.	Second Massecuite	69
11.	Second Sugar	25
12.	Second Syrup	123
13.	Third (Final) massecuite	186
14.	Third Sugar	39
15.	Third Syrup (Molasses)	406-990
16.	Beet Pulp extracted with water at 100°C. for 30 minutes...Dye Value of extract	11,210

-----oOo-----

These results are average figures except for molasses where a range is shown. They clearly indicate the removal of colloids in the process of purification.

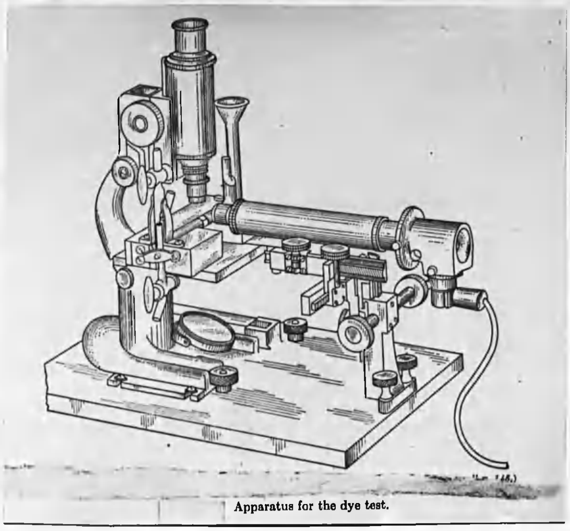


Figure 27 : Ultramicroscopic Cataphoresis Apparatus for Determination of the Isoelectric Point.

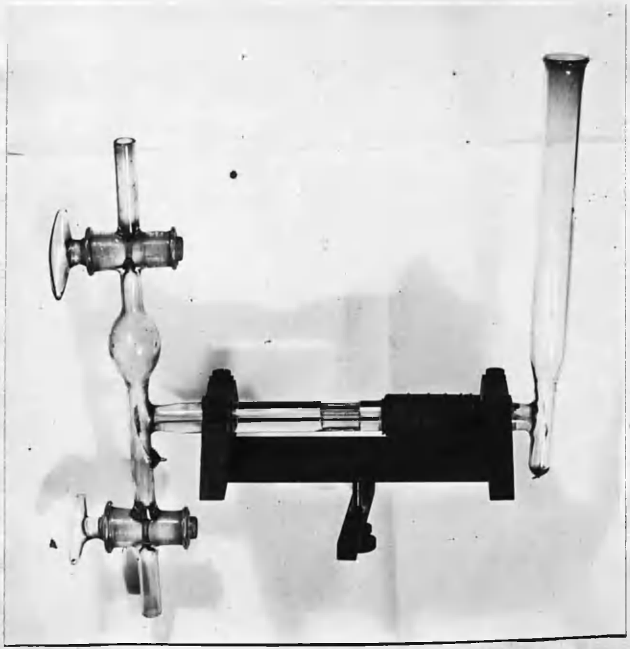


Figure 28 : Cataphoresis Tube from above Apparatus.

COLLOIDS IN SUGAR PRODUCTS.

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SECTION 4 (CONTINUED).

THE PURIFICATION OF RAW BEET DIFFUSION JUICES OF HIGH DENSITY FROM DRIED BEET COSSETTES.

PART 2.

THE ALUMINIUM SULPHATE PROCESS OF DEFECATION.

Outline of the Process.

Aluminium Sulphate Process of Defecation for Diffusion Juices from Dried Beet Cossettes.

Salts of aluminium in the presence of alkalis produce a very bulky precipitate of the hydroxide, which carries down much colloid and colouring matter. Such a reaction was used at least a century and a half ago in the cane sugar industry, being described in a treatise by the Marquis de Casaux in 1778 (Essai sur l art de cultiver la canne, Paris). The property is also included in Howard's patent 3754 of 1813, and the alumina so prepared was for long known as Howard's Finings. A number of other patents have been granted for the use of aluminium compounds in sugar defecation : these are listed on the next page. Patent 244,924 (U.K.), by Majithia and Singh (1926) describes a treatment of the juice (or other liquid) whereby aluminium hydroxide is precipitated therein by adding aluminium sulphate or other soluble aluminium salt, then adding the requisite amount of alkali, such as caustic soda, sodium carbonate, or milk-of-lime to give a slightly alkaline reaction, and heating, preferably to 100°C., afterwards separating the precipitated matter.

A new principle in the purification of sugar juices was embodied in Belgian patent 367,847 (15/2/30) by Dario Teatini of Hougaerde, in the addition to the hot alkaline juice of liquid sulphur dioxide. Teatini claims a large reduction in the amount of lime required as compared with the carbonatation process, and several other advantages.

Arising out of the use of aluminium salts and liquid SO_2, a process was devised by the author, and is described on page 165.

The Stages in the Process.

Aluminium Sulphate Process of Defecation for Diffusion Juices from Dried Beet Cossettes.

The process consists of the following stages:-

1. **Raw Juice Extraction** in diffusion battery at approximately 36-37° Brix (preferably not higher than 40°Brix). The concentration 36-37° Brix is an optimum for defecating efficiency.

2. **Limimg:-** Approximately 0.5 per cent lime, calculated on the weigh of fresh beets, is added at low temperature (say 40-50°C.), and followed by rapid heating. Fifteen minutes contact at 75°C. gives favourable results. The lime is added in the form of a cream of composition 50/50 Buxton hydrated lime and water, or in any other suitable manner. This has proved to be the optimum amount for precipitation of impurities without causing difficulty in filtration.

3. **Secondary Reagent :-** The juice is now treated with approximately 0.3 per cent of an elewtrolyte (for example, aluminium sulphate), which by reason of its electrical charge is able to fix and disperse some of the colloidal and colouring matter which remains after limimg. Contact is maintained for about 5 minutes at 75°C. The juice is brought by this treatment to a pH value of 7.8-8.0 or thereby.

4. **Final Reagent :-** The juice with its precipitate is now treated, either with or without an intermediate filtering, with approximately 0.09 per cent of a suitable acid reagent, using the quantity necessar to obtain the requisite pH value in the final filtered juice.

This acid treatment is preferably carried out before the juice is filtered, as this will accelerate the whole process and a better final juice is obtained. The acid substance added may be acid calcium phosphate, carbon dioxide, or sulphur dioxide, but is preferably sulphur dioxide in liquid form. The addition may be sufficient to give a pH value of 7.3-7.4 where there is a further sulphitation after concentration. Where the juice is not to be further sulphited, or where it is to be treated with carbon, the pH value may be brought down to 6.9-7.0. This acid treatment is carried out at approximately 75°C., although a temperature between the range 65-95°C. may be used in special cases.

5. Filtration:- The solids precipitated are now separated in any suitable manner : as the precipitate is copious, the mud chamber of the filter should have ample capacity. The temperature can be raised at this stage, but the colour of juices containing invert sugar is better when 75°C. is maintained, and filtration is rapid at this temperature. The cake is easily sweetened off, and leaves a hard compact cake which falls readily from the cloths of the filter. No extra filter aid was found necessary in the trials of this method.

6. Multiple Effect Evaporation :- The juice is concentrated to a density most suitable for boiling, say 65-68°Brix.

7. Thick Juice Treatment :- When the juice is sulphited after concentration, the pH before the initial filtration should be kept at 7.3-7.4, and reduction to 6.9-7.0 pH effected on the thick juice Alternatively, the thick juice may be treated with decolorising carbon, when 6.9-7.0 pH is required in the thick juice.

8. Gravity Filters :- The treated thick juice is filtered through gravity filters.

9. <u>After-treatment of filtered thick juice :-</u> <u>FIRST PANS :-</u>

The two-massecuite system is used, charging the first boiling with the carbon-treated remelt sugar, and building up the crystals with thick juice, with the possible addition of treated high wash or high green syrup to bring purity conditions to the correct proportions.

<u>SECOND PANS :-</u> A proportion of high wash syrup is used to grain the second boiling, and the high green syrup is used to build up the crystals. The pan is completed with low wash syrup to the requisite purity.

10. <u>Remelt Sugar :-</u> The remelt sugar (from the second boiling) is washed to the required colour in the centrifugal machines, and dissolved in treated juice of about 35°Brix to make a syrup of 55-60°Brix. This syrup is treated with 0.3 per cent decolorising carbon on the weight of sugar solids in the remelt and filtered.

<u>Note :-</u> The method outlined for after-treatment may be replaced by any suitable process.

RECAPITULATION

<u>STEPS :-</u>

EXTRACTION - 36-40°Brix.
TRIPLE DEFECATION TREATMENT
FILTRATION
EVAPORATION - 65-68°Brix.
SULPHITATION OR CARBON TREATMENT.
GRAVITY FILTRATION
AFTER-TTEATMENT

<u>Advantages :-</u> By this process defecation is accomplished at 36° Brix instead of 10-15°Brix ; there is only one main filtration ; manufacture is speeded up ; and there is saving of steam.

List of Patents for the use of aluminium salts in defecation.

Year	Number	Name	Description
1861	1856	W.E.Gedge	Alumina jelly by pptg. alum with NH_3 (Abridgements, p.23)
1867	3405	W.R.Lake	Neutral Al sulphate on soln. of sugar in lime-water (Abr. p. 4)
1871	2090	Duncan & Newlands	Formation of alum to ppt. K and NH_3 salts from sugar solns. (Abr. p.26)
1874	1989	J.Duncan	Acidification of limed juice by Al sulphate. (Abr. p. 39)
1874	3332	Gill and Martineau	Use of alumina after tannin (Abr. p.41)
1875	4264	Duncan & Newlands	Al.Sulphate, 30 m. contact ord. temp., then lime: or vice-versa. (Abr.p.54)
1876	4433	Geistodt & Plicque	Use of aluminates of barium, etc. (Abr. p. 68)
1877	1902	Loewig	Use of gelatinous Al hydrate with lime. (Abr. p. 3)
1879	1076	Loewig	Lime-water and gelatinous Al hydrate. (Abr. p.17)
1880	861	Gawalowski & Teichmann	Phosphite or phosphate of Al prepared from the sulphate. (Abr.p.25)
1886	3196	Englert & Becker	Neut. or basic Al or Fe sulphite or hydrosulphites. (Abr.p.18)
1893	14373	Evans	Aluminium hydrate, alone or mixed. (Abr.p.3)
1878	4861	Hunt	Use of basic aluminium sulphate. (Abr.p.25)(1897)
1879	3195	Loewig	Basic chloride of Al, prepared from gelatinous Al hydrate (Abr.p.26) (1897)
1903	16750	Hlavati	Al. polysilicates : Al sulphate during diffusion. (Abr. p. 16)
1916	108303	Hayashi & Emura	Clarifying matter made from char and H_3PO_4 with Al salts. (Abr.p.2)
1918	134607	Hood, Clark, & Clark	Granular alumina or magnesia- Al salts may be used, (Abr.p.8)

Analyses of the reagents used in the Purification tests on raw Diffusion Juices.

Hydrated Lime

	%
Calcium Hydroxide	96.17
Calcium Carbonate	1.19
Calcium Sulphate	0.58
Magnesium Carbonate	0.47
Ferric Oxide	0.02
Alumina	0.10
Insoluble in HCl	0.53
Water	1.10

Sieve Test

Through 50 mesh	100.00
100	98.00
150	94.00
200	94.00

17/18 % Aluminium Sulphate

	%
Al_2O_3	17 - 18
Fe_2O_3	0.001-0.007
SO_3 (combined)	39.6-42.0
SO_3 (free)	Nil-0.20
Insoluble matter	Nil-trace
Water	40-43.4

Sulphur Dioxide Gas.

The purity of the gas as supplied in cylinders was 99 - 100 per cent, the pressure being between 30 and 45 lbs., (2-3 atmospheres).

Analysis of Mono-calcium phosphate :-

		Per cent
Mono-Calcium Phosphate,	$CaH_4(PO_4)_2$	82.90
Calcium Oxide,	CaO	24.00
Magnesium, Oxide,	MgO	0.03
Phosphorus pentoxide	P_2O_5	55.74
Ferric oxide & Alumina	$Fe_2O_3 + Al_2O_3$	0.03
Ignition Loss (with ZnO)		20.03
Sulphur trioxide, SO_3		0.07 = 0.12 $CaSO_4$
		99.90

As_2O_3. 0.5 part per million
Pb, 5.0 parts per million

Interaction of lime and aluminium sulphate(as in defecation).

$$Al_2(SO_4)_3 + 3\ Ca(OH)_2 = 3\ CaSO_4 + 2\ Al(OH)_3$$

342.4 + 222.27

That is, 1 part $Al_2(SO_4)_3$ requires 0.65 part $Ca(OH)_2$

Using the hydrated compound :-

$Al_2(SO_4)_3.18H_2O$ = 666.8 requires 222.27 of $Ca(OH)_2$

or 1 part of hydrated Al. sulphate requires 0.33 part $Ca(OH)_2$.

List of Experiments on the Defecation of Dried Beet Juices.

1. Determination of the Optimum amount of Lime.
2. Neutralisation by sulphuric acid.
3. Treatment with lime and calcium phosphate.
4. Optimum for temperature and for time of contact.
5. Effect of decolorising carbon.
6. Effect of variation of amount of calcium phosphate used.
7. Trials with various grades of alumina.
8. After-treatment of limed juices with SO_2 and with CO_2 .
9. Treatment of limed juice with aluminium sulphate.
10. Effect of Temperature on clarified filtered juice.
11. Solid and fractional addition of lime.
12. Further tests on fractional limimg.
13. Defecation of juice from cossettes dried with pure air.
14. Effect of higher density of juice upon defecation.
15. Settling rates of precipitated defecating agents.
16. Behaviour of reducing sugars during the defecation process.
17. Determination of the amount of aluminium sulphate for defecation.
18. Use of SO_2 and of CO_2 after defecation with lime and Al.sulphate.
19. Use of calcium phosphate in the aluminium sulphate process .
20. Effect of juice density in the aluminium sulphate process.
21. Variations in the method of applying reagents in the Al.S.process
22. The use of other aluminium salts in the defecation of dried beet juices.

Experimental work on the defecation of diffusion juices.

1. Determination of the optimum amount of hydrated lime required.

In these tests 500 ccs. of raw diffusion juice was taken for each experiment. The lime was made into a milk in 10 ccs. of water and added in the cold, the well-mixed volume of limed juice being then heated to 75°C. and maintained there for 15 minutes with stirring. It was then filtered and the time of filtration noted.

No.	Gms. Lime	%lime on F. Beets	Brix°	% Sugar	Purity	Colour Stammer	Filt. Rate m.	Filt. Rate sec.	Purity Diffce.	pH
1	0.88	0.08	34.8	31.0	89.1	11.1	7	30	+0.9	6.7
2	1.76	0.15	34.3	30.7	89.5	16.7	8	10	+1.3	7.6
3	2.63	0.24	34.45	30.9	89.7	10.6	5	10	+1.5	7.9
4	3.51	0.32	35.1	31.7	90.3	6.8	6	05	+2.1	8.6
5	4.39	0.38	34.8	31.3	89.9	5.5	6	00	+1.7	9.2
6	5.26	0.47	34.3	30.6	89.3	5.5	5	00	+1.1	10.0
7	6.14	0.55	34.3	30.5	88.9	5.6	4	40	+0.7	--
8	7.02	0.63	34.8	31.0	89.1	5.7	4	15	+0.9	--
9	7.90	0.70	33.9	30.2	89.1	6.3	4	30	+0.9	--
10.	8.78	0.78	32.9	28.8	87.5	6.3	6	50	-0.7	--
Raw Jce.	-	-	34.7	30.6	88.2					4.7

The optimum amount of lime appears to be 0.5-0.6 per cent hydrated lime (on fresh beets), this amount giving the palest juice and a satis-factory rise in purity. Much after-settling out of solid was seen in tubes of juice kept for 5 days, except in No. 10 which had not then precipitated. The Stammer colour degrees were read at 10°Brix. The filtration rate was taken in a standard filter by stop-clock.

2. The Effect of sulphuric acid neutralisation of limed juice.

A typical limed juice was taken in 500 ccs. portions and the influence of sulphuric acid was observed at 20, 75, and 95°C. The contact time was 15 minutes in each test. The lime used was 6 gms. per 500 ccs. juice, equal to 0.54 per cent on fresh beets.

No.	Liming Contact Time mins.	Liming Temp. °C.	Gms. H_2SO_4 added	% on F.B.	Contact Time mins.	Temp. °C.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix
1	15	75	0.5	0.05	5	20	36.7	32.5	88.5	9.1
2	15	75	0.5	0.05	5	75	37.4	33.3	89.0	10.0
3	15	75	0.5	0.05	5	95	38.6	34.2	88.6	12.1
L.J.	15	75	-	-	-	-	39.4	34.7	88.1	5.9

No.	Filtration Rate for 50 ccs. mins.	Filtration Rate for 50 ccs. secs.	Purity Diffce.	pH Value	Remarks.
1	9	15	+ 0.4	7.1	While the purity has risen in each case, the increase in colour makes this method of little value.
2	2	15	+0.9	7.0	
3	1	45	+ 0.5	7.0	

L.J. = Limed juice.

3. The effect of lime and phosphate treatment of diffusion juice.

This test aimed to find the optimum point of application of calcium phosphate. The temperature used was 75°C. for both liming and phosphating, 500 ccs. of juice being used in each test. The contact time was 15 minutes for lime and 5 minutes for phosphate : the quantities required of lime and phosphate were added each in 10 ccs. of water.

No.	Gms. Lime	%Lime on F.B.	Gms. Ca Phos.	%on F.B.	Brix°	%Sugar	Purity	Colour °Stammer : 10°Brix	Filtration Rate mins.	secs.
Raw Juice	-	-	-	-	33.2	29.5	88.9	-	-	-
1	3.51	0.32	0	-	33.1	29.8	90.0	7.1	1	50
2	3.51	0.32	4	0.36	32.2	29.2	90.4	5.1	4	00
3	3.51	0.32	4	0.36	32.3	29.1	90.1	7.1	ex 10	00

No.	Purity Diffce.	pH Value	Remarks
Raw Juice	-	4.7	-
1	+1.1	8.7	Lime alone added
2	+1.5	6.8	Lime added first, followed by phosphate.
3	+1.2	7.5	Phosphate added first, followed by lime.

The most striking feature of the above test was the effect of adding the phosphate before the lime (No.3). Filtration was slowed up at once, and the pH value did not fall as in No. 2. The colour was also darker in No.3, and the filtrate hazy. It is clear that lime must be added first.

4. Determination of optimum temperature and contact time of liming.

(a) Temperature :- 500 ccs. juice per test, adding 5 gms. of lime in 10 ccs. water in each case (= 0.44 per cent on fresh beets).

No.	Temp. °C. 15 mins. contact time	Brix°	%Sugar	Purity	Colour °Stammer 10° BRIX	Filtration rate		Purity Diffce.	pH Value
						mins.	secs.		
Raw Juice	-	40.4	35.8	88.6	-	-	-	-	4.6
1	30	38.4	34.5	89.8	8.0	3	45	+1.2	9.8
2	40	38.5	34.7	90.1	5.4	5	00	+1.5	9.9
3	50	38.2	34.4	90.0	5.7	9	30	+1.4	10.0
4	60	37.4	33.7	90.1	6.25	7	10	+1.5	10.0
5	70	39.3	35.5	90.3	7.55	3	45	+1.7	9.9
6	80	39.4	35.5	90.1	8.0	4	55	+1.5	10.0
7	90	39.3	35.2	89.6	8.3	4	30	+1.0	9.9
8	100	41.6	37.7	90.6	11.1	3	00	+2.0	9.7
9	70	38.3	34.5	90.1	6.7	1	00	+1.5	10.0

(b) Contact Time :- a temperature of 75°C. was used throughout.

	Mins.								
Raw Juice	-	37.7	33.4	88.6	-		-	-	4.8
1	5	35.3	31.4	88.9	8.8	2	10	+0.3	10.0
2	10	35.7	31.9	89.3	7.7	2	20	+0.7	9.9
3	15	36.0	32.2	89.4	7.7	3	10	+0.8	9.8
4	20	36.4	32.6	89.6	8.5	4	00	+1.00	9.9
5	25	36.8	32.8	89.1	8.9	4	30	+0.5	9.7
6	30	37.3	33.3	89.3	9.1	4	55	+0.7	9.6

5. Determination of the effect of decolorising carbons on diffusion juice after liming, but without neutralisation.

A diffusion juice limed with 6 gms. hydrated lime per 500 ccs., equal to 0.54 per cent lime on fresh beets, was treated with three different decolorising carbons using 500 ccs. juice for each test at 75°C. The lime was allowed 15 minutes contact at 75°C. and the carbon contact time was also 15 minutes : carbon and lime were each added in 10 ccs. of water.

No.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Filtration Rate mins.	secs.	Purity Diff.	pH Value	Carbon Gms. and type
L.J.	37.1	33.2	89.5	8.7	2	30	-	7.8	-
1	38.9	35.2	90.5	9.1	2	10	+1.0	7.7	Williams 1 gm. 0.09% on FB
2	38.1	34.6	90.8	8.7	1	30	+1.3	7.7	Esbit 1gm. .09% on F.B.
3	37.8	34.0	89.9	9.1	2	00	+0.4	7.6	Carboraffin 0.25 Gm. .02 % on F.B.

This test demonstrated that it is not satisfactory to apply carbons to juices above the neutral point. While a juice may be decolorised at say 6.9-7.3 pH, it is difficult to decolorise it if its pH value is above say 7.3 pH. The purity rise and rate of filtration were satisfactory in these tests.

The pH value should be reduced to near the neutral point before using carbon : this can be done by means of CO_2, SO_2 or an acid phosphate. It is well known that the decolorising power of carbons is greater, in general, in contact with acid juices.

6. The effect of varying amounts of acid phosphate on limed juice.

No.	Gms. Lime	Contact Time Mins.	Temp. °C.	Gms. Phosphate	% Lime on F.B.	% Phos. on F.B.	Contact Time for Phosphate mins.	Temp. °c. for Phos.	ccs. water for Lime & Phos. (each)
Raw Jce.	-	-	-	-	-	-	-	-	-
1	5	15	75	0	0.43	-	-	-	10
2	5	15	75	1	0.43	0.09	5	75	10
3	5	15	75	2	0.43	0.17	5	75	10
4	5	15	75	3	0.43	0.27	5	75	10
5	5	15	75	4	0.43	0.36	5	75	10
6	5	15	75	5	0.43	0.43	5	75	10

No.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Filtration Rate		Purity Diffce.	pH Value
					mins.	secs.		
Raw Jce.	39.8	34.9	87.7	-	-	-	-	4.8
1	37.9	33.6	88.6	7.9	5	10	+0.9	9.9
2	36.8	32.7	88.9	10.6	10	10	+1.2	8.8
3	37.9	33.8	89.2	17.0	5	30	+1.5	7.8
4	39.7	35.3	88.9	19.0	4	45	+1.2	7.5
5	40.0	35.8	89.5	9.5	5	10	+1.8	7.0
6	40.4	36.2	89.6	5.7	5	10	+1.9	6.8

This test showed satisfactory purity rise and filtration rate : the colour did not improve until the juice was acid.

7. Effect of various grades of alumina on limed diffusion juice.

The juice was limed in 500 ccs. quantities with 5 gms. of hydrated lime, equal to 0.43 per cent on fresh beets, allowing 15 minutes contact time at 75°C., and was then treated with 3 gms. of the aluminium compound for 5 minutes at 75°C. This was equal to 0.27 per cent on fresh beets. Each reagent was added in 10 ccs. of water.

No.	Brix°	%Sugar	Purity	Colour °Stammer 10° Brix	Filtration Rate mins.	secs.	Purity Diffce.	pH Value	Remarks
Raw Jce.	35.2	31.2	88.6	-	-	-	-	4.7	-
1	35.2	31.4	89.2	8.9	2	20	+0.6	9.8	Lime alone
2	34.9	31.4	90.0	9.5	2	00	+1.4	7.8	Dry $Al(OH)_3$
3	34.5	31.0	89.9	6.5	2	00	+1.3	7.8	99% Calcined alumina
4	34.8	31.2	89.7	10.6	2	30	+1.1	7.8	98%
5	35.0	31.5	90.0	11.3	3	10	+1.4	7.8	Crude alumina
6	35.2	31.6	89.8	5.7	2	50	+1.2	7.5	Calcined alumina
7	35.1	31.5	89.7	9.5	2	50	+1.1	7.8	Crude Bauxite

The purifying action of these grades of alumina appears to be in direct ratio to their own purity. No attempt was made to render these alumina samples active by ignition or other treatment.

Filtration rate and purity rise are very satisfactory in all the tests, but only Nos. 3 and 6 gave satisfactory reduction of colour.

8. Treatment of limed juice with acid reagents - use of sulphur dioxide, and of carbon dioxide.

A litre of raw diffusion juice was taken for each experiment. This was treated with 10 gms. of lime, equal to 0.43 per cent on fresh beets, with 15 minutes contact at 75°C., and filtered. The acid reagent was then applied to the filtered limed juice from a cylinder at a temperature of 65°C. to approximately pH 7.0. The neutralised juice was filtered.

(a) Sulphur dioxide treatment :-

No.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Filtration Rate mins.	secs.	Purity Diff.	pH Value	Remarks
Raw Jce.	35.8	31.4	87.7	-	-	-	-	4.7	-
1	36.7	32.7	89.1	5.3	7	00	+1.4	9.9	Lime alone
2	37.1	33.0	88.9	7.7	0	55	+1.2	7.2	Filtered Juice+SO_2

(b) Carbon dioxide treatment :-

3	36.7	32.7	89.1	5.3	7	05	+1.4	9.8	Lime alone
4	37.0	33.0	89.6	7.5	2	10	+1.9	7.0	Filtered Juice+CO_2

An important result in these tests is the great increase in the spedd of filtration. The colour is slightly darker in both finished juices, but the purity is substantially the same after SO_2 treatment. With CO_2 it was observed that it was much easier to control the reaction than woth SO_2; the 'gassing' with CO_2 was not so fast. It is probable that some of the colouring matter is not affected by the acid reagents, which suggests the use of a third reagent to fix and remove this colour.

9. The use of aluminium sulphate as a defecating agent.

The aluminium sulphate reagent was made by dissolving 510 gms. of hydrated salt in 500 ccs. of distilled water and filtering hot. This gave a solution of about 70°Brix which crystallised out below 30°C. It therefore represented saturation at ordinary temperature. The following tests were made :-

(a) 5 gms. lime ;followed by 5 ccs. Al.S. soln. : filtered.

(b) 5 ccs. Al.S. soln. followed by 5 gms. of lime : filtered.

(c) 5 ccs. of Al.S. soln. followed by 5 gms. sodium carbonate.

(d) 5 gms. of soda-ash,followed by 5 ccs. of Al. S. soln.

In each test 500 ccs. of juice was taken, heating for 15 minutes with the alkaline reagent, and for 5 minutes with the Al. S. soln. The temperature used was 75°C. The 5 gms. alkaline reagent represents 0.44 per cent on fresh beet : the Al.S. 5 ccs. soln.,0.22 %.

No.	Brix°	% Sugar	Purity	Colour °Stammer 10°Brix	Purity Diffce.	Filtration Rate mins.	secs.	pH Value	Remarks
Raw Jce.	35.6	31.4	88.2	-	-	-	-	4.7	-
(a)	36.3	32.4	89.2	2.2	+1.0	3	30	5.5	Very acid
(b)	36.9	32.7	88.6	3.9	+0.4	4	00	7.7	Good
(c)	36.0	32.0	88.9	12.7	+0.7	49	00	7.4	Very slow
(d)	37.0	33.0	89.1	9.0	+0.9	38	00	7.0	Slow

There is obviously a great difference in the reaction obtained by the reverse method of addition: the soda gives dark juice and slow filtration.

10. The effect of temperature on Clarified filtered juice.

Additions of reagents are shown as per cent on weight of fresh beet Lime was added to give pH 7.4 using 0.17 per cent: this was followed by Aluminium sulphate solution (0.27 per cent). Lime was again added (0.27 per cent) and the juice was then treated with sulphur dioxide to give a final pH value of 7.5. The first liming was at 75°C. for 15 minutes, the Al.S. solution was for 5 minutes at 75°C. and the final liming was for 5 minutes at 75°C.

Experiment :- Separate 500 ccs. lots of the treated filtered juice were heated for 15 minutes at 80, 85, 90, 95, and 100°C.

No.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Filtration Rate Mins.	Secs.	pH Value	Remarks
Treated Jce.	36.7	32.2	87.7	7.2	-	-	7.5	-
1	37.0	-	-	6.7	1	30	7.5	80°C.
2	37.7	-	-	6.3	0	30	7.5	85°C.
3	38.9	-	-	5.9	0	15	7.5	90°C.
4	40.8	-	-	5.9	0.	15	7.5	95°C.
5	42.0	36.9	87.9	5.7	0	10	7.5	100°C.

The original treated juice was now 'gassed' with SO_2 in the cold, heated to 75°C., and filtered: 50 ccs. filtered in 10 secs.

Brix°	% Sugar	Purity	% Ash	% Reducing Sugars	Colour °Stammer 10°Brix.	pH Value
37.3	32.9	88.2	0.90	1.08	5.0	6.9

The juice has bleached as the temperature increased : the second sulphitation has markedly improved the juice.

11. Investigation of Solid and fractional addition of lime in the Purification of Diffusion Juice.

Various tests were made comparing addition of lime-cream with solid liming, and also with fractional liming, both liquid and solid.

All heating was at 75°C. : 500 ccs. of juice used for each test.

NO.	Gms. Lime added	Form added	Gms. Al.S. added	Form added	Conditions of test
1	5	liquid	-	-	15 mins. heating at 75°C.
2	5	solid	-	-	15 " " " "
3	5	solid	-	-	1 gm. added each min. for 15 mins.
4	5	liquid	3	liquid	Lime 15 mins.: Al.S. 5 mins. at 75°C.
5	5	solid	3	solid	" "
6	5	solid	3	solid	1 gm. Lime each3mins.for15 mins 1 " Al.S. " 1 " " 3 " Al.S. 5 mins contact in all
7	5	liquid	-	-	Lime in 2 lots of 2.5 gms. each: 1st lot 7 mins. 2nd. lot 8 mins. contact.
8	5	solid	-	-	As in No. 7, but using solid lime.
9	5	solid	-	-	First added 2 gms. lime at 75°C. the rest added 1 gm. at a time each 3 mins. thereafter. 15 mins. total time.

Note :- Special care was taken to ensure that the lime added solid was in very finely divided form, and a mechanical stirrer was used to give thorough mixing of the juice and reagents.

11. Continued :- Analytical Results :-

No.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Purity Diffce.	Filtration Rate Mins.	Secs.	pH Value	Form of Addition
Raw Jce.	36.8	31.7	86.2	-	-	-	-	4.8	-
1	37.4	32.5	86.9	9.1	+0.64	8	50	9.9	liquid
2	37.8	33.0	87.3	8.3	+1.04	7	30	9.8	solid
3	38.2	33.2	87.0	5.6	+0.8	8	20	9.3	solid
4	37.5	33.0	88.0	6.7	+1.8	5	20	7.6	liquid
5	39.6	34.3	86.7	7.1	+0.5	7	00	8.0	solid
6	41.0	35.7	87.1	5.1	+0.9	9	10	7.8	solid
7	37.2	32.4	87.0	6.3	+0.8	9	45	9.6	liquid
8	38.3	33.4	87.3	6.6	+1.1	5	00	9.4	solid
9	39.1	33.7	86.3	6.0	+0.1	17	50	9.8	solid

The most noteworthy feature of this series of tests is the great variation in the colours, the purity increases, and the rates of filtration. In Nos. 3 and 6 a very good juice has been produced by fractional addition of the lime. Filtration was remarkably slow in No. 9 test. The general conclusion is that the addition of the reagents is a matter requiring great care as to the actual conditions and method of addition. In every case the colour of the final juice was lighter where the lime had been added fractionally as compared with tests 1 and 2 where it was added in one lot.

12. Further tests on fractional liming of diffusion juice.

Tests made using 500 ccs. juice.

No.	Gms. Lime	Gms. Al.S.	Form added	Lime Contact Time Mins.	Temp. °C.	Al.S. Contact Time Mins.	Conditions of test
1	5	3	liquid	15	75	5	Normal defecation
2	5	-	solid	15	75	-	1 gm. lime added every 3 mins.
3	5	3	solid	15	75	5	Lime added as in No.2, then Al.S. in bulk.
4	5	3	solid	15	75	5	Lime as in No.2, then Al.S. added 1 gm. at a time during 5 mins.
5	6	-	liquid	20	80	-	Normal defecation
6	6	-	solid	15	75	-	Lime placed in vessel and 100 ccs. raw juice added every 3 mins. to total of 500 ccs., all at 75°C.
7	5	5	liquid	15	75	5	Normal bulk additions, completed by adding 1.25 gms. Ca phosphate and giving 5 mins. at 75°C.

No.	Brix°	% Sugar	Purity	Colour °Stammer 10°Brix	Purity Diff.	Filtration Rate Mins.	Secs.	pH Value
Raw Jce.	35.9	30.0	85.5	-	-	-	-	4.8
1	34.2	29.6	86.6	6.3	+1.1	6	00	9.9
2	37.7	32.5	86.2	4.4	+0.7	8	20	7.9
3	37.9	32.6	86.2	4.1	+0.7	6	40	7.6
4	38.1	32.9	86.3	4.3	+0.8	10	30	7.9
Raw Jce.	36.6	31.7	86.6	-	-	-	-	4.7
5	37.2	32.6	87.7	11.1	+1.1	3	30	9.7
6	37.3	32.8	87.8	7.1	+1.2	3	20	9.8
7	36.5	32.3	88.5	4.6	+1.9	4	40	7.0

13. Tests on the defecation of diffusion juice from cossettes dried by pure air.

These tests were made at 75°C. using 500 ccs, of raw juice, and allowing 15 minutes contact time for liming, and 5 minutes for Al. sulphate where it was used. The lime and Al. sulphate were each added in 10 ccs. of water

No.	Gms. Lime	Gms. Al.S.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Filtration Rate Min.	Sec.	Purity Diffce.	pH Value
Raw Jce.	-	-	32.9	29.0	88.0	-	-	-	-	6.0
1	5	-	34.0	30.6	89.9	5.6	3	10	+1.9	9.9
2	7.5	-	33.6	30.3	90.1	5.1	3	50	+2.1	11.3
3	10.0	-	33.0	29.3	90.2	5.8	5	40	+2.2 ex	12.0
4	5	3	33.0	29.8	90.2	4.8	3	50	+2.2	7.8
5	7.5	3	33.2	29.9	90.2	4.1	3	00	+2.2	8.6
6	10.0	3	33.5	30.1	90.0	5.6	9	20	+2.0	11.0
7	5	5	32.9	29.4	89.4	4.5	5	40	+1.4	7.2
8	7.5	5	33.2	30.0	90.5	4.4	6	10	+2.5	8.0
9	10.0	5	32.1	28.9	90.0	4.2	3	10	+2.0	9.8

Discussion of results in Tests 12 and 13:-

The addition of more lime at a higher temperature and time darkens the juice. The method of adding the juice to the lime offers no great advantage over the usual procedure. The filtration rate when using solid lime is slower, and this slowing down is also seen with more heavily limed juices.

14. Tests on the defecation of diffusion juices at higher °Brix.

Diffusion juices at 44° and 55° Brix were prepared and treated by the normal lime/aluminium sulphate process developed in the previous tests, the quantities of reagents used being corrected for the increased density : 500 ccs. of juice were used in each test, with 15 minutes contact time for lime and 5 minutes for aluminium sulphate, and using a temperature of 75°C.

No.	Gms. Lime	Gms. Al.S.	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Purity Diffce.	Filtration Rate		pH Value
								M.	S.	
Raw Jce.	-	-	43.9	38.6	87.8	-	-	-	-	4.7
1	9	-	43.9	38.8	88.3	11.1	+0.5	4	40	9.6
2	6.7	-	43.9	38.7	88.1	8.6	+0.3	4	10	9.6
3	6.7	4	43.4	38.2	88.0	7.5	+0.2	7	05	8.1
Raw Jce.	-	-	57.2	49.3	86.4	-	-	-	-	4.7
4	9	-	58.2	50.4	86.9	17.1	+0.5	150	00	9.7
5	9	5.4	57.9	49.9	86.5	11.5	+0.1	185	00	8.5
6	13.5	-	56.8	49.4	86.9	14.9	+0.5	230	00	10.9
7	13.5	8.1	57.1	48.8	85.5	18.0	-0.9	260	00	8.3

Remarks :- These tests show clearly the impracticability of treating raw juices for a major removal of impurities by ordinary defecation methods when the Brix° is above about 35°. The rate of filtration is very slow, the purity increase small, and the colour poor in all the above trials. The times of filtration given in tests 4-7 are only approximate.

15. Test on the settling rate of reagents as used in the lime/aluminium sulphate process of defecation.

The usual amounts of reagents were allowed to interact in water and the settling rate noted, with the time for complete settling. Distilled water was used, 500 ccs. per test, and the precipitates were settled in a litre cylinder at 20°C. The internal diameter of the cylinder was 6 cms. and the length of each column of liquid was 18 cms.

No.	Conditions of Experiment	Settling Time Mins.	Ppt. Volume Ccs.	Remarks
1	5 gms. of hydrated lime alone	3 24 hrs.	35 34	Complete and rapid settling
2	5 gms. hydrated lime and 3 gms aluminium sulphate	9 24 hrs.	150 80	Complete settl--ing very slow
3	10 gms. of hydrated lime	4 24 hrs.	60 56	Compares well with No. 1
4	10 gms. of hydrated lime and 6 gms. of aluminium sulphate.	8 18	450 380	Settling very much slower.
5	1 gm. lime and 3.3 gms aluminium Sulphate-these are the theoretical reaction quantities	10 20 30 40	490 473 455 435	This produced aluminium hydroxide which settled very slowly.

Where there was an excess of the large lime particles the flocculation was rapid, and this would indicate that an excess of lime is desirable over that amount necessary to interact with the aluminium sulphate, and the amount required to combine with the impurities in the raw juice.

16. Test following the behaviour of reducing-sugars during the lime/aluminium sulphate process of defecation.

The tests were conducted at 75°C., using 15 minutes contact time for the lime and 5 minutes for the aluminium sulphate ; each reagent was added in 10 ccs. water ; 500 ccs. raw juice were used in each test.

No.	Gms. Lime	Gms. Al.S.	Conditions of Experiment
1	5	-	Normal addition of lime alone.
2	5	3	Normal lime/aluminium sulphate process.
3	5	-	3 ccs. 1.16 s.g.HCl added, 15 mins. contact : then the lime added with 5 mins. contact at 75°C.
4	5	3	As in No.3, with after-addition of 3 gms.Al.S. 5m./75°
5	5	3	Normal process with after-addition of SO_2.
6	5	3	" " " " " " CO_2
7	5	3	Lime, aluminium sulphate, and SO_2 added together. 15 minutes total contact time.

No.	Brix°	%Sugar	Purity	Colour °Stam. 10°Bx.	Purity Diff.	Filtration Rate M.	Filtration Rate S.	pH Value	% Reducing Sugars	Invert Ratio
D.C.	-	63.2	-	-	-	-	-	5.0	0.54	0.85
Raw Jce.	36.2	31.7	87.7	-	-	-	-	4.7	0.79	2.49
1	36.2	32.2	89.1	7.9	+1.3	2	50	9.9	0.47	1.46
2	36.9	33.2	90.0	6.9	+2.3	3	10	8.6	0.44	1.33
3	36.8	32.0	87.0	5.0	-0.7	15	00	7.3	-	-
4	36.9	32.7	88.6	6.3	+0.9	5	50	7.8	0.62	1.90
5	36.8	32.6	88.7	6.7	+1.0	9	20	8.1	0.50	1.53
6	37.0	33.5	90.4	5.9	+2.7	9	30	8.0	0.61	1.51
7	35.6	32.0	89.8	4.4	+2.1	4	30	7.7	0.35	1.09

17. Lime/aluminium sulphate process of juice defecation :- Determination of optimum amount of aluminium sulphate.

In these tests 500 ccs. of raw diffusion juice was used and the lime was kept at the optimum amount of 5 gms. except where mentioned, giving 15 minutes contact time at 75°C. The aluminium sulphate was given 5 minutes contact at the same temperature. Each reagent was added in 10 ccs. of water.

No.	Gms. Lime	Gms. Al.S.	Brix°	% Sugar	Purity	Purity Diff.	Colour °Stam. 10°Bx.	Filtration Rate M.	S.	pH Value
Raw Jce.	-	-	34.2	30.3	88.6	-	-	-	--	4.6
1	5	-	33.5	29.8	89.0	+0.4	5.6	3	10	9.9
2	5	1	33.2	29.6	89.2	+0.6	4.8	2	00	9.1
3	5	2	33.6	29.9	89.0	+0.4	5.3	2	45	8.5
4	5	3	32.8	29.3	89.3	+0.7	4.9	3	50	7.9
5	3.51	4	34.2	30.5	89.2	+0.6	4.7	3	20	7.8
6	5	4	33.6	30.0	89.3	+0.7	5.0	3	10	7.7
7	5	5	34.0	30.3	89.1	+0.5	4.9	4	20	7.6
8	5	6	33.6	30 .0	89.3	+0.7	4.7	3	30	7.6

It seems probable that the optimum amount of aluminium sulphate required is 3 gms. per 500 ccs. of raw diffusion juice when using lime at the rate of 5 gms. per 500 ccs. juice. These amounts correspond to 0.43 per cent on weight of fresh beets for lime and 0.26 per cent for aluminium sulphate.

18. The use of Sulphur Dioxide and Carbon Dioxide in the lime/aluminium sulphate process of defecation.

These reagents were used to reduce the pH value of the treated juice to just above 7.0; the normal 5 gms.of lime and 3 gms. of aluminium sulphate were used on 500 ccs. of juice.

No.	Gms. Lime	Time of Contact Mins.	Temp. °C.	ccs. Juice	After -Treatment
1	10	15	75	1000	Filtered -
2				500	F.J. from no.1 treated with SO_2 at 65°C.to 6.9 pH; then added 3 gms. Al. S. with 5 mins. contact at 75°C.
3				500	F.J. from no.1 treated withSO_2 until just colourless to phenolphthalein.
4	10	15	75	1000	Filtered
5					F.J. from no.4 treated with 3 gms. Al.S. with 5 mins.contact at 75°C.
<u>6</u>				500	F.J. from no.4 treated with SO_2 at 65°C. to faint pink to'phthalein. Then added 3 gms. Al.S. + 5 mins.75°
7				250	F.J. from no.5 treated with SO_2 at 65°C.to 6.9 pH.
8	20	15	75	2000	Filtered
9				500	F.J. from no.8 treated with CO_2 at 65°C. to 8.5 pH,then 3 gms. Al.S. for 5 mins. at 75°C.
10				500	F.J. from no.8 treated with 3 gms. A Al.S. for 5 mins. at 75°C. Then CO_2 to pH 7.0

18. Continued :- Analytical results.

No.	Brix°	% Sugar	Purity	Colour °Stamm. 10°Brix	Purity Diff.	Filtration Rate M.	Filtration Rate S.	pH Value	Remarks
Raw Jce.	37.4	32.8	87.7	-	-	-	-	4.8	-
1	36.4	32.1	88.2	5.9	+0.5	7	00	9.8	Lime alone
2	37.2	33.0	88.7	2.4	+1.0	0	40	5.5	SO_2 + Al.S.
3	37.7	33.8	89.7	2.4	+2.0	0	55	5.5	SO_2 + Al.S.
4	37.3	33.3	89.3	6.7	+1.6	7	15	9.9	Lime alone
5	37.7	33.6	89.1	4.4	+1.4	0	30	7.9	Lime + Al.S.
6	38.2	33.8	88.5	3.6	+0.8	0	25	7.3	SO_2 + Al.S.
7	37.9	33.7	88.9	3.3	+1.2	0	25	6.7	Lime+Al.S.+ SO_2
8	37.8	33.7	89.1	6.7	+1.4	7	00	9.9	Lime alone
9	38.2	34.1	89.3	3.7	+1.6	0	35	7.2	CO_2 + Al.S.
10	37.1	33.2	89.5	3.7	+1.8	0	30	7.0	Al.S. + CO_2
11	37.1	32.8	88.4	3.5	+0.7	0	30	6.9	Repeat of 7.
12	36.5	32.6	89.3	4.4	+1.6	0	25	7.3	Repeat of 10.

The filtered juices produced by the above methods were very satisfactory in comparison with those from previous tests. The use of carbon dioxide gives juices almost as good as those from sulphur dioxide treatment. It was noticed that with the carbonated juices there is always a dark shadow in the juice when viewed in a boiling tube, whereas with sulphited juice the tint seems to be more a monochromatic yellow.

Test with filtration rate of water and a pure sucrose solution through the standard filter used in the purification tests.

A solution of pure sucrose was made at 36.57°Brix, and 500 ccs. of this solution was heated to different temperatures and the time of filtration of 50 ccs. noted.

Sugar solution :-	Brix°	% Sugar	Purity
	36.57	35.90	98.17

Results :-

(1) Water

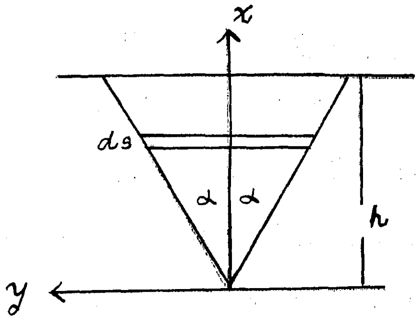
	Temperature °C.						
	30	40	50	60	70	80	90
Time of Filtration for 50 ccs. (a)	50	40	35	33	31	28	25
(b)	48	42	35	31	31	28	25
Average	49	41	35	32	31	28	25

(2) Sugar Solution

	Temperature °C.						
	30	40	50	60	70	80	90
Time of Filtration for 50 ccs. (a)	30	24	22	20	18	17	15
(b)	32	24	22	18	19	18	15
Average	31	24	22	19	18.5	17.5	15

This test was designed to serve as a basis for comparison with the raw juices used in the defecation experiments as regards rate of filtration. It was found that the sugar solution Brix° had risen to 41.2 after the test at 100°C.

The Pressure of Filtration in a Funnel.



Consider a funnel of cone angle 2α, and height h from cone apex.

An element ds will have area $2\pi y\,ds$, where $\frac{ds}{dx} = \sqrt{1+\left(\frac{dy}{dx}\right)^2} = \sec\alpha$

Thus $ds = 2\pi\tan\alpha\sec\alpha\,x\,dx$

The force on the element $= p.ds$ where $p = \rho(h-x)$, and the total force on the cone

$$= \int_0^h \rho(h-x).2\pi\tan\alpha\sec\alpha\,x\,dx$$

$$= 2\pi\rho\tan\alpha\sec\alpha\left[\frac{hx^2}{2} - \frac{x^3}{3}\right]$$

$$= \frac{1}{3}\pi\rho h^3\tan\alpha\sec\alpha$$

where ρ (rho) = density of liquid being filtered.

Total surface area of the cone $= \int_0^h ds = 2\pi\tan\alpha\sec\alpha\frac{h^2}{2}$

Thus the mean pressure per unit area, $\bar{p} = \frac{1}{3}\rho h$.

<u>Example :-</u> In a 6 inch funnel (diameter) with 60° sides :

$h = 4.5"$, and in filtering 30° Brix juice (sp.gr.=1.13)

the pressure, $p = \frac{1}{3} \times 1.13 \times 4.5 \times 0.0361$

$$= 0.061 \text{ lbs. per sq. inch.}$$

(A 1 inch column of water = 0.0361 lbs., per sq. inch)

19. The use of calcium phosphate as neutralising agent in the lime/aluminium sulphate process of defecation.

Lime was applied at the rate of 5 gms. per 500 ccs. raw diffusion juice with 15 minutes contact at 75°C., and aluminium sulphate at 3 gms. per 500 ccs. at the same temperature, allowing 5 minutes contact. The varying quantities of phosphate were allowed 5 minutes contact at 75°C., the treated juice then being filtered.

No.	Gms. Ca phos. added	Brix°	% Sugar	Purity	Colour °Stammer: 10°Bx.	Filtration Rate M.	Filtration Rate S.	Purity Diffce.	pH Value
Raw Jce.	Nil	39.8	34.9	87.7	-	-	-	-	4.8
1	"	37.9	33.6	88.6	7.9	5	10	+0.9	9.9
2	1.0	39.8	35.4	88.9	5.0	12	00	+1.2	7.8
3	1.5	39.8	35.5	89.2	4.2	17	00	+1.5	7.7
4	2.0	40.5	35.9	88.5	4.0	17	15	+0.8	7.6
5	1.0	39.9	35.3	88.5	4.7	19	00	+0.8	7.9

In all tests the lime was added in 10 ccs. of water ; in Nos. 2 and 5 the difference lay in adding the Al.S. and phosphate solid in No. 2 and in 10 ccs. water each in No. 3.

These results were satisfactory with regard to colour and purity of the final juices, but the filtration rates were slow, and the phosphate is a relatively expensive reagent. The same results are achieved by sulphur dioxide or carbon dioxide with very much better filtration. This test emphasises the well-known tendency of the phosphate defecants to give close-grained, slow-settling, and/slow-filtering precipitates.

20. The effect of juice density in defecation by the lime/aluminium sulphate process.

The effect of lime, and of lime and aluminium sulphate were observed on the same raw diffusion juice diluted from 40°Brix to 30° 20°, and 10°Brix, the weights of reagents used being calculated in proportion to the amounts of solids in 500 ccs., for each juice.

Brix°	Lbs. Solids per Gallon	Gms. Lime used	Gms. Al.S. used	Example 30° Brix
40	4.72	5.00	3.00	Lime =
30	3.38	3.58	2.16	$\frac{5 \times 3.38}{4.72}$
20	2.17	2.30	1.40	Al.S.=
10	1.04	1.10	0.67	$\frac{3 \times 3.38}{4.72}$

All tests were made at 75°C. with 15 minutes contact time for lime, and 5 minutes for aluminium sulphate : the reagents were added each in 10 ccs. of water.

No.	Gms. Lime	Gms. Al.S.	Brix°	%Sugar	Purity	Colour °Stam. 10°Bx.	Filtration Rate M.	S.	Purity Diff.	pH Value	Remarks
Raw Jce.	Nil	Nil	40.1	35.3	88.0	-	-	-	-	4.7	Original
1	5	Nil	41.0	36.5	89.0	6.8	14	00	+1.0	9.3	Lime alone
2	3.58	2.16	40.6	36.1	89.0	5.6	9	10	+1.0	7.2	Lime & Al.S.
3	Nil	Nil	30.4	26.7	87.8	-	-	-	-	4.7	Raw Jce.
4	3.58	Nil	31.9	28.3	88.7	6.8	4	50	+0.9	9.6	Lime Alone
5	3.58	2.16	31.5	28.0	88.9	7.3	4	10	+1.1	7.1	Lime & Al.S.
6	Nil	Nil	20.7	18.3	88.4	-	-		-	4.7	Raw Jce.
7	2.30	Nil	20.9	18.5	88.5	9.3	1	10	+0.1	9.0	Lime alone

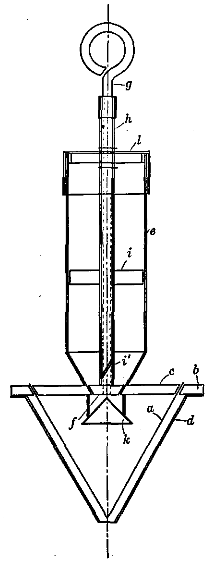
20. Continued :-

No.	Gms. Lime	Gms. Al.S.	Brix°	%Sugar	Purity	Colour °Stam. 10°Bx.	Filtration Rate M.	Filtration Rate S.	Purity Diff.	pH Value	Remarks
8	2.30	1.40	21.4	19.0	88.8	7.3	1	50	+0.4	7.4	Lime & Al.S.
9	Nil	Nil	10.5	9.3	88.5	-	-	-	-	4.7	Raw Jce.
10	1.10	Nil	11.4	10.2	88.6	9.3	1	00	+0.1	8.7	Lime alone
11	1.10	0.67	10.9	9.7	88.8	4.8	0	40	+0.3	7.7	Lime & Al.S.
12	10.00	3.00	41.3	36.5	88.4	8.3	6	30	+0.4	9.7	Lime & Al.S.

The raw juice used in this test was of poor quality : even with the lime quantity doubled the result was not good, the colours being darker than usual. The filtration rate increases apparently in direct ratio to the dilution, but the colour was better at 40°Brix than at 20° or 30°.

Comparison of Filtration Rates :-

The apparatus used was similar to that shown in Fig.35. The paper filter a is held fast at its upper edge by the covers b and c. The jacket d serves as heat insulator. The juice to be filtered is placed in vessel e which is closed by stopper f on rod g. This rod is surrounded by a hollow spindle h to which two stirrers i and i' are fixed. The cone k serves to distribute the liquid.



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Apparatus for determining filterability of sugar juices.

Figure 29

21. Variations in the method of application of aluminium sulphate in the lime/aluminium sulphate process of defecation.

The juice used in this test was dark and of poor quality: 500 ccs. were used for each test with 10 gms. of lime added in 20 ccs. of water and 15 minutes contact time. This gave 0.89 per cent lime on fresh beets, and did not give a finished juice of better colour. The aluminium sulphate was given 3 minutes contact time.

No.	Gms. Al.S.	Temp. °C.	Brix°	%Sugar	Purity	°Colour Stammer 10°Brix	Filtration Rate		pH Value	Remarks
							M.	S.		
Raw Jce.	-	-	31.8	28.0	88.3	-	-	-	4.5	-
1	Nil	75	31.3	27.8	88.8	6.2	4	30	10.9	Lime alone
2	3	75	30.8	27.4	89.0	3.9	4	00	8.3	Standard procedure
3	3	95	32.5	28.7	88.4	5.3	5	20	7.7	Limed at 75°
4	3	75	31.6	28.0	88.6	5.1	5	00	7.6	Lime & Al.S. added together
5	3	95	32.1	28.5	88.8	5.4	4	55	7.4	

In test No. 5 the lime and aluminium sulphate were added together at 95°C.

It is clear from these tests that this beet juice containing relatively large amounts of reducing sugars cannot be treated at a temperature much above say 80°C. without attack on the reducing sugars and consequent darkening of the colour. The addition of the reagents together has not given so good a result as the usual method of separate additions. The increased lime used in this test was necessary with the poor quality juice, and this shows the need for cautious regulation of the amounts of reagents used in proportion to the quality of the juice.

22. Use of aluminium salts in defecation after liming:-

In this series of tests 500 ccs. of raw diffusion juice was used for each test, and 5 gms. of lime was added giving 15 minutes contact at 75°C. Three gms. of each aluminium salt was used with 5 minutes contact at 75°C., except in the case of the powdered metal where 10 minutes contact was allowed.

No.	Salt added	Brix°	%Sugar	Purity	Colour °Stammer 10°Brix	Purity Diff.	Filtration Rate M.	S.	pH Value
Raw Jce.	-	36.1	31.6	87.5	-	-	-	-	4.7
1.	Lime alone	34.0	30.0	88.2	7.1	+0.7	4	10	9.9
2	Al. sulphate	36.3	32.0	88.1	5.4	+0.6	3	25	7.4
3	" metal (powder)	37.0	33.0	89.2	7.7	+1.7	9	15	7.1
4	Al. acetate	36.2	32.1	88.7	6.3	+1.2	6	15	7.5
5	Al. Carbonate	36.0	32.2	89.4	5.3	+1.9	5	30	7.5
6	Al. Nitrate	36.6	32.6	89.1	8.3	+1.6	5	30	7.1
7	Al. Oleate	37.3	33.5	89.8	9.1	+2.3	9	10	7.7
8	Al. Phosphate	37.2	33.1	89.0	14.3	+1.5	6	30	7.7
9	Al Silicate	36.2	32.2	89.0	7.7	+1.5	3	50	7.0
10	Al. Silico-fluoride	36.7	32.6	88.8	7.5	+1.3	7	00	7.5
11	Al. Tannate	35.6	31.4	88.2	8.3	+0.7	9	10	7.3

The best result was obtained with the carbonate, but in general no great advantage is visible with any of these salts in comparison with aluminium sulphate. The juice from silicate treatment was dim, and that from nitrate very dull in appearance.

ANALYSES OF PRODUCTS FROM EXPERIMENTAL CLARIFICATION

PRODUCT	RELATIVE YIELD LBS.	% SOLIDS	% SUCROSE	% REDUCING SUGAR	% ASH	% OTHER ORGANIC MATTER (by diff.)	% LIME SALTS
Fresh Beet	400	23.55	70.91	1.27	2.91	7.12	0.17
Dried Cossettes	100	92.16	68.14	0.87	3.18	8.07	0.55
Diffusion Juice	160	36.22	87.10	1.56	2.02	9.32	0.44
Filtered Limed Jce.	158	36.12	87.50	1.41	2.13	8.96	0.94
Filtered Juice after $Al_2(SO_4)_3$	160	35.79	87.80	1.42	2.79	7.99	0.78
Filtered Juice after Sulphitation	160	35.79	87.44	1.29	2.71	8.56	0.39
Filtered Juice after Carbonatatn.	160	35.86	89.82	1.33	2.68	6.17	0.75
First Massecuite	63.5	91.00	89.80	1.46	2.65	6.09	0.43
First Syrup	31.1	82.00	79.49	3.63	4.98	11.90	0.97
First Sugar	32.4	0.02[x]	99.85	0.02	0.07	0.04	--
Second Massecuite	27.2	93.20	84.49	3.92	3.17	8.42	--
Second Syrup	15.0	82.00	67.24	6.98	6.20	19.58	--
Second Sugar	12.2	1.00[x]	97.00	0.75	0.80	1.45	--
Third Massecuite		94.00	76.20	5.73	16.60	11.47	--
Third Syrup (Final Molasses)		86.80	58.80	7.80	10.20	23.20	--
Third Sugar		98.00	94.20	1.33	1.43	3.04	--
Waste Pulp	350	12.25	3.51	--	--	--	--
Dried Pulp		88.80	2.25	--	7.23	--	--
Dried Pulp (Ordinary Process)		86.52	0.92	--	4.32	--	--
Filtered Juice (Solid liming)	155	37.00	87.30	1.49	2.24	8.97	0.65
F.Jce.(Dble. Lime)	160	35.92	87.14	1.42	4.09	7.35	2.53

ANALYSES OF PRODUCTS FROM EXPERIMENTAL CLARIFICATION

PRODUCT	% SOLUBLE PECTIN	% PROTO) PECTIN	% PENTO -SAN	% TOTAL N_2	% ALBd. N_2	SO_2 P.P.M.	SO_3 P.P.M.
Fresh Beet	trace	4.67	9.13	0.64	2.19	below 1	5.75
Dried Cossettes	0.33	5.59	6.31	1.37	7.31	90	21.2
Diffusion Jce.	0.11	1.38	0.39	0.77	3.56	110	7.4
Filtered Limed Juice	0.019	--	0.27	0.80	5.00	69	0.4
Filtered Jce. after $Al_2(SO_4)_3$	Nil	Nil	0.20	0.75	4.69	56	0.9
Filtered Jce. after SO_2	Nil	Nil	0.31	0.67	4.19	(0.33%)	0.8
Filtered Jce. After Carbn.	Nil	Nil	0.26	0.67	4.19	110	0.8
First M/cuite.	trace	Nil	0.11	0.68	4.25	75	0.9
First Sugar	Nil	Nil	Nil	--	--	16	--
First Syrup	trace	Nil	trace	1.10	6.88	42	1.6
Second M/cuite	trace	Nil	0.20	1.20	7.50	20	1.4
Second Syrup	Nil	Nil	0.33	1.63	10.18	46	2.1
Second Sugar	Nil	Nil	Nil	--	--	22	--
Third M/cuite	Nil	Nil	0.15			73	2.0
Third Syrup (Final molasses)	trace	Nil	0.22			60	3.6
Third Sugar	Nil	Nil	Nil			21	0.4
Waste Pulp	2.69	13.55	17.96	1.06	6.63	--	--
Dried Pulp	0.44	17.57	18.47	1.98	6.13	75	--
Dried Pulp (Ord.process)	1.96	21.84	23.58	1.96	12.25	--	1.4
Filtered Jce. (Solid Liming)	Nil	Nil	0.51	0.70	4.38	135	0.5
Filtered Jce. (Double Lime)	Nil	Nil	0.36	0.67	4.19	84	0.6

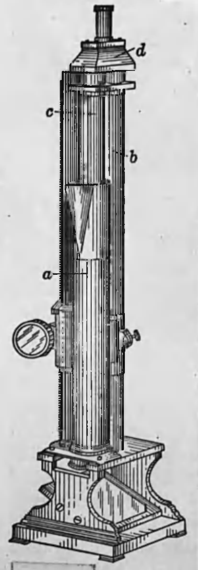
<u>Ammoniacal Nitrogen :-</u> Fresh Beet, 0.29 % : Dried Cossettes, 0.20 % : Diffusion Juice, 0.20 %.

BALANCE OF ASH AND INVERT SUGAR IN EXPERIMENTAL DEFECATION.

PRODUCT	LBS. WET	PER CENT SOLIDS	LBS. DRY	PER CENT ASH ON DRY	PER CENT REDUCING SUGARS ON DRY	LBS. DRY ASH	LBS. DRY REDUCING SUGARS
DRIED COSSETTES	100	92.16	92.16	3.18	0.87	2.93	0.80
RAW JUICE	160	36.22	58.0	2.02	1.56	1.17	0.90
PURIFIED JUICE	160	35.86	57.4	2.68	1.33	1.54	0.76
FIRST M/CUITE	63.5	91.00	57.8	2.65	1.46	1.53	1.06
FIRST SYRUP	31.1	82.00	25.5	4.98	3.63	1.27	0.93
FIRST SUGAR	32.4	99.98	32.3	0.07	0.02	0.02	0.01
SECOND M/CUITE	37.2	93.2	34.7	3.17	3.92	1.10	1.36
Second SYRUP	20.5	82.00	16.8	6.20	6.98	1.04	1.17
SECOND SUGAR	16.7	99.00	16.5	0.80	0.75	0.13	0.12

This balance shows some discrepancies, but on the whole is probably as close as could be expected for the experimental conditions in a pilot plant using relatively small quantities of material. Part of the second crop sugar was used as a footing for the final boiling made, so that the balance is not complete. The yield from the first massecuite was approximately 51 per cent crystals, and from the second massecuite 45 per cent.

FIGURE 30 - "SPEKKER" PHOTOELECTRIC ABSORPTIOMETER.



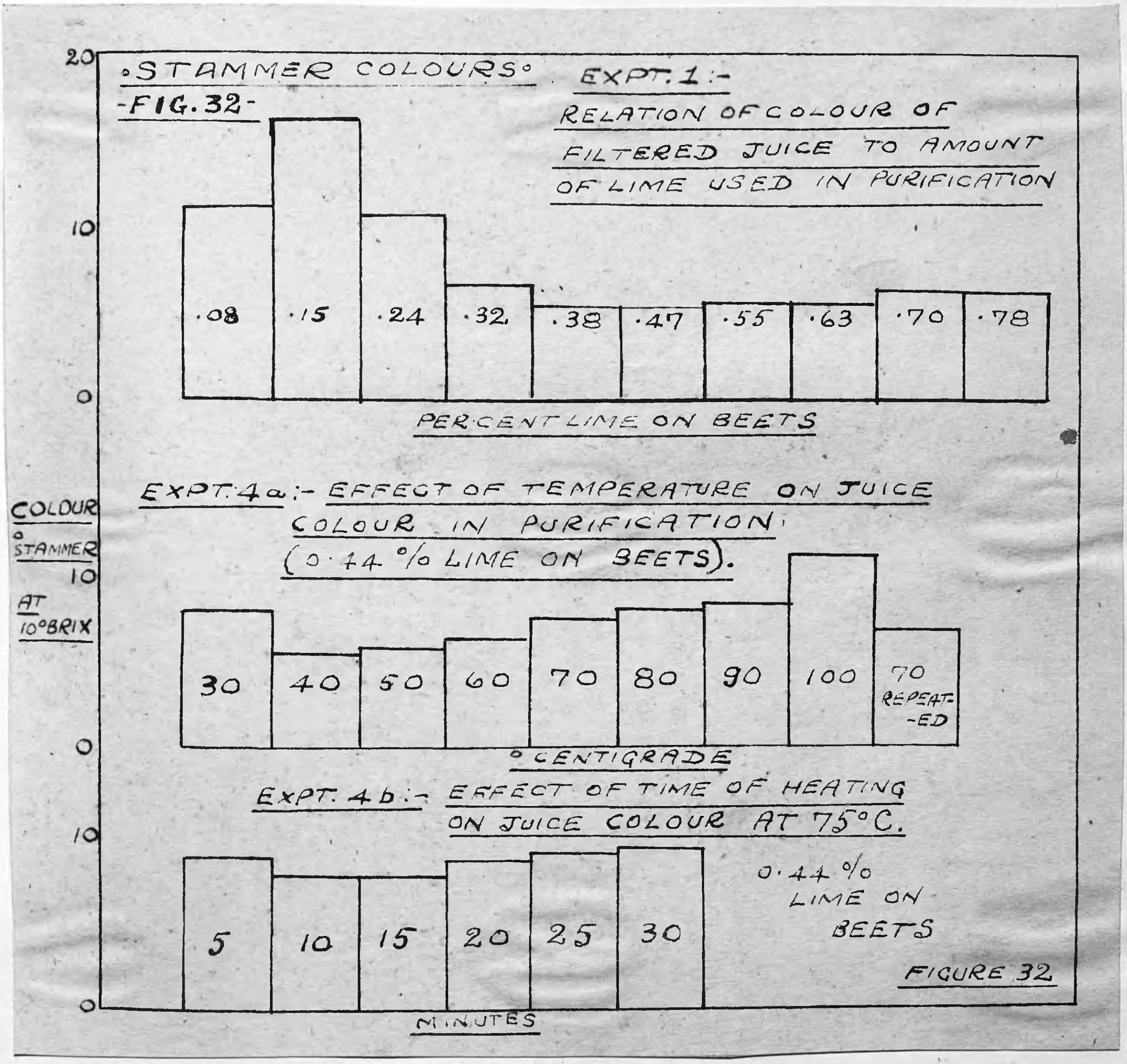
Stammer's colorimeter.

FIGURE 31.

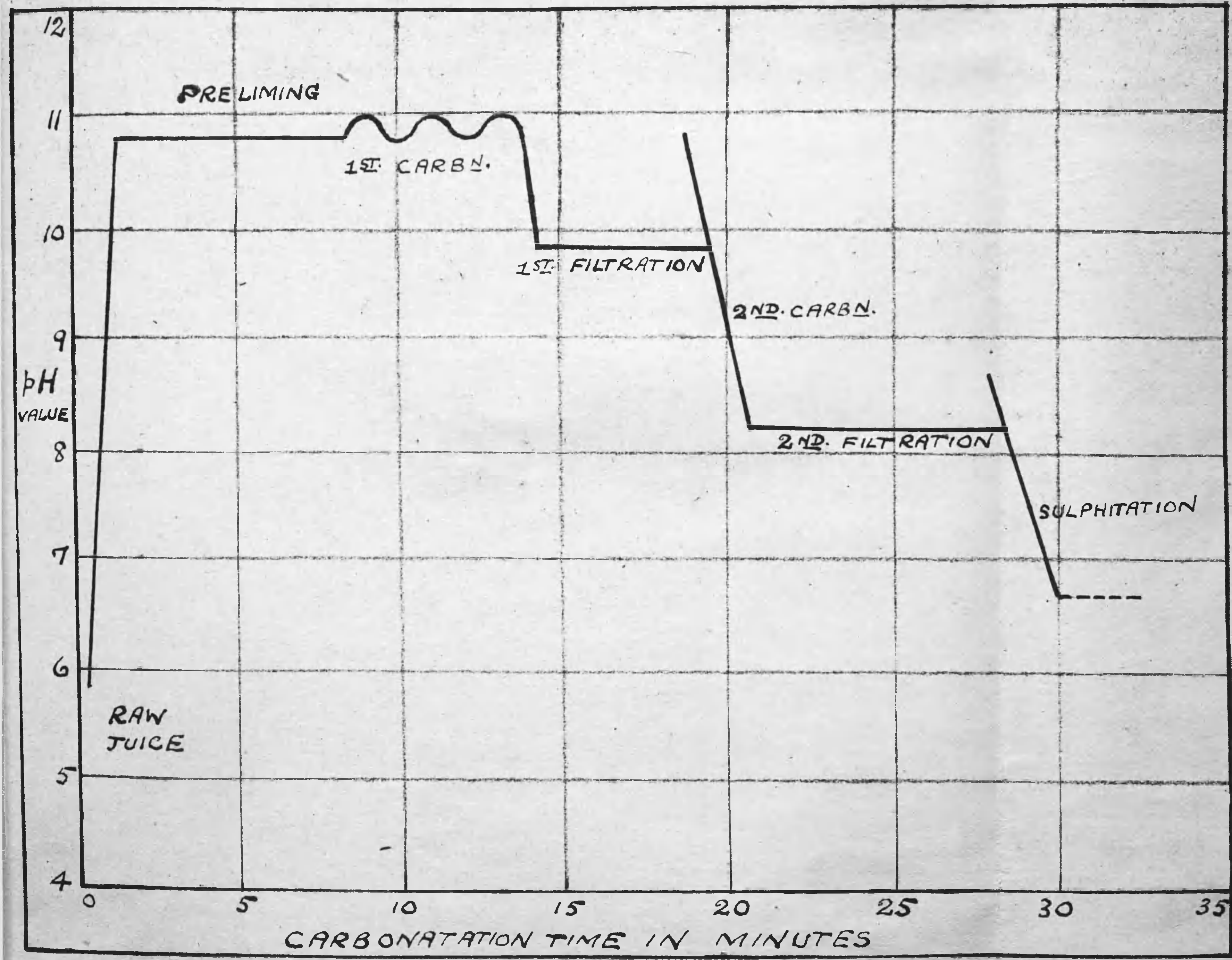
The Stammer Colorimeter.

The original Stammer colorimeter was described inStammer's "Zuckerfabrikation",p.747,1887. Discs of coloured glass were used to give a reproducible colour standard,and a value of 100 was given by Stammer to a solution which matched the standard disc for a scale reading of 1 mm. The colour value of any liquid in Stammer degrees is found by dividing 100 by the reading of the scale in mm.

This colorimeter was used in all the defecation tests described in this work,and the Stammer glasses were checked by a method due to Sandera (Z.Zuckerind.cechoslovak. Rep.,57,44,1932/33). This consists of comparing the glass discs with a standard solution which has practically the same absorption curve as the glass. The solution is made by dissolving 1 gm. nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$, 1.2 gms. cobalt ammonium sulphate,$CoSO_4.(NH_4)_2SO_4.6H_2O$, and 0.019 gm.potassium dichromate in dust-free distilled water, and diluting to 100 ccs. The Ni and Co salts are first recrystallised from water and dried in dust-free air on a glass plate. The recrystallised potassium dichromate is dried at $150^\circ C$. These salts are stored in glass stoppered bottles, and made fresh as required. The standard solution has a colour of exactly 5°Stammer, that is, 1°Stammer is defined by a thickness of 20 mm. of the solution. If a normal glass to be checked is found to be matched in the colorimeter by say, 22.8 mm. of the solution, then all results obtained with this glass must be multiplied by $\frac{22.8}{20}$, or 1.14, to convert the observed degrees into standard Stammer degrees. A complete spectrophotometric analysis of the normal Stammer glass is given by Spengler and Landt (Z.ver.d.Zucker-Ind. 83,223.1933).


·STAMMER COLOURS·
-FIG. 32-
EXPT. 1:-
RELATION OF COLOUR OF FILTERED JUICE TO AMOUNT OF LIME USED IN PURIFICATION
20
10
0
·08
·15
·24
·32
·38
·47
·55
·63
·70
·78
PER CENT LIME ON BEETS
EXPT. 4a:- EFFECT OF TEMPERATURE ON JUICE COLOUR IN PURIFICATION.
(0·44 % LIME ON BEETS).
COLOUR
°STAMMER
AT
10°BRIX
10
0
30
40
50
60
70
80
90
100
70 REPEATED
° CENTIGRADE
EXPT. 4b:- EFFECT OF TIME OF HEATING ON JUICE COLOUR AT 75°C.
10
0
5
10
15
20
25
30
0·44 % LIME ON BEETS
FIGURE 32
MINUTES

ooo FIGURE 33 : pH VALUES IN SIMPLE CARBONATATION ooo



(AFTER HONIG.)

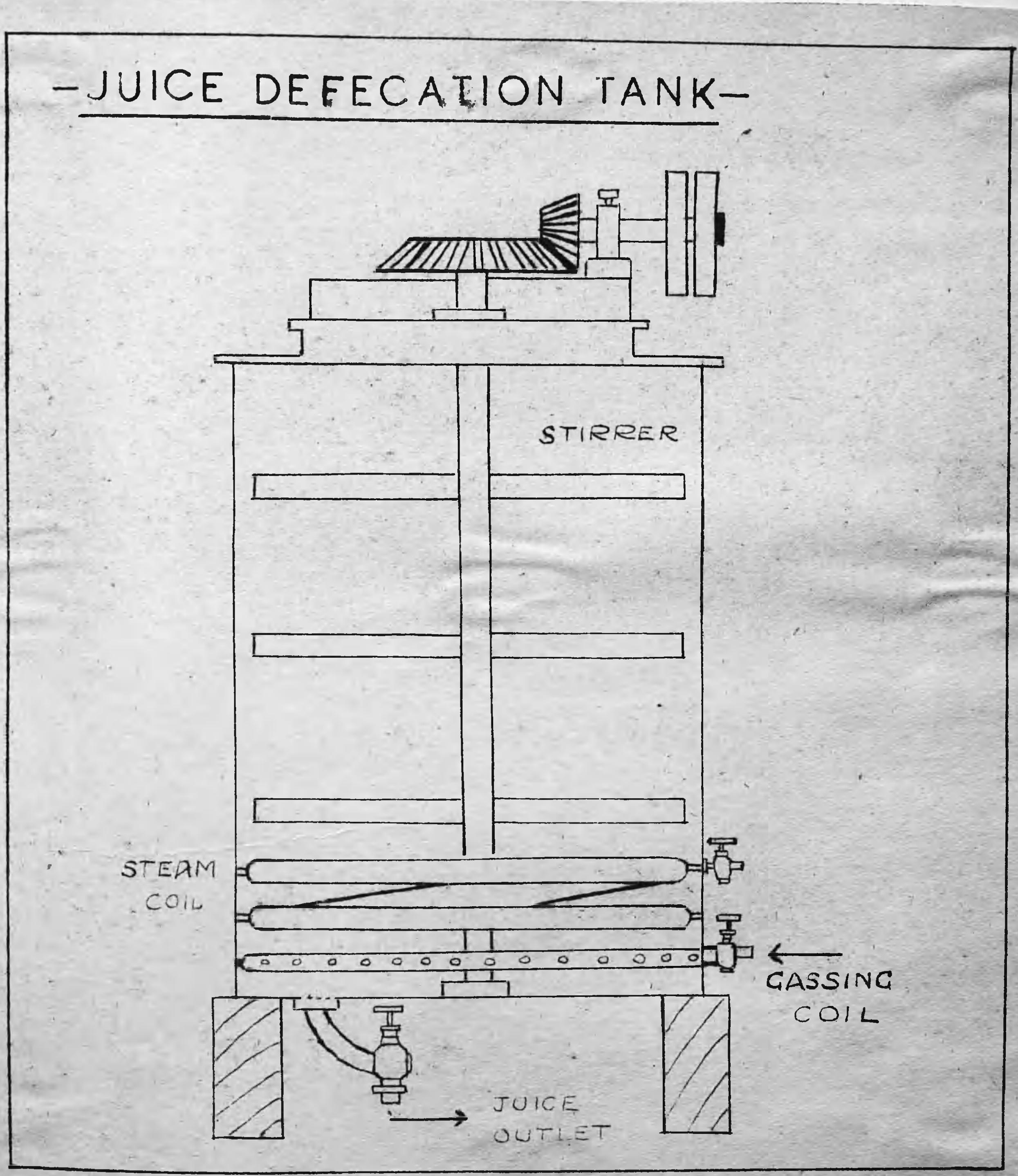

-JUICE DEFECATION TANK-
STIRRER
STEAM COIL
GASSING COIL
JUICE OUTLET

FIGURE 34.

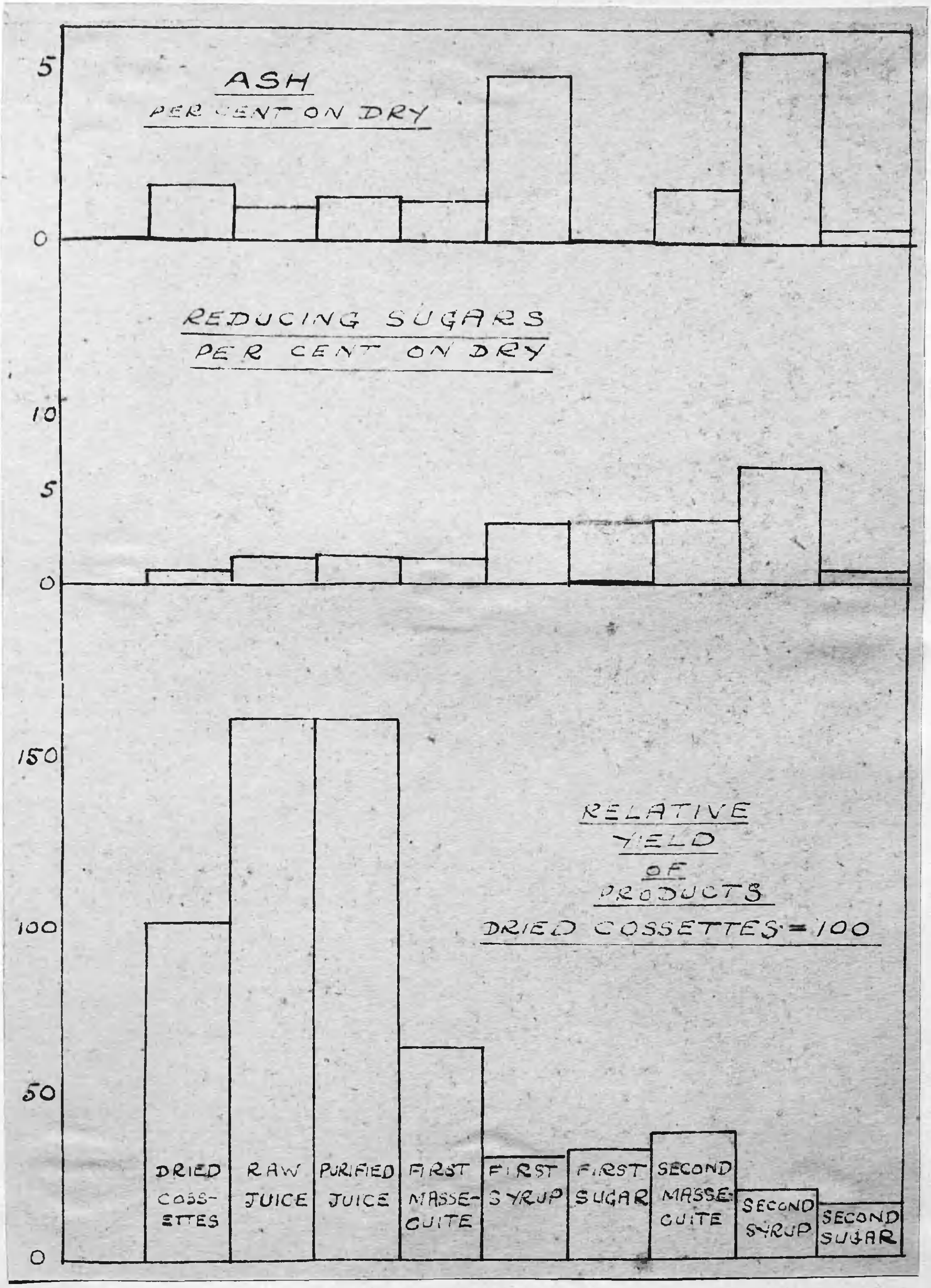

ASH
PER CENT ON DRY
5
0
REDUCING SUGARS
PER CENT ON DRY
10
5
0
RELATIVE
YIELD
OF
PRODUCTS
DRIED COSSETTES = 100
150
100
50
0
DRIED COSSETTES
RAW JUICE
PURIFIED JUICE
FIRST MASSECUITE
FIRST SYRUP
FIRST SUGAR
SECOND MASSECUITE
SECOND SYRUP
SECOND SUGAR

FIGURE 35.

SECTION 5.

PART 1 : Summary of Analytical Methods used for the determination of the apparent sucrose (polarization) and reducing sugars in fresh beets and Dried Cossettes.

1. Sampling :

2. Polarization :

3. Reducing sugars.

NOTE :- The methods of analysis for polarization and reducing sugars in fresh beets and dried cossettes have already been given in brief outline in section 1 (Composition of the Sugar Beet).

In the present section these methods are described in detail.

METHODS OF ANALYSIS

Analysis of fresh beet slices :- Sampling:-

In a plant working over the full 24 hours of the day the perfect method of sampling would be the taking of a sample almost continuously, about every 3 minutes, with removal of the average sample to the laboratory every two hours. Properly carried out, this method is beyond criticism. In practice, the sample may be taken every quarter of an hour, and removed to the laboratory at once. These samples are composited and analysed every hour, taking care to mix thoroughly and to take smaller lots from different parts of the pile.
The average sample is passed through a mincer of the Russwin or Universelle type (Gillet) with exterior knives, taking care that no juice is expressed from the sample.

Polarisation :- The normal weight, 26 gms. is weighed out in a tared nickel capsule and transferred to a 200 ccs. Kohlrausch flask with distilled water. The necessary volume of neutral lead acetate solution (or of Lead subacetate solution) is added to the flask before adding the cossettes. Usually 5-7 ccs. will be sufficient. The volume in the flask is made to 160/170 ccs. with warm sugar-free water, and the flask is transferred to a thermostatically controlled water-bath regulated in advance to 88°C. The flask is left in for 30 minutes, and then withdrawn and the volume completed to the mark without cooling. The flask is replaced in the bath and digested for a further 30 minutes. It is now cooled, froth removed by application of ether vapour, and the volume completed. After shaking well the liquid is filtered with addition of a drop of glacial acetic acid if neccessar

Analysis of Dried Cossettes :- **Sampling :-**

Samples are collected along the breadth of the discharge end of the Drier (for drying control), taking care to sample the depth of the layer as well. These samples should be taken at quarter-hour intervals. During extraction control the samples are taken from the conveyor belt bringing the cossettes from storage.

The sample is thoroughly mixed and a representative portion ground in an impact type mill with a 3/8 inch screen to yield about 200 gms. as sample. The Harrison-Carter mill with four beater arms is satisfactory.

Polarisation :- The estimation is carried out exactly as described for fresh beet, but taking a half-normal weight (13 gms.)

Determination of Reducing Sugars in Fresh beet and Dried cossettes.

The weights used are 60 gms. for fresh beet and 15 gms. for dried cossettes, taking marc volume at 2.8 ccs. and 0.7 cc. respectively. If the marc volume allowance be included in the weight the amounts taken will be 59.2 for fresh beet, or 14.8 gms for dried cossettes. Digestion is made in each case exactly as for the polarisation and preferably at the same time, but with the use of neutral lead acetate as required . The final filtrate obtained is used for the reducing sugar determination by the Bertrand-Saillard method, 100 ccs. being deleaded with potassium oxalate (dry), and filtered.

For the actual estimation 50 ccs. of the deleaded filtrate is placed in a 150 ccs. conical flask , 20 ccs. of mixed Bertrand-Saillard Copper reagent added, and the whole heated for 22 minutes exactly in a water bath maintained at 62-63°C.

The filtrate, which must be perfectly clear, is polarised in a 400 mm. tube at close to 20°C.

The Digestion bath used should be cylindrical, preferably of copper, and fitted with a constant level device arranged so that the water level is always a little above the gauge mark of the flasks. The bath should hold atleast five flasks, and will have a perforated tray in the bottom, on which the flasks rest. The thermostatic control should keep the temperature of the bath within ± 0.5°C. of 88°C.

Marc Volume:- This was taken as 1.2 ccs. per Normal weight of fresh beet. The final volume in the flask must therefore be 201.2 ccs. Alternatively this allowance may be made in the Normal weight and the volume made to 200 ccs.-li.e. 25.7 gms. weighed instead of 26 gms. or 12.85 in place of 13, or 51.4 in place of 52 gms. according to the weight required for a particular estimation.

Notes :- The saccharimeter zero point should be checked frequently with a standard quartz plate reading around 35°, and the instrument should be accurate to 0.05°. It is not recommended to use tubes longer than 400 mm., as in practice the reading errors will outweigh the additional accuracy due to the longer tube.

The first few drops of filtrate should be thrown away and all the remaining liquid filtered and mixed before filling the tube, taking every precaution to avoid evaporation. A very little Analytical grade Celite (kieselguhr) may be used to aid clarity in difficult filtrations : this must be added after completion to volume.

The use of Haynes special volumetric flasks carrying a lateral tube of small diameter is convenient for making to volume when there i

SECTION 5.

METHODS OF ANALYSIS.

PART 2 : Determination of Major Constituents other than Water.

- Polarisation
- Sucrose
- Reducing Sugars

Part 2 :- Determination of Major Constituents other than Water :

METHODS OF POLARISATION :-

Expression : Extraction : Digestion :

- Application to Dried Beet Cossettes.

Adsorption of Sucrose by the Marc.

EXPERIMENTAL :-

Tests on polarisation of Fresh Beets and Dried Cossettes :

Experiments on the influence of temperature in hot digestion of :-

1. Fresh Beets : 2. Dried Cossettes :

Comparison of Methods for the Polarisation of Sugar Beets :

Consideration of Results.

Experiments on the determination of the Polarisation and Reducing-Sugar content of Dried Beet Cossettes :-

1. Effect of size of material and mode of Digestion :
2. Cold v. Hot Digestion for Reducing Sugars estimation :
3. Influence of concentration on Polarisation :
4. Extended Tests on the influence of concentration on polarisation :

The Bertrand-Saillard Method for Determination of Reducing Sugars : Application to Dried Beet Cossettes :

Experiments on the Determination of Reducing Sugars :

1. Digestion with N/28 Sodium Hydroxide :
2. Variation of Digestion c onditions :
3. Use of different filtebing media :
4. Check of method using Standard Invert Sugar Solution :
5. Use of Neutral and Basic Lead Acetate :

THE POLARISATION OF SUGAR BEETS AND SUGAR PRODUCTS.

The readings of the saccharimeter scale indicate percentage of sucrose only if other constituents are without effect upon the reading, and results obtained with impure materials are thus more correctly expressed as degrees "polarisation".

The clarifying agents used may have considerable influence upon the reading and must be selected with great care and used in minimum amount which will ensure sufficiently rapid filtration, a bright filtrate, and the smallest possible error due to its use.

Methods of polarisation:-

In polarising plant materials the methods in general use are expression, extraction, or digestion. The material should be in a very finely divided condition for all of these.

In prinsiple the method of expression is the most accurate since it eliminates errors due to the uneven nature of the juice, the presence of colloid water, or the adoption of a fixed figure for marc content. The main difficulty with this method is to ensure that the same pressure is used in all cases.

The extraction method using hot water is liable to cause solution of optically active gums, hemi-celluloses, and pectic acid, leading to considerable errors in the polarisation taken as sugar. This particular error is eliminated by alcoholic extraction, since these substances are relatively insoluble in ethyl alcohol. The alcoholic method has been regarded as giving an accurate estimate of the sugar in a plant substance, but Herzfeld long ago admitted that its absolute accuracy had not been proved. It is not now regarded as the standard method. The principal errors which may arise in alcoholic extraction are the effect of alcohol on the polarisation of the non-sugars present, and the effects on both the sugars and the non-sugars of the prolonged period of heating,and of the excess lead and acetates formed in the clarification of the solution. Alcoholic extraction normally gives lower results than obtained by expression of the juice, and it is also tedious and long requiring fragile apparatus. Its use as a standard for judging the results by other methods has been abandoned on these grounds by some continental countries.

Digestion method :- These may be regarded as a combination of the methods of extraction and expression, and are generally rapid. The principle is to digest a weighed amount of pulp with a large excess of water or alcohol for a time long enough to ensure complete diffusion of the sugar throughout the liquid. The volume is then made up at standard temperature after clarifying, and the solution filtered and polarised. With hot digestion a coarser pulp may be used but the time required is greater : this method is often used in routine control. Cold digestion methods are well adapted for rapid testing - e.g. in beet selection trials or the polarisation of beets entering the factory when hundreds of samples may have to be analysed each day.

Dried Beets :- These are high in both sugar and marc content. Spengler, Paar, and Mück (Z. verein Deut. Zuck. Ind.,87,594,1937) have found that the marc volume of dried beets upon digestion with water is 4.5 ccs. per Normal weight, and the marc volume for dried cossettes from the Steffen hot juice extraction process is 9.6 ccs.

Extraction or digestion methods are probably not suited for accurate work with dried products, since caramelisation and inversion of sucrose may occur during the drying process.

The method adopted for dried beet polarisation should employ not more than a half-normal weight in a 200 ccs. flask with allowance for marc volume,and making the reading in a 400 mm. tube Using Spengler's figures (ibid.) for marc volume, the volume would be made to 202.25 ccs. It is generally more convenient to take a smaller normal weight (12.86 gms. in place of 13 gms.) rather than have flasks marked specially at 202.25 ccs.

<u>ADSORPTION OF SUCROSE BY THE MARC :-</u> <u>Martraive</u>, (Bull. Assoc.Chim., 52, 775,1935 : 53,609,1936 : 55,441,1938) has shown that hot aqueous digestion of a beet pulp with and without added sucrose gave a lower result than that expected where sucrose had been added,and ascribed this to adsorption of sucrose by the marc. It is also possible that this may be due, at least in part, to the dehydrating effect of sucrose on the marc. It has also been suggested that the lead subacetate added causes shrinkage of the marc hydrate by withdrawing colloid water. Beets with 3.96 per cent dry marc were found to have 0.12 gm. colloid water,and beets of 5.47 per cent marc contained 0.20 gm. colloid water. It would appear therefore that a normal weight of average beet pulp will contain about 0.15 gm.(or cc.) of colloid water.

Tests on the Determination of the polarisation of fresh beet and Dried Cossettes :- Using various weights and volumes, the standard hot digestion procedure was followed.

FRESH BEET.

Weight taken Gms.	Volume of flask Ccs.	Marc Volume Allowance Ccs.	Reading 400 mm. tube	% Polarisation
6.5	100	0.3	7.8	15.6
13.0	100	0.6	15.6	15.6
26.0	100	1.2	31.2	15.6
26.0	200	1.2	15.8	15.8 x
52.0	200	2.3	31.4	15.7
26.0	300	1.2	10.6	15.8
52.0	300	2.3	21.0	15.7 x

DRIED COSSETTES.

Weight taken Gms.	Volume of flask Ccs.	Marc Volume Allowance Ccs.	Reading 400 mm. tube	% Polarisation
6.5	100	1.2	30.4	60.8
13.0	100	2.3	60.2	60.2
6.5	200	1.2	15.3	61.2
13.0	200	2.3	30.7	61.4 x
26.0	200	4.6	61.1	61.1
13.0	300	2.3	20.4	61.2 x
26.0	300	4.6	40.4	60.6
39.0	300	6.9	60.2	60.2

The tests marked 'x' appear to give the most satisfactory results : there is much wider discrepancy in the dried cossettes, and the ratio of water to cossettes in the flask is obviously important.

Test on the inclusion of the marc allowance in the weight taken.

FRESH BEET.

Weight taken Gms.	Volume of flask Ccs.	Marc Allowance per N wt.	Neutral Lead Acetate added Ccs.	Reading 400 mm. tube	% Polarisation
12.85	200	1.2	3	11.2	22.4
12.85	200	1.2	3	11.2	22.4
25.70	200	1.2	5	21.2	21.2
25.70	200	1.2	5	20.8	20.8
51.40	200	1.2	9	42.2	21.1

EXPERIMENTS ON THE INFLUENCE OF TEMPERATURE IN THE HOT DIGESTION METHOD FOR THE POLARISATION OF FRESH BEET AND DRIED COSSETTES.

1. Fresh Beet : Series (1) :- 3 Normal weights in 300 ccs. flasks

Temperature °C.	% Sugar (Polarisation)	% Reducing Sugars	Average % Polarisation	Average % Reducing Sugars
80	14.8	0.150		
	15.0	0.155	14.90	0.152
85	15.0	0.165		
	15.1	0.167	15.05	0.166
90	15.1	0.181		
	15.15	0.184	15.12	0.182
95	15.2	0.190		
	15.3	0.192	15.22	0.191

Series (2) :-

	% Sugar (Polarisation)			
Temp. °C.	Sample 1	Sample 2	Sample 3	Sample 4
Alcoholic	15.0	14.7	16.3	16.0
70	15.0	14.8	16.2	16.2
75	15.4	15.1	16.3	16.1
80	15.3	15.0	16.3	16.2
85	15.3	15.0	16.4	16.3
90	15.4	15.1	16.3	16.4
95	15.4	15.3	16.4	16.4

The alcoholic method was used as comparison for series (2) employing the standard Scheibler alcohol extraction process (see Browne and Zerban, "Sugar Analysis" 3rd, Ed. 1941, p.353.)

2. Dried Cossettes :- A three-quarter N wt. in 300 ccs.

Temp. °C.	% Sugar (Polarisation)	% Reducing Sugars	Average % Polarisation	Average % Reducing Sugars
80	60.2 60.0	1.38 1.32	60.10	1.35
85	60.3 60.2	1.34 1.38	60.25	1.36
90	60.0 60.o	1.40 1.36	60.0	1.38
95	60.4 60.4	1.42 1.41	60.4	1.41

Conclusions and notes :- The method used was the standard hot digestion method (see p.*208*). The reducing sugar content tends to increase as the temperature is raised, and there is a similar tendency to increase in the polarisation. A temperature of 70°C. appears to be too low : there is maximum extraction at 95°C.

Comparison of methods for the polarisation of sugar beets :-

Proved methods of preparing samples for analysis have shown that provided there is thorough disintegration of the cellular tissue and no loss by leakage of juice or by evaporation, almost any of the numerous raspers, shredders or graters may be used. The Keil-Dolle segment rasp is the standard machine used in beet sugar factories in this country, the U.S.A., and much of continental Europe. Some comparisons of methods of preparation and analysis are here shown :-

COMPARISON OF METHODS FOR THE POLARISATION OF SUGAR BEETS.

SAMPLE	S. Le DOCTE 1.	S. Le DOCTE 2.	ALCOHOLIC	STRÖHLEIN COLD	STRÖHLEIN HOT	MILL ALCOHOL	MINCED	SAW
1. High	16.1	16.0	15.9	16.1	16.7	16.1	15.7	16.5
Low	15.8	15.7	15.7	15.3	13.6	16.4	--	--
2. High	18.1	18.2	18.0	18.0	18.9	18.3	17.6	18.6
Low	17.5	17.5	17.5	17.9	18.2	18.1	--	--
3. High	18.0	18.0	17.9	17.2	18.4	18.6	17.5	18.3
Low	15.0	14.9	14.9	16.2	16.8	17.9	--	--
4. High	18.0	17.9	17.7	18.0	18.5	18.2	17.3	18.3
Low	14.4	14.2	14.1	14.8	14.3	14.3	--	--
5. High	21.6	21.5	21.5	20.5	21.1	21.4	20.7	21.9
Low	16.1	16.0	15.9	14.0	15.3	14.6	--	--
6. High	17.9	17.6	17.8	17.7	19.1	18.6	17.1	18.0
Low	11.7	11.5	11.5	10.5	11.6	11.4	--	--
7. High	18.0	18.2	17.9	17.6	18.2	17.8	17.1	18.5
Low	17.6	17.5	17.4	16.9	17.6	17.5	--	--
8. High	19.7	19.4	19.6	18.8	19.6	21.4	18.2	21.6
Low	13.8	14.0	13.9	13.5	14.7	15.0	--	--
9. High	18.4	18.5	18.3	18.9	19.2	19.0	18.0	18.6
Low	16.3	16.8	16.7	16.1	17.0	17.0	--	--
10. High	18.5	18.9	18.7	19.4	19.9	19.0	17.7	18.9
Low	15.5	15.6	15.5	15.0	15.4	15.2	--	--
11. High	15.7	15.6	15.5	16.3	17.2	16.8	16.0	17.3
Low	13.7	13.5	13.6	11.7	12.5	11.2	--	--
12. High	17.6	17.3	17.3	17.7	18.4	18.5	17.1	18.3
Low	16.4	16.4	16.4	15.8	16.3	16.8	--	--

<u>Consideration of results</u> :- The method of simple polarisation for the determination of sucrose in beets assumes that the only material present which is optically active is the sucrose, and also assumes that the sucrose rotation is unaltered by accompanying impurities. These assumptions are both incorrect. Normal beets contain small amounts of invert sugar, raffinose, asparagine, glutamine, gums, and other optically active substances, which by themselves may cause a quite appreciable plus or minus error. In addition the rotation of some of these is considerably affected by the addition of basic lead acetate. For example, asparagine, which is slightly levorotatory in aqueous solution becomes strongly dextrorotatory in presence of lead subacetate, while with glutamine the reverse is true. It is evident that there will be errors which may or may not be mutually compensating. The extraction of highly dextrorotatory gums is also likely to occur even with the cold water digestion methods, if the beets are unripe, frosted, diseased, or otherwise abnormal. The alcohol method eliminates this particular error, since these gume are insoluble in alcohol.

Usually agreement between the water and alcohol methods is very close. The cold-water method is only suitable where the pulp can be prepared in adequate fineness : the hot water method is generally preferred for factory loss-control routine.

Many of the other optically bodies present may change rotation under the influence of heat, and some substances may be hydrolysed by heat producing optically active bodies when acids, alkalis, or enzymes are present. In general the tendency is towards dextrorotation, so that the apparent polarisation is always higher than the true sucrose content. As a rule a plant containing a glucoside has also present a corresponding enzyme capable of hydrolysing it, the enzyme being also present in similar species which do not contain the enzyme. Glucoside and enzyme do not exist in the same cell, but are brought together if the cell structure is damaged. Thus the finer the pulp the more the cells ruptured and the more intimate the contact of enzyme and glucoside, producing dextrose usually and increasing the polarisation.

The Ströhlein mill produced a pulp which was extremely finely divided, and which yielded in general appreciably higher results than other methods. The sampling by means of a saw also seems to give high results, while preparation of the sample by passing through an ordinary mincer, gave abnormally low results, apparently due to incomplete extraction. The samples done by the Sachs-Le-Docte method were prepared by the standard beet rasping method, and this pulp was also used for the alcoholic extraction.

Cumulative experience of these methods has shown that the Sachs-Le-Docte method, where a constant volume of water and lead acetate is added, gives a fair and relatively accurate estimate of the sugar present in the beet, particularly where the cycle of analysis is arranged so that each capsule is allowed to stand for at least 20 minutes before polarising. In addition it is probably the only feasible method where a very large number of samples have to be analysed each day. It is the standard method in this country for commercial valuation of sugar beets.

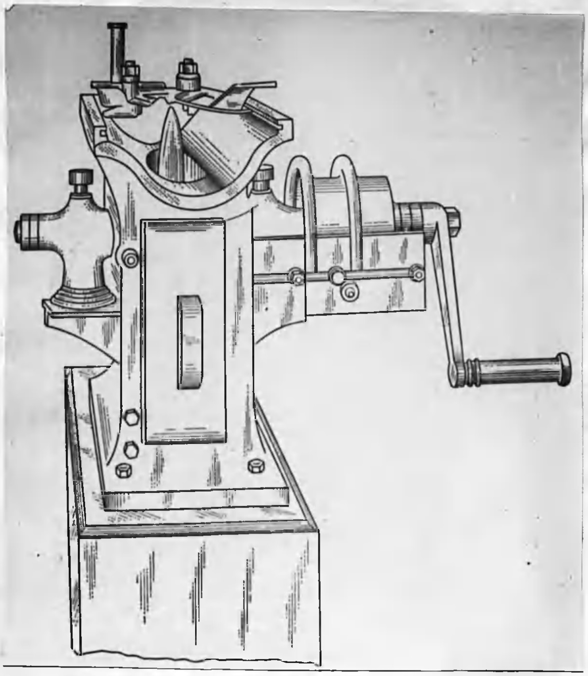


Figure 35a...The Keil-Dolle Segment Rasp.

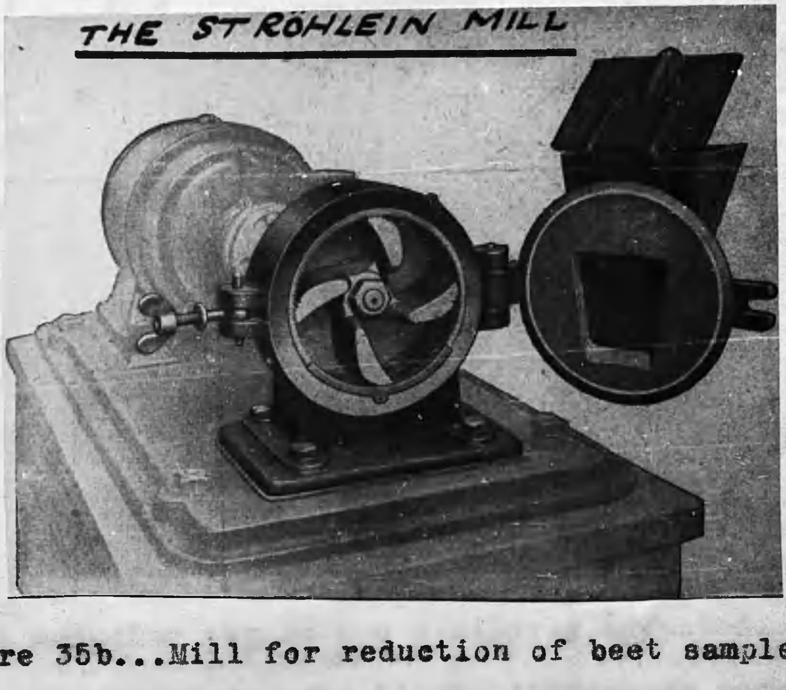


Figure 35b...Mill for reduction of beet samples.

Experiments on the determination of the polarisation and reducing-sugar content of dried beet cossettes.

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1. Effect of size of material and mode of digestion

(a) Hot water digestion : 35 minutes at 88°C.:-

Gms. taken in 200 ccs. flask	Marc allowance	(A) Hand ground in mortar % Sucrose	(B) Through mill: holes 20 per sq.in. % Sucrose	(C) Through mill: holes: 144 per sq. inch. % Sucrose
6.5	1.2	64.8	65.6	65.6
13.0	1.7	64.8	64.8	64.8
26.0	3.4	63.8	64.0	64.2

(b) Cold water digestion : 2 hours standing:-

Gms. taken in 200 ccs. flask	Marc allowance	(A) Hand ground in mortar % Sucrose	(B) Through mill: holes 20 per sq.in. % Sucrose	(C) Through mill: holes: 144 per sq. inch. % Sucrose
6.5	1.2	60.2	62.4	62.4
13.0	1.7	61.6	63.2	63.2
26.0	3.4	60.0	63.6	63.8

Reducing sugars by Bertrand-Saillard method :-

		(A)	(B)	(C)
(a) Hot digestion : 35 mins.		1.18	1.40	1.43
(b) Cold digestion :2 hours		1.07	1.13	1.12

It is clear from the above results that cold digestion is not sufficient to bring all the sucrose into solution from the plant cells : the reducing sugars are similarly affected. The fineness of grinding would appear to make little difference once a certain size has been reached. The use of 6.5 gms. is not advisable.

2. A contrast of cold and hot digestion methods for the estimation of reducing sugars by the Bertrand-Baillard method.

<u>Test (a) :-</u> 15 gms. in duplicate, using 5 ccs. neutral lead acetate solution (10%), 20 ccs. mixed copper solution and 100 ccs. water 2 hours digestion in cold :- Reducing sugars)1(0.65% :)2(0.67 %.

<u>Test (b) :-</u> 15 gms. in duplicate, other details as above with 30 mins. digestion at 88°C. :- Reducing sugars (1) 1.07 % : (2) 1.10 %.

Sucrose in cossettes 62.0 per cent.

This once again brings out the necessity for hot digestion.

---

3. The influence of concentration on the polarisation found.

In this test all marc volumes were allowed for at 1.2 ccs. per Normal weight of fresh beet, and calculated back from the polarisations.

	In 200 ccs. flasks		
gms.	6.5	13.0	26.0
After 30 mins, digestion	66.10	65.80	63.45
After 60 mins. digestion	67.35	65.40	65.30
Lead acetate used, ccs.	4	7	10
<u>Second series on same cossettes</u>			
After 30 mins. digestion	64.0	64.5	63.2
After 60 mins. digestion	67.3	64.6	63.2

The results show that 6.5 gms. introduces too large a multiplier, while 26 gms does not allow sufficient liquid for complete extraction of the sucrose. The use of 13 gms. would seem best.

4. Extended tests on the influence of concentration on the polarisation of dried beet cossettes.

With marc allowance calculated at 1.2 ccs. per Normal weight of fresh beet. All in 200 ccs. flasks.

Polarisations

Using 6.5 gms.	Using 13 gms.	Using 6.5 gms.	Using 13 gms.
64.0	64.2	56.8	56.4
64.0	62.4	66.0	64.4
63.6	62.8	64.4	65.0
64.8	63.2	56.4	53.6
64.0	61.6	53.2	52.8
57.2	56.4	62.4	60.8
64.0	62.8	64.4	63.8
63.6	61.2	60.0	57.6
58.4	56.0	64.0	64.0
64.0	62.0	61.2	59.0
63.6	65.2	64.0	62.8
61.6	60.0	64.0	61.6
62.4	62.4	61.6	61.2
64.0	60.4	62.4	57.2
64.0	63.2	60.4	63.2
60.8	57.2	61.6	61.2
59.2	60.6	64.6	64.0
64.0	62.0	64.0	61.6
62.4	62.0	56.8	56.4
61.6	59.2	59.2	57.2
60.8	60.0	64.8	64.0
60.0	59.2	60.4	58.4
64.6	62.4	62.4	62.0
63.2	61.2	64.8	62.4
60.0	59.2	61.6	61.6
65.0	63.2	59.2	58.6
60.8	57.6	63.2	62.8
62.0	61.4	62.4	60.4
61.6	58.0	61.6	61.2
61.6	6o.8	62.4	61.2
64.0	63.2	62.4	61.6
63.2	61.2	61.6	57.6
63.2	60.2	62.8	61.6

(66 results)
Averages 62.09 60.74

Difference 1.35

4. (Continued) Influence of concentration on the polarisation of Dried beet cossettes. Details as in previous test.

Polarisations.

Using 6.5 gms.	Using 26 gms.	Using 6.5 gms.	Using 13 gms.
62.8	63.0	64.0	58.6
61.6	58.7	58.4	58.9
61.6	56.2	58.4	57.2
62.0	58.8	58.8	57.8
61.2	60.6	57.2	54.6
63.6	55.9	64.8	61.9
63.6	54.8	64.0	55.6
63.6	60.4	64.4	61.5
59.2	58.7	60.8	57.2
58.0	51.5	62.0	50.5
60.5	60.8	64.0	61.8
60.0	57.8	64.4	62.8
66.0	58.5	62.0	55.0
60.0	57.8	60.8	60.7
58.0	57.5	62.4	57.8
61.6	54.6	65.2	60.8
59.2	58.2	58.8	57.6
59.6	55.6	58.8	54.8
59.6	57.6	59.2	54.9
62.0	59.1	60.8	57.1
59.2	57.5	63.6	57.7
60.4	55.2	60.8	57.0
64.0	62.0	66.4	63.6
58.4	56.3	58.8	55.8
57.6	55.1	61.2	58.8
65.6	61.0	64.0	61.5
64.0	57.2	64.0	51.1
64.0	62.0	65.2	61.0
63.2	59.9	64.0	61.9
64.4	60.7	64.4	62.2
62.3	61.0	64.8	61.5
65.6	63.4	(63 results)	
	Averages	61.89	58.32
	Difference	3.57	

The first series of tests using 6.5 and 13 gms. cossettes show considerably less difference than the second series using 6.5 and 26 gms. There is not enough liquid present when 26 gms. are taken. The adoption of 13 gms. would seem the best compromise, since with 6.5 the reading must be multiplied by 4.

THE BERTRAND - SAILLARD METHOD FOR THE DETERMINATION OF REDUCING-SUGARS - APPLICATION TO DRIED BEET COSSETTES :

The precipitated cuprous oxide is filtered through a sintered glass crucible, washed with water and dissolved in 10 ccs. of ferric sulphate solution. This solution is titrated against a standard potassium permanganate solution until faintly pink. The amount of reducing sugars present is found from specially prepared tables.

Solutions :- Fehling s solution as modified by Bertrand-Saillard :-

A. COPPER SOLUTION - 69.3 gms. $CuSO_4.5H_2O$ per litre

B. ALKALINE SOLUTION - 346 gms. Sodium Potassium Tartrate (Rochelle Salt), per litre.

130 gms. NaOH per litre.

A and B mixed in equal volumes just before use.

The alkalinity of this solution is very much reduced from that of the normal Fehling s solution, which minimises the effect of alkali on the sucrose, and gives results nearer the truth than would be possible with say, the methylene blue method of titration.

POTASSIUM PERMANGANATE SOLUTION :-

6.75 gms. $KMnO_4$ in 5 litres solution

1 cc. = 2.5 mgms. Copper

This solution is standardised by titration against 125 mgms. of ammonium oxalate which is dissolved in water in a conical flask with addition of 2 or 3 ccs. of 5 N sulphuric acid, heated to 70°C., and the $KMnO_4$ solution added to a faint pink colour. This should require 22 ccs.

FERRIC SULPHATE SOLUTION :- Sulphuric acid - 200 gms.

Ferric sulphate - 50 gms.

This is made up with water to just under 1 litre, filtered through a sintered glass funnel, and completed to volume.

Further check on the Bertrand-Saillard method :-

In addition to the titration with ammonium oxalate, the following check should be made :-

A solution of 9.5 gms. of pure sucrose in slightly less than 100 ccs. of approximately 0.6 N hydrochloric acid is kept for a week at room temperature (or heated for 7 minutes at 67-70°C. as in the Clerget-Herzfeld conditions of inversion) and is then diluted accurately to 1 litre and bottled. This acid 1 per cent solution of invert sugar will keep unchanged for many months. For standardisation it may be neutralised with sodium hydroxide solution and suitably diluted.

The neutralised solution does not keep for more than a day or two.

A volume of the solution corresponding to 25 mgms. of invert sugar is placed in a conical flask with 20 ccs. of the mixed Bertrand-Saillard solution and made up to 100 ccs. with water. The reduction and titration with permanganate are carried out in the standard way and comparison made with the figure shown in Saillard's table for sucrose = 0.

The burette used for the permanganate should read to 0.05 cc. each division being at least 1.5-2 mms. broad. It must have a glass stopcock.

REFERENCES :-

The so-called Bertrand method was first proposed by Schwarz (Ann. 84,84,1852),who dissolved the cuprous oxide in $FeCl_3$ solution made acid with Hcl, and titrated the ferrous iron formed with $KMnO_4$.

Saillard :- Betterave et Sucreries des betteraves,Paris, 1913.

Lane and Eynon,J:S:C:I., 32T.,1923

Experiments on the determination of reducing sugars

1. Dried cossettes digested with N/28 sodium hydroxide by standard digestion method, using neutral lead acetate and dry deleading with potassium oxalate. Compared with ordinary method used simultaneously. Both tests in duplicate.

	Av. %Reducing Sugars	Av. pH Value	(after digestion).
Alkaline digestion	1.00	7.5	
Ordinary method	1.10	5.4	

This test was an attempt to prevent inversion of sucrose during digestion. The results show very little difference between the two methods, in any case not enough to make the change desirable.

---

2. Further tests were made using different conditions of digestion.

Digestion using	% Reducing Sugars (Bertrand-Saillard method)	pH
10 ccs, neutral lead acetate	0.76	6.0
10 ccs. N310 Sodium carbonate	0.75	7.2
Water alone	0.76	5.3
1.5 gms. Calcium carbonate	0.74	6.5

Each test was made in duplicate. Filtration was very slow where lead was not used. The calcium carbonate gave the next best filtration. The usual method of adding neutral lead acetate before digestion appears to be the most satisfactory.

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3. Test on the use of different filtering media in Bertrand-Saillard method :-

	Asbestos (Gooch)	Paper pulp	Sintered glass
% Reducing Sugars	0.57 : 0.58	0.58 : 0.58	0.58 :0.58

It is seen that the filtering medium has no influence on the results and its choice is therefore a matter of individual preference.

4. Check on the Bertrand-Saillard method using standard invert-sugar solution.

Five gms. of specially purified white sugar was inverted by standing for a week with 0.6 N HCl and made to 1 litre after neutralising. 1 cc. therefore contains 5.26 mgms. invert-sugar. $KMnO_4$ solution 1.035 factor against ammonium oxalate.

Invert Solution taken ccs.	Titration ccs. $KMnO_4$	Mgms. Copper	Mgms. Invert-Sugar
10	Theoretical content (18.4 ccs.)	92.0	52.6
10	18.3	91.5	52.3
10	18.4	92.0	52.6
10	17.6	88.0	50.3
10	18.7	93.5	53.4
10	18.4	92.0	52.6
10	18.4	92.0	52.6
10	18.5	92.5	52.8
10	18.6	93.0	53.1
10	18.4	92.0	52.6
Average	18.37	91.83	52.48

A check was made on this invert solution using the gravimetric method for estimating the copper :-

(a) Reduction to Cu by alcohol	(b) Weighing direct as Cu_2O
1. 0.185 gm. Cu	1. 0.205 gm. Cu_2O
2. 0.185 " "	2. 0.215 " "
3. 0.185 " "	3. 0.210 gm. Cu_2O
Theoretical 0.184 gm.	**Theoretical** 207 mgms.

These results indicate that the Bertrand-Saillard method can be considered reliable for the estimation of small amounts of reducing sugars in presence of excess of sucrose.

5. The effect of neutral and of basic lead acetate in the Bertrand-Saillard method for reducing sugars.

This test was carried out on raw diffusion juice from dried cossettes, using varying quantities of the two lead solutions for defecation.

Lead solution used, ccs.	% Reducing sugars using Basic Lead Acetate solution	% Reducing Sugars Using Neutral Lead Acetate solution
2	0.68	0.70
4	0.74	0.77
8	0.85	0.67
10	0.75	0.70
12	0.69	0.58
16	0.78	0.86
17	0.76	0.72
Average	0.750	0.714

These results are rather inconclusive. Possibly precipitation of reducing non-sugars may occur in some cases, while invert-sugar or its components may be precipitated in other cases.

The effect of lead acetate on the polarisation was found in the following test :- 13 gms. dried cossettes in 200 ccs. flask with 2.3 ccs. allowance for marc volume : digestion by standard method.

1. + 6.5 ccs. Basic Lead Acetate	2. + 6.5 ccs. Neutral Lead Acetate	3. + 6.5 ccs. Ammoniacal Lead Acetate
64.6	64.6	64.6
64.6	64.8	64.8

There is apparently no difference : These results are all within experimental error.

SECTION 5.

METHODS OF ANALYSIS

PART 3 : Determination of some Minor Constituents in the Sugar Beet.

Density of Fresh Beets and Dried Cossettes :

Determination of 'marc' in the beet :

The estimation of Raffinose.

NOTE :- The density of fresh beets and dried cossettes is included in this section for convenience.

ESTIMATION OF THE SPECIFIC GRAVITY OF DRIED COSSETTES AND MARC

1. Dried Cossettes :- The cossettes tested contained 7.5 per cent of water and 64.4 per cent polarisation. The sp. gr. was taken by weighing 5 gms. of the fine cossette 'flour' in petroleum ether of sp. gr. 0.79216 at 20°C. The average of six tests gave 1.4300 at 20°C.

2. Dried marc :- The above method gave 1.19012 sp. gr. as the average of six determinations.

Note :- The sp. gr. of Sucrose is 1.588 at 20°C.

Check from Composition of Dried Cossettes:-

Assuming 644per cent sucrose at 1.5877 density in the dried cossettes and 7.5 per cent water, this leaves 28.5 per cent marc and soluble non-sugars which can be assumed to have density 1.19.

On this basis:- 64 at 1.5877/100 - 1.016
28.5 at 1.19 - 0.339
7.5 at 1.00 - 0.075
Total - 1.430

Weight per cubic foot of fresh beets and Dried Cossettes :-

Loose Dried Cossettes vary rather widely in weight per cubic foot according to the conditions of packing of the slices.

DRIED COSSETTES :-	Lbs. per cu.ft.	Cu. ft. per ton
Composite sample over 7 days	14.9	150.8
Average from storage bins	19.0	120.0
Stanek and Sandera[1]	25.0	89.6
Fresh Beets (cossettes)	26.2	85.5
Washed Beets (Claassen)	34-37	65-60

[1] Zeit. Zuckerind. czechlslov.,525,1929 :I.S.J.,501,1929.

Zeit. Zuckerind. czechlslov.,525,1929 :I.S.J.,501,1929

'MARC' IN THE SUGAR BEET.

Claassen defines marc as the residue remaining after complete xtraction of the sugar from the beet, and of the easily soluble non-ugars under conditions similar to those in factory operations,working s rapidly as possible to prevent the formation of soluble substances y the decomposition of hemicelluloses, pectin, and like bodies.

This marc, or insoluble cellular matter,is sometimes assumed to be resent at a constant percentage of 5.0 or 4.75 per cent. This cannot e exact since the percentage of cellular matter varies considerably ith locality and climatic conditions,and also with other conditions such as the age of the plant and the soil fertility.

It is apparent from the indefinite nature of Claassen's attempt t definition that marc cannot necessarily be considered the water-nsoluble portion of the beet, since this figure will vary with the article size of the beet pulp, the length and mode of treatment dopted, and in particular the temperature and the quantity of water sed. The temperature must be at least 60°C. to destroy the protoplasm.

The corrections generally accepted for the volume error due to arc in determinations of sugar in the beet by digestion are those of Rapp and Degener (Z. VER. DEUT. ZUCK IND., 32,786,1882) who assumed 4.8 as the average dry marc content of the beet, and 2.0 as the density of the marc, giving a correction of 0.6 cc. per Normal weight.

Heintz (Z. analyt. chem. 262,1874) found that dry sugar beet marc would adsorb water from sugar solutions, and Schiebler,(Ibid.,176,256, 879) later showed the presence of colloid water in beet marc. e found an average of 2.5 ccs. volume for the hydrated marc per Normal weight of beet, this being much higher than the volume occupied by the dry marc.

A summary of the principal conclusions regarding marc volume is shown below:-

Year	Authority	Reference	Correction per N wt.	Remarks
1882	Stammer	Z.V.Deut.Zuck.Ind., 32,634,1882	--	Original method
1916	Claassen	ibid., 66,359,1916	--	Improved method
1882	Rapp and Degener	ibid, 32,786,1882	0.6	Density,2.0 : % dry marc,4.8
--	Fribourg	"Analyse Chimique" p.253	0.75	
1906	Pellet	Z.V.Deut.Zuck.Ind., 56,903,1906	0.80	
	Sidersky	"Manuel" p.241	1.35	
1926	Spengler and Brendel	Z.V.Deut.Zuck.Ind., 76,880,1926	2.42	Density,1.13 : % dry marc,3.0-4.5 av. 3.5 %
1930	Müller and Pucherna	Z.Z.C.R. (Czecho-Slovakia),54,99,1929/30	1.7	
1927	Staněk and Vondrák	ibid.,51,101,113, 1926-27	1.54	In presence of Lead acetate
1931	Kopecký	Z.V.Deut.Zuck.Ind., 81,447,1931	1.30	
1933	Spengler and Paar	ibid.,83,342,1933	0.83	In presence of Lead acetate
1937	Spengler, Paar, and Mück	ibid.,87,594,1937	2.1	
1934	Bachler	Facts about Sugar, 29,191,1934	2.31	
1934	Osborn	I.E.C.,anal.ed. 6,37,1934	1.00	
1938	Staněk and Pavlas	Z.Z.C.R., 62,357,365,1937/38	1.06	In presence of Lead acetate

METHODS OF ESTIMATING MARC IN SUGAR BEET

Stammer's method :- Twenty gms. of the finely divided sample are digested in a beaker with 300-400 ccs. water for 30 mins. The solution is removed by suction and the digestion and filtration repeated until the filtrate is free from sucrose as indicated by α-naphthol. The residue is treated with boiling distilled water and collected on a dry weighed filter-paper and washed with alcohol and then with ether. It is then dried first at low temperature and finally at 100-110°C. to constant weight. The marc is then ignited and the ash weight deducted from the total weight first obtained. The per cent of dry marc is then five times this figure.

Claassen's method :- Twenty-five gms. of ground pulp is placed in a beaker marked at 400 ccs. and boiling water is poured in up to the mark. The pulp is digested for 2 mins. and rapidly filtered through a Büchner funnel. The pulp is returned to the beaker and the process repeated thrice. After the fourth digestion the marc is collected on a tared filter-paper, washed with a few ccs. of alcohol and dried for 6-8 hours at 105-110°C. The calculation is made as in the above method.

It is clear from a study of these methods that the marc result obtained will depend on the temperature of digestion primarily. During exhaustive hot water extraction certain normally insoluble pectins are known to hydrolyse and pass into solution, and it may well be that other cell constituents will behave similarly.

EXPERIMENTS ON MARC :-

1. Quantities of 6.5, 13, and 26 gms. of dried cossettes ground in the standard way in an impact mill were digested in a beaker with water at 50°C., transferred to a tared filter-paper, and washed with water at 50°C. until there was no reaction with the alpha-naphthol test for sucrose. The residue was dried at 105°C. for 6 hours and weighed.(It was then ashed and re-weighed - not reported).

Cossettes taken gms.	Wt. of Marc gms.	Per cent Marc	Sp. Gr. Marc	Occupied Volume ccs.	Apparent Volume occupied, ccs.
6.5	1.5190	23.37	1.19	1.31	2.08
6.5	1.5950	24.54	1.19	---	---
13.0	3.2240	24.80	1.19	2.71	6.40
13.0	3.2170	24.75	1.19	---	---
26.0	6.0790	23.38	1.19	5.21	7.80
26.0	6.3190	24.30	1.19	---	---

The occupied volume was found by dividing the gms. weight of marc by the specific gravity of the marc. The apparent volume occupied was found by putting the dry marc into a dry 100 ccs. flask in each test and adding water from a standard burette up to the 100 ccs. volume at 15°C. This took no account of occluded air.

2. Indirect estimation of marc error :- Amounts of 100 gms. of dried cossettes were washed free from sugar as above, and the mass was semi-dried so that it would wet easily. Half-normal weights of dry sugar were then taken and varying amounts of this semi-dried pulp added. The sugar was dissolved in a little water, and the volume

made up to 200 ccs. at 20°C. The readings were then taken.

% Moisture in the semi-dried pulp = 40.6

Pulp taken gms.	Equiv. Dry Weight gms.	% Polarisation	Difference	Diffce. per gm. wet pulp	Diffce. per gm. Dry pulp
Nil	0	24.5	-	-	-
2.5	1.02	25.9	1.4	0.56	1.37
5.0	2.03	26.7	2.2	0.44	0.80
7.5	3.05	28.1	3.6	0.48	1.40

3. 195 gms. of white sugar made to 1 litre, and 100 ccs. of this solution used for each test. A quantity of dried cossettes was Continuously extracted with cold water for 9 hours until sugar free to alpha-naphthol, the resultant pulp being dried for 6 hours at 105°C.

Pulp taken gms.	% Polarisation	Difference	Difference per gm. of Marc
0	38.1	-	-
1	38.3	0.20	0.20
2	38.9	0.80	0.40
3	39.5	1.40	0.47
4	40.2	2.10	0.52
5	40.9	2.80	0.56
6	41.2	3.10	0.51
7	41.5	3.40	0.49
8	41.9	3.80	0.48
			Av. 0.454

Discounting the result with 1 gm. of the pulp, the average is 0.49-i.e. roughly 0.5 difference per gm. of marc present.

A repeat experiment was carried out with a different sugar solution, but with details otherwise as above :-

Pulp taken gms.	% Polarisation	Difference	DIfference per gm. of Marc
0	36.9	--	--
0.5	37.2	0.3	0.60
1.0	37.3	0.4	0.40
2.0	37.5	0.6	0.30
3.0	37.8	0.9	0.30
4.0	38.2	1.3	0.33
5.0	38.6	1.7	0.34
6.0	38.8	1.9	0.32
7.0	39.3	2.4	0.34
8.0	39.9	3.0	0.38
		Average	0.368

This test has given results differing rather widely from those in the previous test : the dried cossettes in this case were not the same which probably had some influence.

4. Direct Estimation of marc :-

In this test a finely ground 'flour' was made from the dried cossettes sample. Smaller amounts were used in each test than in Test No. 1, the product, after washing free from sugar, being ashed. The details were otherwise as in No. 1 test.

Weight Cossettes taken ; gms.	Weight Pulp found	Gms. ash found	% Marc	% Marc (ash-free)	% Ash
3	0.625	0.062	20.83	18.76	2.07
3	0.636	0.073	21.20	18.77	2.43
4	0.862	0.097	21.30	18.87	2.43
4	0.859	0.096	21.48	19.08	2.40
4	0.869	0.104	21.73	19.13	2.60
		Average	21.31	18.92	2.39
2	--	--	19.60	17.00	2.60
20	--	--	20.61	18.11	2.50

The results of various similar estimations on fresh beet and dried cossettes are summarised below :-

MARC PER CENT FOUND IN BRITISH SUGAR BEETS GROWN IN OXFORDSHIRE AND BUCKINGHAMSHIRE, WITH PER CENT MARC IN DRIED BEET COSSETTES.

FRESH BEET

Sample No.	% Marc
1	4.2
2	4.0
3	5.4
4	5.4
5	5.2
6	5.1
7	4.9
8	4.8
9	4.6
10	4.7
11	4.8
12	5.0
13	4.9
14	5.0
15	4.6
AVERAGE	4.84

RANGE:- 4.0 - 5.4

At say 78% water = 22.00(%Marc on dry)

DRIED COSSETTES

Sample No.	% dry Marc
1	22.4
2	22.7
3	23.4
4	24.5
5	24.8
6	24.8
7	23.4
8	24.3
9	26.7
10	21.4
11	21.7
12	22.4
13	20.8
14	21.2
15	21.3
16	21.5
17	21.7
18	19.6
19	20.6
20	19.7
AVERAGE	22.45

D.C. RANGE :- 19.6-26.7

At 8% Water = 20.24 % Marc

Occurrence of raffinose in the sugar-beet.

The trisaccharide raffinose was obtained by Loiseau[1] in 1876 from beet sugar. It was first described by Johnston[2], who isolated it from eucalyptus manna in 1843, and it was then named melitose by Berthelot[3]. Raffinose occurs normally in the sugar beet in very small amount : it accumulates in the molasses and is recovered in large quantities as a by-product of the Barium Process for the recovery of sucrose from the molasses. It is commercially available from the Great Western Sugar Company, Denver, Colorado.

Raffinose crystallises in long needles of composition $C_{18}H_{32}O_{16}.5H_2O$, and giving $(a)_D^{20}$ of 105.2° in 10 per cent aqueous solution, without mutarotation. It is not readily oxidised and does not reduce Fehling's Solution. On hydrolysis it yields first a mixture of levulose and melibose, and further hydrolysis of the melibiose gives glucose and galactose.

Saillard[4] has observed progressive formation of raffinose in the sugar beet as the season advanced, due to the gradual lowering of temperature, and has pointed out that in the south of France where the temperatures are higher, the raffinose content of the beet is much less than in the colder north. He also states that the raffinose is higher in wet seasons, and believes that raffinose may form while the roots are lying in silos before entering the factory.

Dahlberg[5] found that where the roots are not exposed to frost no raffinose accumulated in the molasses, and Hungerford and Nees[6] report an inexplicable variation in the raffinose content of beet grown in the Rocky Mountain region, U.S.A., from 0.01 to 0.10 per cent in different years.

Estimation of Raffinose :-

Since raffinose nearly always occurs in association with sucrose, it is necessary when these two sugars are present to use a method which combines their hydrolysis equations. With two unknown quantities two equations are sufficient, but complication is caused by the presence in the sugar beet of other optically active bodies mainly nitrogenous in character. The nature of these substances varies with the soil and growing conditions among other factors, for example Paine and Balch[7] mention a preponderance of dextro-rotatory non-sugars in beets grown in Idaho, while in beets from Utah, Colorado and Nebraska, the non-sugars were levo-rotatory.

The well-known Creydt[8] formula for the estimation of raffinose uses the relation that raffinose has 1.852 times as great a rotatory power as an equal weight of sucrose (anhydrous raffinose, 123.2°: sucrose, 66.5°). One of Creydt's equations states that the direct polarization is the sum of the rotations of the sucrose and raffinose, and the other states that the invert polarization is the sum of the rotations of the products of hydrolysis. The Creydt formula is thus only valid in the absence of other optically substances than sucrose and raffinose. Owing to the presence of the optically active non-sugars mentioned above, the precision of the Creydt method may appear good but its accuracy is doubtful, and for this reason the double enzyme method[9], or, in some localities, the double acid method of Osborn and Zisch[10] is required. Browne and Zerban[11] suggest that no greater accuracy than 0.5 per cent can be expected by any of the methods for determining raffinose in mixtures, since caramelization products, gums, and organic acids may indicate raffinose when none is present. They suggest that even the two-enzyme procedure of Paine and Balch[9], while much more reliable than Creydt's method, should be used only in the investigation of substances in which raffinose is likely to occur, and should never be used as a test for raffinose in unknown mixtures. For unknown products, the raffinose should be isolated in crystalline form, and its physical and chemical properties confirmed.

EXPERIMENTAL WORK.

With the above limitations in view an attempt was made to apply both the double enzyme method[9], and the Osborn and Zisch method[10] to the analysis of fresh beet slices and dried cossettes. It was thought that the fourfold sucrose content of the dried cossettes afforded an excellent opportunity to secure a positive result for raffinose.

The results found are,of course,difficult to assess,since other optically active bodies are still present amd may in fact have altered their optical properties during the drying process.

It is thus necessary to regard the figures with reserve, as they merely indicate that raffinose may provide the largest proportion of the percentage called "Raffinose".

DETERMINATION OF RAFFINOSE IN FRESH BEETS GROWN IN SOUTHERN ENGLAND.

(a) Seed beets and beets from Trial Fields :-

No.	Direct Poln.	% Sucrose	% Raffinose		No.	Direct Poln.	% Sucrose	% Raffinose	
			Acid Method	Double Enzyme Method				Acid Method	Double Enzyme Method
1	13.4	13.20	0.08	0.01	13	17.1	16.98	0.06	0.09
2	13.7	13.45	0.13	0.06	14	17.3	16.86	0.34	0.27
3	14.4	14.10	0.16	0.14	15	17.5	16.99	0.35	0.19
4	14.8	14.27	0.28	0.27	16	17.6	16.79	0.41	0.37
5	15.1	14.82	0.22	0.31	17	17.6	17.37	0.12	0.10
6	15.6	15.40	0.06	0.02	18	17.8	17.59	0.11	0.27
7	16.2	15.77	0.19	0.23	19	18.0	17.49	0.29	0.38
8	16.35	15.91	0.23	0.26	20	18.0	17.90	0.01	0.18
9	16.7	16.12	0.36	0.47	21	18.2	17.72	0.21	0.23
10	16.7	16.21	0.49	0.24	22	18.2	18.15	0.03	0.07
11	17.0	16.72	0.15	0.19	23	19.0	18.42	0.39	0.33
12	17.1	16.70	0.25	0.24	24	19.7	18.71	0.27	0.19

(b) Factory Cossettes:- January to February :

1	16.0	15.77	-	0.11	5	15.5	15.49	-	Nil
2	15.9	15.81	-	0.04	6	15.7	15.49	-	0.11
3	15.7	15.64	-	0.03	7	15.8	15.62	-	0.03
4	15.9	15.72	-	0.09	8	15.6	15.61	-	Nil

Range :- Nil to 0.49 per cent raffinose; it is clear that part of this apparent raffinose is due to the rotation of non-sugars.

DETERMINATION OF RAFFINOSE IN DRIED COSSETTES.

AVERAGE WATER CONTENT :- 7.5 per cent.

No.	Direct Polarization	Sucrose per cent	Sucrose per cent on dry	Raffinose per cent	Remarks
1	66.0	65.31	70.62	0.69	These samples do not
2	64.2	62.81	67.92	1.48	correspond to the
3	63.4	63.25	68.37	0.15	fresh beet samples
4	62.8	61.95	66.99	0.85	in the previous table.
5	62.0	60.05	64.94	1.95	
6	64.0	63.17	68.29	0.83	
7	64.2	63.75	68.92	0.45	
8	64.8	64.62	69.85	0.18	
9	69.2	67.75	73.24	1.49	
10	64.8	64.13	69.36	0.67	
11	65.6	64.83	70.09	0.47	
12	64.0	63.65	68.82	0.18	

Range 0.15 to 1.95 per cent : this figure is more correctly named 'apparent Raffinose'.

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INVERSION

The action of an inverting agent such as an acid or the enzyme invertase on the sucrose molecule gives rise, by the addition of one molecule of water to one molecule each of glucose and fructose, the mixture being known as invert sugar.

$C_{12}H_{22}O_{11}$ + H_2O = $C_6H_{12}O_6$ + $C_6H_{12}O_6$
Sucrose (342) Glucose(180) Fructose (180)
Invert Sugar 360

Inversion by acid follows the unimolecular reaction law, by which the rate of the reaction $\frac{dx}{dt} = k(a-x)$, where a is the amount of sucrose originally present, x the quantity inverted at the end of time t after the start of the inversion, dx the infinitesimal quantity inverted during the infinitesimal time interval dt, and k a constant termed the velocity constant of the inversion. Integration gives the following value for $k = \frac{1}{t} \log \text{nat.} \frac{a}{a-x}$, or changing to common logarithms :-

$$k = \frac{1}{0.4343t} \log_{10} \frac{a}{a-x}$$

From the above 1 part of sucrose is converted into $\frac{360}{342}$ or 1.05263 parts of invert sugar. Taking the specific rotation of sucrose as --66.5 at 20°C., and that of the half normal weight of invert sugar as -20.28 at 20°C. the relation of the optical activity of one part of sucrose before inversion to that after inversion is given by :-

66.5 : 1.05263(- 20.28) = 66.5 : -21.3473 = 87.8473 decrease in specific rotation. For 1 degree of the saccharimeter scale the decrease is $\frac{87.8473}{66.5}$ or 1.3210. Thus the total decrease in the saccharimeter readingat 20°C. of the half normal weight of product after inversion, divided by 1.3210 and then multiplied by 2, gives the percentage of sucrose if no other optically active component is hydrolysed and there is no change occurring in the specific rotation of other optically active bodies present.

Clerget systematised this process and gave the formula $S - \frac{100D}{134}$, where S is the per cent sucrose, D, the algebraic difference between the direct and the invert polarisations, and 134 is the factor corresponding to 1.3210 above, and similarly derived for 20°C. Herzfeld (Z. Ver. deut. Zucker-Ind., 38, 699, 1888) and Schrefeld (ibid., 70, 402, 1920-), have further modified the original Clerget formula, and the current form accepted by the American Association of Official Agricultural chemists is $S - \frac{100(P - P')}{143-0.5t}$, where P and P' are the direct and invert polarisations, and t is the temperature.

This method is essentially one requiring strict adherence to detail in order to get comparable results.

Application of the method to the determination of Raffinose :-

The hydrolysis of raffinose with hydrochloric acid under the conditions of the Clerget method proceeds according to the equation:-

$$C_{18}H_{32}O_{16} + H_2O = C_6H_{12}O_6 + C_{12}H_{22}O_{11}$$

Raffinose		d-Fructose	Melibiose
$(\alpha)^{20}_D = +104.5$ for raffinose hydrate before hydrolysis		-92	$+143$

$(\alpha)^{20}_D = +53.5$ for raffinose hydrate after hydrolysis.

The normal weight for raffinose for the Ventzke scale, corresponding to 26.026 gms. of sucrose (a_D 66.5 at 20°C.) is 16.562 gms. for the hydrate (a_D 104.5 at 20°), and 14.051 gms. for the anhydride (a_D123.1)

By Schrefeld's method, these weights of raffinose, polarising 100° Ventzke, show after hydrolysis a polarisation of --51.40° Ventzke at 20°C., or a decrease of 48.60°V., or 0.486°V. for the weight of raffinose reading 1°V. The calculation of pure raffinose may then be expressed :- $R = \frac{P-P'}{0.486}$, where R = per cent raffinose, and P and P' the polarisations of the normal weight before and after inversion. For the scale using 26 gms. normal weight for sucrose the weights of raffinose taken are 16.545 gms. for the hydrate or 14.037 gms. for raffinose anhydride.

This is probably the commonest application of the Clerget inversion principle apart from sucrose, since raffinose occurs in beets and beet products. Sucrose is then invariably present in addition to raffinose, and the formula above is therefore of little practical value. Creydt (Z.Ver. deut. Zucker-Ind., 37, 153, 1887) combined the equations for the calculation of sucrose and raffinose, and was able to estimate the two sugars in mixtures. Thus if a substance contains S per cent sucrose and R per cent raffinose, and the suwrose normal weight in 100 ccs. is polarised in a 200 mm. tube, the sucrose polarisation will be S, but the raffinose polarisation willbe 1.852 R, since 1.852 is the ratio of the normal weights of sucrose and raffinose anhydride. The direct polarisation P will be shown by the formula $P = S + 1.852 R$, whence $R = \left(\frac{P - S}{1.852}\right)$. If the sucrose normal weight is now inverted by Schrofeld's method, its polarisation at 20°C. will be represented by -0.33S (since 1°V. sucrose before inversion reads -0.33°V. after inversion). Similarly the raffinose after hydrolysis will be 1.852 R x 0.514.

This arises since for a raffinose solution reading 100°V., each 1°V. before hydrolysis, reads +0.514°V. at 20°C. after hydrolysis by Schrefeld's method. The invert polarisation P' (the sum of the raffinose and sucrose invert polarisations) is shown then by the formula

$$P' = -0.33S + 1.852\,R \times 0.514 \qquad (2)$$

By substituting the quantity $\left(\frac{P - S}{1.852}\right)$ of equation (1) for R in equation (2) we get :-

$$P' = -0.33 + 0.514\,(P - S), \text{whence } S = \left(\frac{0.514(P-S)}{0.844}\right) \qquad (3)$$

R is then got from $R = \left(\frac{P - S}{1.852}\right)$. By substituting the quantity $P - 1.852\,R$ of equation (1) for S in equation (2) we obtain the formula :- $P' = -0.33\,(P - 1.852R) + 0.9519\,R$, and from this,

$$R = \frac{0.33\,P - P'}{1.563} \qquad (4)$$

By formula (4) the raffinose may be calculated from the direct an invert polarisations immediately. The results are not quite exact as formulae (3) and (4) do not correct for variations in P' due to changes in the concentrations of sucrose and raffinose.

Example illustrating the use of the formulae :-

A beet molasses free from reducing sugars gave a direct pol. of +49.75°V., and an invert pol. of - 14.80°V.

By formula (3), per cent sucrose $= \frac{(0.514 \times 49.75) - (-14.80)}{0.844}$

$= 47.83$

By formula (1), per cent raffinose $= \frac{49.75 - 47.83}{1.852} = 1.04$

By formula (4), per cent raffinose $= \frac{(0.33 \times 49.75) + (-14.80)}{1.563}$

$= 1.04$

SECTION 5.

METHODS OF ANALYSIS.

PART 4 : DETERMINATION OF WATER AND TOTAL SOLIDS :

INTRODUCTION

THE PRESENCE OF WATER IN SOLID SUBSTANCES:

1. Adsorbed and sorbed water ; the states of water in solid materials :
2. The mode of retention of water in a colloidal material :
3. The removal of water from biological materials :

THE DETERMINATION OF WATER CONTENT :

4. Methods of determination :
5. The importance of moisture determinations :

SURVEY OF THE LITERATURE ON MOISTURE DETERMINATION :

6. Oven methods in general :
7. Method of the Chicago Malt Standardization Committee :
8. Ovens and oven temperature :
9. The influence of humidity on moisture determinations :
10. The determination of water in organic materials :

THE DETERMINATION OF WATER IN SUGARS AND OTHER FOODSTUFFS :

11. Behaviour of heat-sensitive materials on drying :
12. Reasons for discrepancies in results by oven methods :

THE SOLUBILITIES OF CARBOHYDRATES.

THE PRESENCE OF WATER IN SOLID SUBSTANCES.

ADSORBED AND SORBED WATER.

Water vapour is generally adsorbed by substances exposed to the atmosphere. This adsorption takes place on their surface and is relatively large at small pressures, changing rapidly in this region with the vapour pressure. The relation between the amount adsorbed and the tension of aqueous vapour is given by the adsorption isotherm : the effect of temperature is adsorption decrease as temperature rises.

If glass is heated to a temperature above 150°C. it is wetted by water only with difficulty, and this effect is also apparent at 110°C. Thus the weight of a dish may slowly increase as the water film returns after heating : final equilibrium is reached more rapidly from the wet side than from the dry. By reason of this water film also, changes of atmospheric humidity and temperature will cause change in the weight of a glass container.

Finely divided substances attract water from the atmosphere and hold it on their surfaces : equilibrium is usually reached in 5 to 10 minutes. Such water is called hygroscopic water, and will increase in amount with increasing suffface area, and with increasing humidity of the air. Many substances of a colloidal nature have a very large internal surface development and can adsorb very large amounts of water. In such cases equilibrium is very slowly attained and the process is called a sorption process.

This water is often called water of imbibition. Thus starch, agar, cellulose, and silica-gel in air-dried condition may contain 20-30 per cent of water and still appear to be perfectly dry powders.

The water content of such substances changes with humidity, for example, potato starch may have 10 per cent of water at relative humidity 0.20, and 21 per cent water when the relative humidity changes to 0.70. It is not easy as a rule to determine the water content of such materials. At 100-115°C. the water is given off very slowly ; moreover it is impossible to remove the last traces of water since there is humidity in the surrounding air, and the sorption at very low aqueous vapour pressures is still relatively large. If heating is taken to 180-200°C. there is grave danger of decomposition occurring, especially with organic materials.

It is therefore necessary to use a vacuum oven at 70-100°C., removing the water vapour given off, or drying must be done by a current of perfectly dry air.

THE STATES OF WATER IN SOLID MATERIALS.

1. Non-essential or adventitious water :- Hygroscopic water is usually very small in quantity after a substance has been heated. The water taken up by a substance in this mechanical way can be very large indeed since it is adsorbed at both the external and the internal surfaces. Internal surfaces arise from say, the precipitation of extremely fine particles from relatively concentrated solutions at room temperature. The very fine crystals thus formed have come into being so rapidly that they may have a discontinuous structure and consist of microscopic units containing few ions or molecules and fitted together like the bricks in a wall.
These discontinuities give rise to an internal surface and the total surface of such crystals is much larger than that measured by the microscope

Adsorbed water is not always removed quantitatively at 100-130°C. since the adsprption and desorption processes are reversible.

2. Occluded water :- This can be present in almost any solid, and is not usually removed by heating at 100°C. but disappears continuously at much higher temperatures. Water may be occluded in cavities containing mother-liquor in the solid, or may occur at the internal surfaces. It is also possible for water to be distributed homogeneously throughout a solid, e.g., natural glasses may contain several per cent of water.

3. Water of Imbibition or Colloidal water :- This may be taken up in various ways :-

(a) The water is sorbed without changing the lattice of the original material:-This may be due to the presence of vacant spaces in the dry lattice which are easily accessible to water or other vapour, and water may condense in these spaces, e.g., zeolites. Again , the crystallites in lyophilic organic colloids such as starch and agar may absorb water at their surfaces, and a swelling results.

(b) The sorbed water changes the lattice of the material :-
This can be caused by water penetrating into the crystal lattice, giving rise to a continuous increase of the distance between the planes of a layer lattice, and therefore resulting in a swelling, e.g., Graphitic acid, (Katz and Derksen, Rec. Trav. Chim., 53, 652, 1934). A second way in which the lattice changes is by formation of a definite hydrate.

4. Essential Water:- This may be (a) Water of Crystallisation, (b) Water of Constitution.

Water of crystallisation occurs in hydrated salts which are stable in air between certain humidity limits.

Water of Constitution is not present as water, but in the form of hydroxyl or hydrogen, chemically bound in the compound.

On heating, decomposition takes place with the formation of water which may be called water of constitution.

Occurrence of non-essential water :- W.F.Hillebrand, discussing the analysis of silicate and carbonate rocks (U.S.Geol.Survey Bulletin 700, p.64, 1919), gives the following classification of the occurrence of non-essential water :-

1. In liquid solution : (deliquescent powders, amorphous materials, and supercooled liquids.
2. Held by surface forces -
    - (a) Adsorbed on surfaces in films of monomolecular thickness -
        - (i) On walls of cavities within grains of aggregates
        - (ii) On exteriors of grains.
    - (b) Held by Capillarity, in liquid form -
        - (i) In colloids with mesh structure
        - (ii) In definite openings within grains of aggregates
        - (iii) In spaces between separate grains.
3. Included -
    - (a) As liquid droplets in cavities
    - (b) As included grains of minerals belonging to one of above classes.

MODE OF RETENTION OF WATER IN A COLLOIDAL MATERIAL :-

The water in a colloidal material is held in part relatively loosely by capillarity in the fine pores of the structure (absorbed) while the remainder is held much more tenaciously in very thin layers on the surfaces (adsorbed). There is no fixed division between these processes, which merge gradually into each other.

The most firmly held water on such surfaces is in the form of a monomolecular layer, in which each molecule is necessarily in direct contact with the adsorbing surface, and is bound to it by strong inter-atomic forces comparable with the forces binding the constituent atoms in ordinary compounds. The water layers immediately above this first layer are not quite so firmly held, and as further water layers form, the forces of adsorption rapidly become less, until they are no greater than the capillary absorption forces which hold most of the water.

When attempt is made to remove this water it is probable that various compounds, particularly hydrated substances where the water is loosely held will release water before the last surface-adsorbed water is driven off. It cannot therefore be said precisely how much of the water removed from a colloidal material was adsorbed, how much absorbed, and how much truly combined.

It is therefore clear that the water content of a colloidal material can be stated only in terme of the result given by a specified method.

Water which has been adsorbed into the colloidal structure of a material is of slightly higher density, slightly lower specific heat, and of much lower vapour pressure than free water. This last difference is important since it means that the amount of water vapour contained in an atmosphere in equilibrium with the colloidal material is always less than that of an atmosphere in equilibrium with a free water surface at the same temperature.

The lower the water content of the material, the more tightly the water molecules are bound, and hence the less free they are to escape to the atmosphere. Thus the relative humidity of an atmosphere in equilibrium with a colloidal material is lowest at low water contents, and may approach 100 per cent as the water content increases.

If the temperature of the colloidal material be increased, the vapour pressure of its contained water will also increase almost exactly as does that of a free water surface, so that the relative humidity remains almost constant. The effect of temperature for wheat at constant relative humidity is about 0.6-0.7 per cent decrease of water content for each 10°C. temperature increase.

Results obtained by various workers for the relation between the water in grain and atmospheric relative humidity are shown in the combined graph in Figure 35a, due to Oxley ("The Scientific Principles of Grain Storage,"Northern Publishing Co.,1948,p.18).

In spite of the diversity shown here, the general form is a sigmoid curve rising steeply above 80 per cent relative humidity. There is reasonable agreement around 78-80 per cent relative humidity, but as Oxley points out, all the workers started with grain near this humidity and conditioned it upwards and downwards with greater or less success.

Oxley suggests that a more accurate curve would result by adding liquid water or water vapour to wheat, and after a suitable time interval, determining the relative humidity of the intergranular atmosphere. Normal humidities in Britain are near the inflection points of the curves shown, and a rather small increase in relative humidity will correspond to a large increase in equilibrium water content.

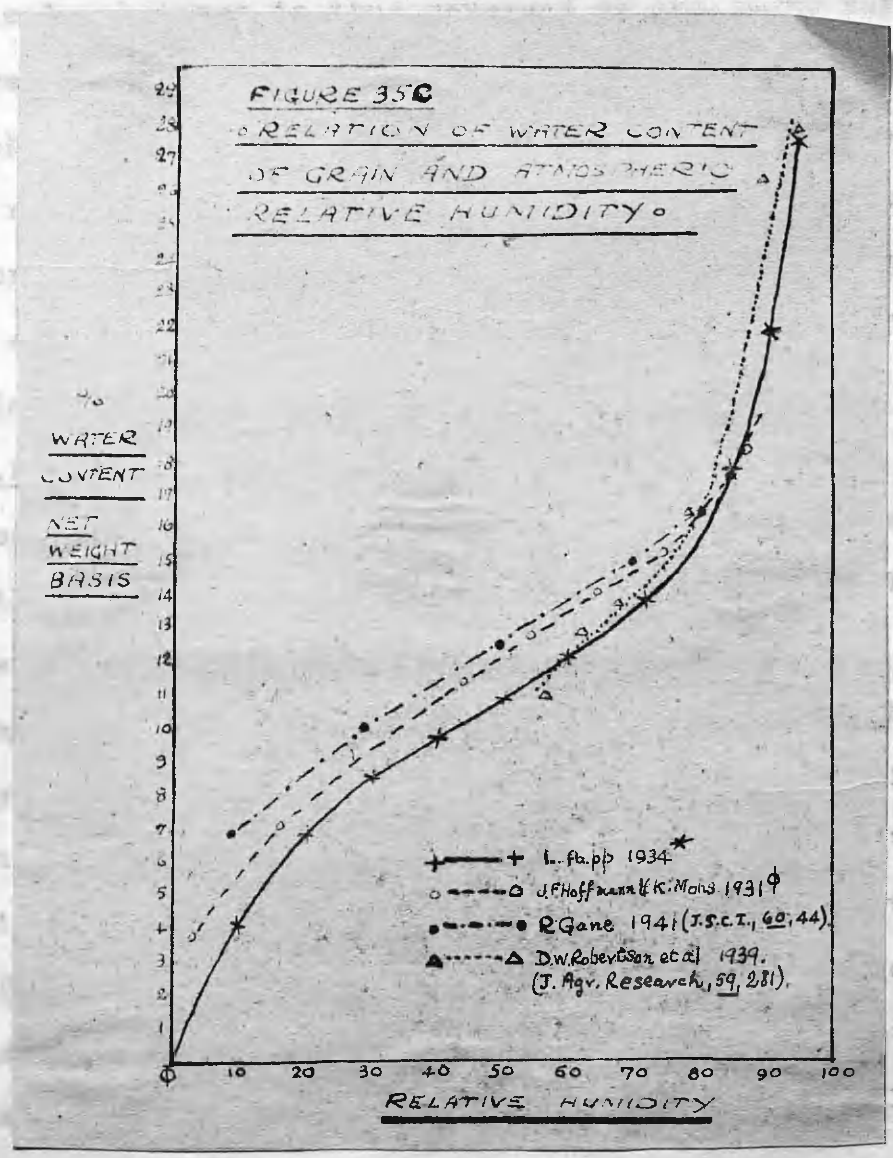

FIGURE 35C

• RELATION OF WATER CONTENT OF GRAIN AND ATMOSPHERIC RELATIVE HUMIDITY •

* Mezögazdasági Kutatások 7, 177, (Hungarian).

φ "Das Getreidekorn" Paul Parey, Berlin.

THE REMOVAL OF WATER FROM BIOLOGICAL MATERIALS.

Water is held with great tenacity upon surfaces, and if the surface is that of a colloid gel, appreciable amounts of water may remain in the material after it has been heated to a fairly high temperature. Nelson and Hulett (I.E.C., 12, 40, 1920) showed that water is retained by biochemical products at least to temperatures as high as 365°C., the critical temperature of water.

The purely empirical process of determining the moisture in a biological substance is thus governed by the three variables - time, pressure, and temperature. As R.A.Gortner has remarked ("Outlines of Biochemistry", 2nd. Ed., John Wiley, p.231, 1938) :-

" The removal of water from a biocolloid is merely shifting one equilibrium between a colloid surface and water to a new equilibrium, and the extent to which the equilibrium is shifted is determined by these three variables. "

R.Newton (J.Agr. Sci.,12, 1, 1922) in a study of the winter hardiness of the wheat plant, concluded that under the stimulus of cold, the water in the tissues of the wheat plant is 'bound' on the surface of the hydrophilic colloids.

There is considerable experimental evidence to show that there is a hydration shell connected with hydrophilic colloids, and that the water molecules in this shell differ from the state which characterises the water molecules in ordinary liquid water.
Heat of hydration, dielectric constant measurements, and the contraction of the system 'colloid-water', all indicate that the water molecules in bound water are rather more closely packed and

are

probably specifically oriented in relationship to each other, possibly in a more or less true crystal lattice which is more densely packed than the crystal lattice of ice. It has been shown that such oriented molecular films may be many molecular diameters in thickness. Experimental data shows also that 1 gm. of dry gelatine carries 0.5 gm. of closely bound water. One molecule of gelatine (mol. wt. 34,500) is therefore closely bound to 960 of water, a figure very close to the calculated number of possible co-ordination centres. It can be concluded therefore that the forces which bind water on the surface of lyophilic colloids are of the same nature as the forces which cause the association of water in bulk, although the actual magnitude of these forces is probably greater in the colloidal system. Similar forces immobilise water in the ice crystal lattice. The presence of colloidal matter appears to induce some change in the water molecule from the condition which characterises water in bulk.

Two hypotheses are current for bound water :-

1. The orientation of water molecules at the interface :
2. Selective adsorption of oriented layers of hydrogen and hydroxyl ions to form a shell surrounding the micelle.

Presumably under (1) for a positively charged colloid we should have an orientation with the oxygen end of the water molecule oriented towards the particle, and the hydrogen end oriented toward the body of the liquid. The reverse orientation would occur if the micelle were negatively charged. Nutting has shown that the water film thickness at a silica-water interface represents a layer of water from 100 to 120 molecular diameters deep , and that the energy of adsorption is by no means confined to the first molecular layer. It is not yet possible tosay whether this corresponds with what the biologist calls 'bound' water. It is, however, logical to think that bound water consists of an oriented shell, a layer or layers of water molecules or hydrogen and hydroxyl ions more or less firmly bound at the interface of the colloid particle,and that hydration is closely connected with the orientation of the water dipoles. The solubility of a particular compound may be zero in completely orientated water,whereas in the non-orientated water it will be normal, and between these limits we probably have the case of partly orientated water. It is possible that after orientation of dipoles a shifting of the equilibrium between H_2O and $(H_2O)_n$ occurs when water is 'bound'.

Gortner (loc.cit) sums up the position by saying- "The present evidence available points strongly to the conclusion that biochemical products in general contain appreciable quantities of water which cannot be removed by the ordinary methods of drying... no biological material can be completely dried without destroying the organic structure. I do not believe there is any sharp line of demarcation between free and bound water, but that we must postulate an insensible gradation between molecules of water having the normal activity of pure water, and molecules of water where this activity has been so reduced that such moleculas have become to all intents and purposes a part of the solid upon which they are adsorbed." He emphasises that different methods for determining bound water will show different results since they draw the dividing line at different activity values for the water molecules.

THE DETERMINATION OF WATER CONTENT.

Most methods are based on either of two assumptions :-

1. That all the water can be removed by some process (e.g. heating or chemical combination), and that the amount removed can be estimated directly or by loss in weight ; or,
2. That some other property of the sample (e.g. dielectric constant, or equilibrium water vapour pressure) can be correlated with the water content.

The difficulty of removing or attacking All the water in a sample makes assumption 1 faulty, while assumption 2 is often rendered inaccurate by variations in different samples.

It is apparent that the term 'water content' is itself an indefinite concept, but the practical utility of its determination outweighs the inherent defects of the methods used.

Oxley cites as criteria for a good method :-

1. Its precision :
2. Its ability to show accurately known amounts of water added to or subtracted from the sample.

METHODS OF ESTIMATION.

1. OVEN METHODS :- These are the most popular, since the results are reproducible. They are laborious as a rule, and require grinding of the sample and careful standardisation of the procedure.
2. DISTILLATION METHODS :- These have the same faulty assumption of the oven method that heating for a certain time will remove substantially all the water from a sample : there may be less oxidation with many samples.

3. KARL FISCHER REAGENT :- The basic assumption of this method is that **all** the water present in a sample can be removed by treatment with dry alcohol, and this is just as erroneous as the assumptions underlying the oven and distillation methods.

4. ELECTRICAL METHODS :- These methods involve the assumption that the physical condition and distribution of the water in the sample is always the same for a given water content, irrespective of the previous history or variety of the sample. The main advantage here is that of speed. The methods have been largely developed for grain, and they differ in the property measured. Thus the Tag Heppenstall meter measures pure resistance, while other systems use alternating current and measure various combinations of resistance and dielectric constant.

5. METHODS BASED ON HUMIDITY MEASUREMENT :- These can only give very approximate results since the relation between water content and relative humidity of the atmosphere in contact with a sample is far from constant. It must be remembered that relative humidity largely determines the liability of vegetable substances and foodstuffs generally to attack by fungi or insects, and is thus a very important figure in the study of storage conditions.

The importance of moisture determination.

1. In drugs exact content important since if excessive mould growth and enzyme action are favoured, and these are both injurious to the drug.
2. Water increases the weight of a substance and decreases its value so that commercially the buyer does not want to pay for useless water and for its transport.
3. In making estimates of stock in process water content is important for raw material entering, materials in process and finished products leaving.
4. Moisture absorbing power of electrical insulation is also important since it influences the insulating qualities of the materials.
5. A process may be held up until a moisture figure is determined, hence rapid estimation is often necessary. More efficient control is possible by cutting down the time of estimation.
6. Moisture estimation is essential in dehydration and drying processes generally.
7. For hygroscopic substances.
8. For proper interpretation of legal definition of buying and selling standards.
9. The moisture content of a commodity is closely related to its intrinsic value, its keeping quality, and its transportability.
10. Quick methods lessen cost of testing.
11. For beet sugar work small errors in purity determinations cause large variations in calculating per cent ELIMINATION.

12. For evaluation of research data.
13. Control of plant operations, and of the intermediates and finished products.
14. In interpreting manufacturing costs.

Fairbrother , (Ind. Chem. p.243, (1929)) points out the importance of the moisture content of wheat and flour. If wheat is too dry it mills 'flinty' and the flour is contaminated with much offal. If, on the other hand, it is too damp, it mills 'sticky' and the mills get clogged and the yield of flour is reduced.

The moisture content of flour has also great influence on the keeping properties of the flour. Low moisture is essential for prevention of mildew and prevention of the development of mites.

Refs: Shuey:- Collaborative Study of Moisture Methods,
Cereal Chemistry Vol. II, p.319
L.H. Bailey : : Vol. I, p.183
Fisher and Halton : : Vol. V.
Fisher and Jones J. Science, Vol. 18, part IV. p.42.

Summary - Importance of the estimation of moisture.

1. For buying raw materials - water increases weight and decreases value.
2. For stock in process - rapid estimation necessary for routine purpose - exact estimation necessary for stock balance.
3. Finished products and their keeping qualities - high moisture content favours mould growth, enzyme action, and the development of mites in foodstuffs, drugs, etc.

4. The hygroscopicity of electrical insulators and many other materials must be estimated and controlled.
5. Legally defined moisture limits must be controlled by an exact method.

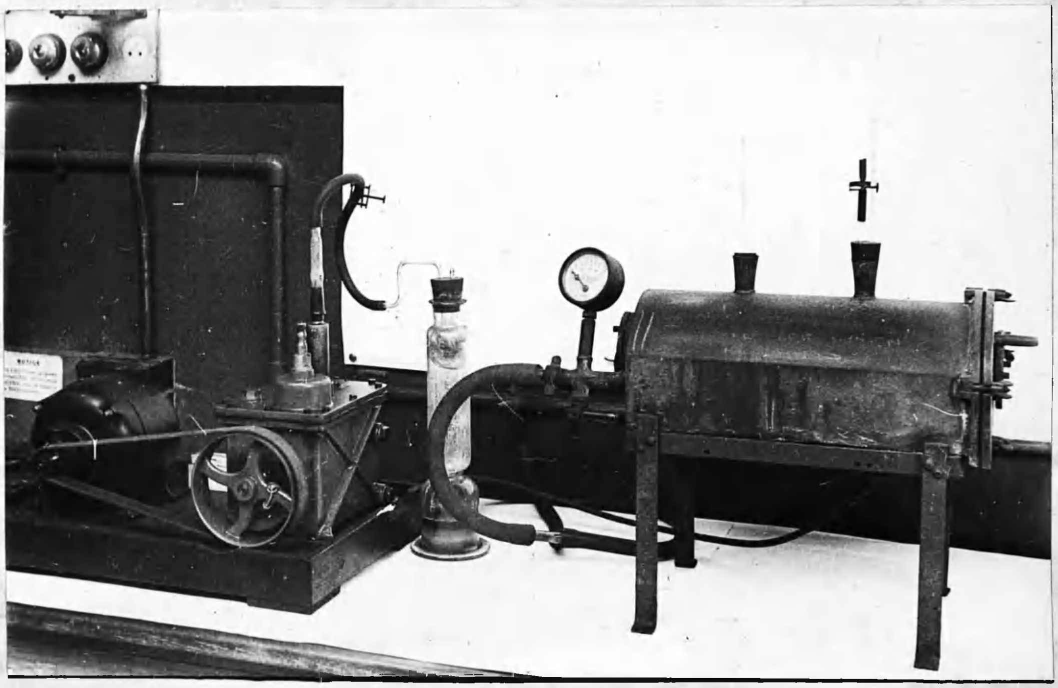

Figure 36 : Vacuum Oven used in tests : the switchboard with rheostats is in left hand upper corner : the drying tower is used when 'breaking' vacuum.

THE DETERMINATION OF WATER CONTENT-

SURVEY OF THE LITERATURE.

Forms in which water occurs.

Snyder and Sullivan (1924) recognised the term moisture or water in foods to mean all the water present in a free state, i.e. not combined in any form with the ingredients of the material, and other substances volatile at the temperature of drying.

For example, the main part of the free water of flour is given off in water-oven drying, much of that expelled at higher temperatures being in a different form. Many investigators supposed that water-oven temperature was the dividing line between free water and water in other forms. Water is still held tenaciously at higher temperatures as physically bound water, and some may be held as water of hydration of the carbohydrates and proteins.

Coleman and Snider (1935) again define moisture as the water which may be added to or taken from a product without changing the chemical composition of the product, and does not therefore include water of crystallisation or water of constitution.

C.B. Morison (1926) pointed out that the inherent difficulties in making an accurate determination of the total water content of foods composed largely of water are well recognised.

Nelson and Hulett (1920) emphasised one of these difficulties:- The layer of water adsorbed on the surface of colloids has quite different properties from ordinary water. Its vapour pressure is much lower, and if this layer is of molecular dimensions it cannot be removed by the best desiccating agents in a vacuum desiccator.

Schneller (1926) in a comparison of drying, densimetric, and refractometric methods of determining water in sugar products containing invert-sugar stated that apparent agreement of results was due mainly to compensation of errors such as persistent retention of moisture by film formation; oxidation; inversion of sucrose; and decomposition of invert-sugar especially levulose. He found that vacuum drying on sand at 70°C did not give constant weight after a week; 30-36 hours heating, however, gave a result which agreed fairly closely with the densimetric reading. Distillation with toluene was not found better than the drying method, as the end-point was not sharp and much time was required.

de Whalley (1936) stated that drying at room temperature in vacuo can be said to give true solids, which when corrected for combines water in dextrose gave solids which differ only 1.72 per cent from refractometer solids corrected for invert sugar: Whereas drying at 60°C in vacuo gives solids which differ 3.49 per cent from refractometer solids corrected for invert sugar. This work was carried out on golden syrup and molasses and led to the conclusion that all the advantages lie with the refractometer as a practical method of determining water.

Gustavson and Pierce (1924) carried out tests on the volatile compounds evolved by beet molasses at 104°C. They found an acid fraction at 90° and a strongly alkaline distillate at 104°C. pointing to decomposition of an amido component of the molasses at this temperature. The analyses of Wiley and Browne had shown the presense in molasses of such amido bodies (see Sherman, p.421, 427, and 431.)

Coleman and Snider (1935) carried out an extensive investigation of methods of determining water in barley malt. As a preliminary step a sample was sent to about twenty laboratories connected with brewing and malting. The figures returned showed differences as high as 2.5 per cent in moisture content, and there were wide variations in the temperatures, apparatus, and methods used. Thus the amounts weighed varied from 2 to 10 grams, temperatures from 98° to 132.5°C., and drying time from 10 minutes to 5 hours.

In consequence the authors set out to test ten existing methods, with the aim of selecting and standardising any likely procedure. They mention that the ideal moisture method is the one which least disturbs water of constitution or water of crystallisation while removing all the hygroscopic water. This they believe to be possible with vacuum desiccation at room temperature.

They found that a large difference was caused in oven methods by even 1° lowering of the oven temperature. The water oven was found to give low results compared with vacuum desiccation. High results were obtained where the temperature was about 130°C., these being ascribed to caramelisation, and decomposition of amino acids. The vacuum oven yielded low results.

Their final conclusion was that low temperature vacuum desiccation and an oven method such as that carefully standardised by the Chicage Malt Standardisation Committee, were the best procedures. This Chicago method is worth quoting in full as an attempt to standardise the heat of a drying oven.

Oven method for moisture recommended by the Chicago Malt Standardisation Committee.

1. The oven should be provided with automatic temperature control to keep within 0.5°C. temperature.
2. The oven should accommodate all the samples on one shelf, and so that no sample is outside the area indicated by test to give comparable results in duplicate samples.
3. The oven is to be standardised at the lowest temperature below 106°C. which will give a moisture content which after 3 hours of drying will be within 0.1 per cent of that attainable at the same temperature within 4 hours.
4. The weighing bottles are to be of glass or aluminium with tight-fitting cover - 40 mms. diam. for a 5 gms. sample, and 55 mms. for 10 gms.
5. The ventilators of the oven shall be open during the whole drying period, and the door is on no account to be opened during the 3 hours of drying.
6. The sample shall be of the same fineness as finely-ground malt for the determination of extract.
7. The sample shall be weighed as soon as cold.
8. Results shall be reported to the nearest 1/10th per cent.

Coleman and Snider found that their oven was at 104-105°C. while under load, but when empty, the temperature rose to 106.5°C.

Coleman and Snider finally plotted moisture contents by the various methods including the standard method, and thus got a basis for obtaining the true moisture content when the determination had been made by any method not standard.

Nowak and Enders (1936) also state that the only absolute method is vacuum desiccation using P_2O_5. They found that the water content by heating 3 hours at 105°C. was on the average 1.44 times the water by vacuum desiccation over P_2O_5, the material tested being hops.

Anderson (1936) paid special attention to water estimations in the vacuum oven. He worked out the energy requirements for the operation, showing that twice as much heat was necessary to raise the sample to oven temperature as for the actual removal of water from it. The conduction of heat to the sample was limited by the thickness of the metal shelves and by the area of the shelf which was in contact with the dish: the heat conductivity of the brass in a vacuum chamber is approximately 3,600 times as great as that for air. He found that samples still showed loss after 54 hours heating in the vacuum oven. The same author comments that if the sample is ground the true loss of water cannot be established owing to mechanical loss.

Grissinger (Great Western Sugar Co.) states that experiments have indicated that glass and aluminium vessels give identical results in oven methods.

Brown, Sharp, and Nees (I.E.C.,945,1928) tried to devise a method for the accurate determination of dry substance in beet house syrup using absorption on sand at 90°C. in a vacuum oven with an atmosphere of CO_2, and heating for 72 hours. Individual desiccators with fresh P_2O_5 were used, allowing the sample to stand 3 days or more before weighing. They found that the weight obtained after cooling say, 3 hours in a desiccator is invariably higher than that after 3 days or more. The drop after 3 days is usually 0.6 to 0.8 mgm. and the weight remains constant within ± 0.2 mgm. This difference they believed to be due to the slow dispersal of static charge from the aluminium dishes used.

"If a thoroughly dried dish after 3 days in the desiccator is weighed, replaced in the desiccator for three hours and re-weighed, it is found to have gained 0.5 mgm. or more : after three more days the weight goes back to the original value". These investigators state that the dish may pick up 1 mgm. of water during weighing. They used P_2O_5 since sulphuric acid allowed the dried material to increase in weight. In this connection Mellor and Thompson ("Text-book of Inorganic Quantitative Analysis",Griffin,London,1938,p.6) state that large glass and porcelain vessels and platinum crucibles and basins are particularly liable to condense wateron their surfaces while being weighed. Ostwald held the opinion that rapid weighing would minimise error by absorption, but J.L.Smith recommended leaving the dish in the balance-case for 20 minutes after removal from the desiccator so that it may regain its normal film of moisture. Mellor also comments on the remarkable facility with which some substances, e.g. clays, will absorb the dry gases in an ordinary desiccator, as much as 1.5 per cent being absorbed in some cases.

OVENS AND OVEN TEMPERATURE.

It is important to place the thermometer in an oven very close to the samples being dried or a false idea is easily obtained as to the temperature of drying. Thus L.H.Bailey (I.E.C., 6, 585, 1914, see also R.G. Grimwood, J.S.C.I., 32, 1040, 1913) tested a number of different ovens and found a very marked variation of temperature :-

TYPE OF OVEN	THERMOMETER READING	MAX. TEMP. RANGE	
		TOP SHELF	BOTTOM SHELF
	°C.	°C.	°C.
1. Electricallyheated and controlled	107	99-114	90-108
2. Gas-heated, porcelain lined	90	88-92	92-102
3. Gas-heated, air-jacket	100	94-96	105-118
4. Gas-heated, steam-jacket, constant water level	98	96-99	95-98

The atmosphere in some air-baths and sream ovens is quite humid and contaminated with sulphurous gases arising from the products of the gas burning beneath the oven. Dust from corroded metal walls in the oven may also fall on to the materials being dried : this may be prevented by lining the oven with tiles or smooth asbestos board. Bailey comments:- "Elaborately designed and expensive ovens are no more reliable than the more simple and inexpensive types : only those surrounded by boiling water and steam were capable of maintaining an approximately uniform temperature."

VARIOUS FACTORS INFLUENCING THE DETERMINATION OF WATER BY OVEN METHODS.

In any analytical estimation the natural trend is to prefer methods which are either more convenient, more accurate, or more rapid than the standard methods, and if all three criteria can be found then the operator is indeed fortunate.

In the attainment of rapid drying in moisture determinations there must be rapid transfer of heat to the sample, and rapid removal of the vapour driven off, and the sample should be heated to the highest possible temperature without causing decomposition.

Data obtained by a committee for Methods of Analysis of the American Association of Cereal Chemists in 1926, showed that a tolerance of 0.3 per cent between results could be reasonably expected from different laboratories working on cereal products such as flour. The limits allowable between duplicates in the same batch of samples with the same operator varied from 0.1 to 0.5 with an average of 0.23 per cent. This committee recommended that the methods should specify a definite time of heating rather than a heating to constant weight, and also advocated a specific time of cooling in the desiccator.

Snyder and Sullivan (1924-26) criticised the vacuum-oven method on the grounds of fluctuations of pressure and inequality of temperature in the oven. They were unable to obtain satisfactory results by drying at room temperature using sulphuric acid or phosphorus pentoxide.

Spencer (1925) working with wheat flour found fair agreement between duplicates on any one day, but irregularity on different days when weighings were made under different atmospheric humidity

Smith and Mitchell (1925) using the steam, vacuum, and electric ovens on flour studied the effect of different positions in the same oven, and the effect of different cooling conditions prior to weighing. Their duplicates showed as high as 0.47 per cent difference for identical conditions. The vacuum oven gave higher and more uniform results for different days and positions than the electric oven and much more so than the water-oven. They emphasised the care necessary to avoid re-absorption of water during transfer from the oven and while weighing.

Mitchell and Alfend (1924) showed that flour dried with covers left loosely over the sample gave higher and better agreeing results than with covers off, and noted that it was apparently not material whether the covers were under the dishes or removed from the oven.

Bailey and collaborators reported that the temperature of the interior of the water-oven was recorded by two collaborators as 94.6° and 95.5° respectively. It must be remembered that water oven drying will show a boiling-point according to the altitude.

Leavitt (1910) working on grain studied drying at temperatures carefully regulated to 97°, 98°, 99°, 100° and 101°C., found differences up to 1.75 per cent on moisture content of 8-10 per cent.

Anderson (1936) reduced the time taken by the sample to reach the oven temperature from 90 to 10 minutes by circulating steam through the brass plate on which the sample was placed.

Lanning (1935) studied the temperature changes in a small oven operating at 130°C. and concluded that there was considerable difference of temperature at various locations in the oven, that the position of the thermometer was important, that the time taken for the oven to regain its temperature after introduction of the samples should be definitely fixed, and that the maximum and minimum number of samples to be dried at one time should also be controlled.

Davis (1935) studied the effect of forced draught in ovens as an aid to moisture determination, and concluded that different oven ventilation conditions had very little effect on results in the air-oven method (130°C). He pointed out that variability of results appeared to be caused by low results near the oven door. This could be due to radiation, lack of convection currents at that part of the oven or recovery of water by the sample when the door was opened.

Leatherock (1922) sent sealed samples of flour to 69 operators. The average result was 14.19 per cent water and the range was from 13.22 to 15.00 per cent. Air-ovens showed 14.15 per cent average and vacuum ovens 14.50 per cent average. The investigation showed that the results were affected by the type of oven used, the weight of sample taken, and the shape and dimensions of the container. The gain in the vacuum oven results was put down to the relative absence of oxidation as compared with the air oven. There is also the possibility of the loss of fine particles of flour by the suction. Leatherock also states that water-jacketed ovens give regular results if attention is paid to the size, lagging and fitting of the door. He mentions an inside oven temperature of 98.5°C., and thinks the largest variation likely is 98-99°C. at sea-level. Distilled water should be used in the jacket since there may be a steady increase with tap-water through time due to the concentration of soluble salts.

In 1924 the referee on Cereal foods for the A.O.A.C. reported the results of a collaboration on determination of water by three methods viz. vacuo at 70°C., vacuo at 100°C., and air-oven at 103-105°C. Vacuo at 100°C. showed consistently higher results than the air-oven, while the results at 70°C. were lower and less concordant than those by the other methods. It was also reported that the copper water-jacketted oven is less efficient than the electric type of oven and gave lower results even when the samples were dried to constant weight at the same temperature. Experimental work indicated that errors due to mechanical loss by suction were improbable.

C.W. Ofelt (Cereal Chem. p.650, 1940) compared the official air-oven moisture method and the rapid aluminium plate method. (Sandstedt, ibid. 813, 1938). The official method was interpreted to mean 1 hour of total time in the oven. The two methods when used on flour samples gave results which are in agreement well within the limits of error of either method. There is a lesser tendency for variation due to oven position with the rapid Al. plate method than with the official method. Samples must not be placed too near the front of the oven when using the official method. With Ground Wheat the Al.

plate method requires more than the stipulated 20 minutes heating; 40 mins. seem necessary for comparable results. (The official A.O. A.C. method is drying for 1 hr. at 130°C.).

Putnam and Jolitz Cereal Chem. p.653 (1940) recorded the results from 26 collaborators on comparisons of the Al plate and official methods on flour and ground wheat. Seven samples of flour and six of ground wheat were tested. Each oven load was 8 samples only on the assumption that speed is less when a larger number of samples is accumulated before drying is started. General precautions used:- All oven vents open; avoiding large temperature drops by loading the oven quickly; avoiding placing of samples under the pilot light; placing lids atilt on the dishes while drying; placing lids on before removal from oven; 20 minutes in desiccator. (above for Al plate method).

For the official method 130° plus or minus 3° was maintained; no forced draught or Al plate was used. The thermometer was placed with the bulb tip level with the top of the dishes but not directly over a sample. For the Al plate method directions were:- place the ½ inch (or more) thick Al plate on the lowest shelf support of the oven; keep Al plate temperature at 140° plus or minus 1°; place thermometer bulb in a small can filled withfine sand; dry 15 minutes for flour and 20 minutes for ground wheat.

Flour Results Sample No.

	5.	6.	7.	8.	9.	10.	11.
A.O.A.C. Method	9.71	12.61	12.13	12.10	13.06	8.95	11.74
Al Plate Method	9.66	12.53	12.08	12.04	12.99	8.92	11.70

Ground Wheat Results

	12.	13.	14.	15.	16.	17.
A.O.A.C. Method	8.66	8.82	6.38	8.64	13.71	6.30
Al Plate Method	8.57	8.71	6.19	8.50	13.58	6.12

The chief advantage of the Al plate method is the even distribution of heat over the shelf area; its chief trouble is the difficulty of measuring its temp. accurately.

Probable Sources of Error in Ovens.

Bailey (1914) spoke of non-uniformity of drying-oven temperatures; Lenning (1935) showed that a poorly designed thermostat gave uneven temperatures. Davis (1935) found that different oven ventilating conditions had little influence on results by the official method (1 hr. at 130°C.) Putnam and Jolitz recommend The one hour period of drying begins when the oven temperature regains 130°C. It should be stated where the tip of the thermometer shall be placed in relation to the samples.

The Influence of Humidity on Moisture Determinations.

Ludwig Papp (1934) studied the effect of humidity on moisture determinations on flour. He instanced limits of 30% relative humidity on a bright cold winter day at a temperature of 15°C., and 65% relative humidity at 25°C. in hot damp summer weather. The possible variation for the same sample with these conditions were from 13.26 in winter to 12.66 in summer. The absolute humidity is lower in winter than in summer so that in the winter higher moisture results are obtained. The figures cited relate to the oven method at 105°C., and Papp points out that the influence of the humidity is even greater at temperatures below 105°C., since the pressure of saturated water vapour is lower, which gives a higher absolute humidity in a room than the humidity at the drying temperature. For example 50% relative humidity at 20°C. corresponds at 105°C. with a relative vapour pressure of 0.97%, and at 95°C. with a relative vapour pressure of 1.38%, the corresponding water percentages being 13.00 and 12.73. Papp used P_2O_5 in order to determine the water left in his samples after oven-drying at 105°C. He found that a sample first dried at 105°C. and then placed in a container with P_2O_5 and re-dried had 0.53 per cent of residual water. On drying at 20°C. 0.25 per cent of water remained after months of exposure. He concludes that materials with a gel-structure cannot be dried completely when water-vapour is present in the atmosphere. Similarly if air is bled through a vacuum oven the vapour tension is decreased in proportion to the vacuum, and higher values are got for moisture content, the effect of humidity and temperature being reduced.

Mason (1939) comments on the wide diversity of opinion as to which method should be considered the standard in moisture determinations, and considers that there is some weight of opinion in favour of the vacuum oven method even with all the varied conditions advocated. His own experience indicated that the vacuum oven method gave higher results than the electric oven method.

The following advantages of the vacuum oven are enumerated by Mason:-

(1) Economy of time for each determination.

(2) Less risk of aerobic oxidation due to prolonged heating in air.

(3) Lower temperatures may be employed, thereby reducing the dangers of thermal decomposition.

(4) The effects of varying conditions of humidity are reduced to a minimum.

(5) The liberated moisture is removed speedily from the heating chamber.

Shuey (1925) using a vacuum oven at 98-100°C. and a maximum pressure of 25 mms. also obtained slightly higher results than by air-oven method at 125°, 130°, and 135°C.

Davies (1935) stated that forced air-draught did not materially improve the air-oven method, and argued that as ventilation conditions were not of vital importance this favoured the use of the air oven method as a standard.

Koster (1936) defended the use of 130°C. for 1 hour on the grounds that temperature and humidity fluctuations have less influence than they have while heating at 105°C. for 3 to 8 hours.

THE DETERMINATION OF WATER IN ORGANIC MATERIALS.

Methods for Determination of Water or Total Solids from Chemistry in Commerce, Newnes, 1934-1935.

No.	Material	Weight used gms.	Temperature °C.	Type of Oven	Details
1.	Balsams	---	Room	Vac. H_2SO_4 desiccator	Cocking, p.912 Time - 48 hours.
2.	Butter	3-5	100	Electric	--- p.434 Time -min.2 hours
3.	Brewer's Malt	5	Boiling water	Bath	Oliver, p.327 Time - 3 hours
4.	Cacao Beans	3	Steam-oven	Steam-oven	--- p.1382 Time - 3 and to constant weight.
5.	Chocolate	---	100-105	Air-oven	--- p.1384 Time - 3 hours.
6.	Casein plastics	3	100	Well-designed air oven	Hand, p.597 Time - to constant weight.
7.	Coal	5	105-110	double-walled oven	Mills, p. 1178 Time - 1 hour.
8.	Corned Beef and Meat Pastes	5	100	Cellular water-bath	Cross, p. 383 Time - 18 hours.
9.	Flour	10	130 (Wheat) 120 (Flour)	Electric	Fairbrother p.935 Time - 2 hours

No.	Material	Weight used gms.	Temperature °C	Type of Oven	Details
10.	Flour	2	a. 98-100 b. 130	a. electric b. vacuum	Thomas, p.1171 a. to constant wt. b. 1 hour (A.O.A.C. methods)
11.	Glycerol	1 (absorbed on asbestos)	Room	Vac. H_2SO_4 desiccator	Davis, p. 373 Time ÷ about 48 hours.
12.	Inks	small	105	double-walled	Harman, p. 1030 Time - 3 hours.
13.	Leather	1	98.5-100	Water or steam-oven	Hepburn, p.922 Time - 3-4 hrs. then to constant weight.
14.	Meat Extract	2	100	Cellular water-bath	Cross, p.104 and 105. Time - 22-36 hours.
15.	Milk	---	Room	Vacuum Desiccator	Hawley, p. 1058 Time - 18 hours.
16.	Milk	5 ccs.	100-102	Electric	--- p.193 Time - av. 2-3hrs.
17.	Pigments	---	105	an oven	Bryson, p. 1063 Time - 2 hours.
18.	Pigments	5-10	100 (1 hr.) 82 (2 hrs.)	an oven	Wilson, p.1353 Method dependent on nature of sampl
19.	Rubber	10	100	---	Scott, p.416 Time - to constant weight.

No.	Material	Weight used gms.	Temperature °C.	Type of oven.	Details
20.	Rubber Mixings	2-5	110	an oven	Scott, p.1500 Time - 2 hours.
21.	Shellac	---	Room	Vac.H_2SO_4 Desiccator	Bryson, p.1374 Time - 48 hours.
22.	Sugar	10	100-105	Electric	de Whalley, p.1278 Time - 3 hours.
23.	Sticky Sugars	10 with sand admixed.	100-105	Electric	de Whalley, p.1278 Time - 3 hours.
24.	Drugs	Oven method not recommended. Distillation with tetrachlorethylene suitable. Electrometric method (dielectric constant) for routine.			Middleton, p.414.
25.	General	Description of the oven method, distillation method and chemical methods.			Hepburn, p.113.

CONCLUSIONS

The Determination of Water in Organic Materials.

A study of the methods described above reveals that there is no great liking for the vacuum oven, practically all the operators preferring the steam-oven or the electric oven. In some cases official methods are used, and with some products the method of vacuum desiccation is employed (balsams, glycerol, milk and shellac). The dishes used include clock and watch glasses, porcelain crucibles, aluminium or nickel flat dishes or basins, stainless steel dishes without lids,flat porcelain dishes, and tall or squat glass weighing bottles. Petri dishes and silica dishes have also been recommended. Several operators take to constant weight: solenoid weighing is specified by one worker and the use of a chainomatic balance by another. In one case the open dish is covered by a watch-glass while weighing. With flour and sugar it is stated that higher results are obtained in the vacuum oven. Chocolate is dried in thin flakes, and cacao beans are roughly broken up. Sand and asbestos are specified in certain instances as absorbing media. Sulphuric acid desiccators are used by several analysts, and the usual time of cooling (where mentioned) is 20 minutes.

With such a wide diversity of dishes, ovens, times, weights taken, temperatures, cooling times, and weighing directions, it is apparent that uniformity between different observers is hardly possible and it must be remembered that in many instances it is never required. It is also evident that no one method could be expected to be applicable to all the products listed.

The behaviour of heat-sensitive materials on drying:-

Occurrence of water :- All commodities and chemical systems contai water unless special care has been taken to prevent its entrance. The determination of water is one of the most familiar and frequent operations in analytical laboratories, and the mode of estimation has been a major problem almost since the introduction of the balance.

Water may occur as free or mechanical water which is often an equilibrium amount remaining constant at constant atmospheric humidity. It may occur as water of crystallization or as water of constitution, which last is usually termed combined water. Finally, in organic compounds of natural origin or from living tissues, bound water may be present.

Water removal :- Free water is easily removed by heat, but water of constitution and bound water provide the main difficulty in the accurate estimation of water. The temperature may be raised to remove this type of water, but the degree to which this is permissible is naturally governed by the type of material under test.

The dilemma is that if the temperature is not raised sufficiently all the water is not driven off, and if it is raised, much more than water may be driven off.

Oxidation :- With thermally sensitive substances oxidation is an important factor, and the end-point in an oven method for moisture is often the point at which the loss due to the last trace of water is balanced by the gain by oxidation or other changes.

Oxidation is minimised by vacuum oven drying, the maintenance of the vacuum removing water vapour from the neighbourhood of the sample and hastening the drying of the sample, particularly when a small air leak is allowed.

Water may be retained very persistently due to the formation of surface films, or to the high surface tension of concentrated syrups, even when absorbent substances such as sand or pumice are used to disperse the sample.

Sources of error :- Variations between observers are usually due to differences in the details of methods, especially when oven methods are used.

Relative humidity variations and differences in atmospheric pressure are particularly liable to cause discrepancies in results from different laboratories, and even in those from the same laboratory.

Choice of method :- Drying over desiccating agents at room temperature has been proposed as an absolute method for standardizing other methods, but the process is extremely slow, and there is the usual difficulty when a time factor is involved, of deciding when to stop. With acid desiccating agents, absorption of acid vapours may occur. As with many other methods, the removal of the last traces of water is difficult, generally taking about 90 per cent of the total drying time. The nature and freshness of the desiccating agent are important in this method, as they are also in the process of cooling oven-dried samples

In many cases the method of desiccation at room temperature will show alternate loss and gain from day to day, as the water passes back and forth from sample to desiccating agent.

Similarly, drying to constant weight does not ensure accuracy, since constant weight is limited by the conditions of drying, and also by the conditions of desiccator cooling and subsequent weighing. The necessity of having fresh desiccating agent in the desiccator is thus apparent ; dry sand as well as the dried sample will absorb appreciable amounts of water from many desiccating agents, and are in fact, better drying agents in many instances than that in the desiccator.

Ideally, the same percentage of water should be found in a given sample by any number of analysts who adhere rigidly to the conditions laid down by the method. In choosing a suitable method for any material many factors must be taken into account, and some of these are described below.

Factors in oven drying :- The time factor in a method should be kept as low as possible. This can be aided by taking as small a sample as is consistent with accuracy. Errors in weighing may become unduly large when less than 0.5 g. of sample is used.

It is doubtful whether the reduced pressure in the vacuum oven is an important factor in rapid drying, since the rarefied atmosphere acts more like an insulator than a conductor of heat. On the other hand, the removal of water vapour by the pump is an advantage over steam-oven drying.

The time necessary for drying rapidly decreases with increase of drying temperature. It may be expected that removal of moisture from solids will cease when the vapour pressure of the remaining water is in equilibrium with the vapour pressure of the atmosphere in the hot oven. It seems certain that drying to say 105°C. or to constant weight can only give comparative results at best and often not particularly quickly. Some substamces have not lost all their moisture at such a temperature, and others have already started to decompose - for example, the caramelization of sugars begins near their melting points, and this is dangerously close to 105°C.

Among the many factors influencing the results obtained by oven drying are the state of division of the substance, the amount of water used to mix absorbent and substance, the ratio of absorbent to substance, the pressure, and the time and temperature of heating. The size, shape, and material of the dish are also significant, and the rate of evaporation may vary from dish to dish even when the dishes appear to be uniform. The position of the dish in the oven, the closeness of its contact with the oven bottom, and the continuity of the heating in the oven will also influence results. The ventilation conditions in the oven are important with regard to removal of water vapour expelled from the sample.

Chemical methods :- These have been advocated for substances which decompose easily, which oxidise readily, or which are very volatile The usual errors in these methods are caused by combination of the reagent used with constituents other than water in the sample.

Various reasons for discrepancies and poor agreement in the Determination of moisture by oven drying.

1. State of division of substance.
2. Usual errors of weighing - carelessness, etc.
3. Adsorption of gases either while in oven or in desiccator.
4. Ratio of adsorbent to sample.
5. Amount of water added to mix sample and adsorbent.
6. Time : temperature : pressure.
7. Ventilation of oven.
8. Atmospheric humidity.
9. Rate of evaporation from dish to dish whether of the same material or of different materials.
10. Nature of substance, e.g., Ash/Reducing sugars ratio.
11. Difference between ovens.
12. Closeness of contact with oven bottom.
13. Size of dish : height, diameter, shape, knobs.
14. Position in Oven.
15. Continuity of heating in oven.

In vacuum drying the rarefied atmosphere is an insulation.
The heat conduction to a sample in an oven is limited by the thickness of the metal shelves (note effect of perforated shelves), and by the area of the shelf which is in contact with the shelf.

Heat transmission may vary from dish to dish - this variation is likely to be more between glass dishes then for say metal dishes of uniform thickness.

Vogel, Quantitative Analysis, 1939, p. 209.

Electrification of the surface of a weighing vessel due to rubbing may cause a comparatively large error, particularly if both the atmosphere and the cloth are dry. It is slowly dissipated on standing, but is best removed by placing a piece of pitchblend or other radioactive material in the balance case to ionise the air.

The time of cooling in a desiccator will depend on the temperature and the size of the dish, as well as upon the material of which it is composed and the nature and mass of the sample within. Pt. crucibles should be left 25 minutes, and crucibles of other materials for 35 to 40 minutes before being weighed.

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A Note on the Determination of Water in Coal :-

In Methods of Analysis of Coal and Coke (Fuel Research Board, Survey Paper No. 44, H.M.S.O., 1940), it is recommended that the weight of coal taken and the diameter of the dish should be arranged to give a layer of coal weighing not more than 0.3 gm. per sq. cm. of exposed surface.

Coals which oxidise readily should be dried in a bath through wh which a slow current of nitrogen is being passed.

SOLUBILITIES OF CARBOHYDRATES

In the experimental work on the estimation of water it was necessary to prepare solutions of various sugars. The solubilities of the principal sugars are conveniently grouped in Figure 37 :-

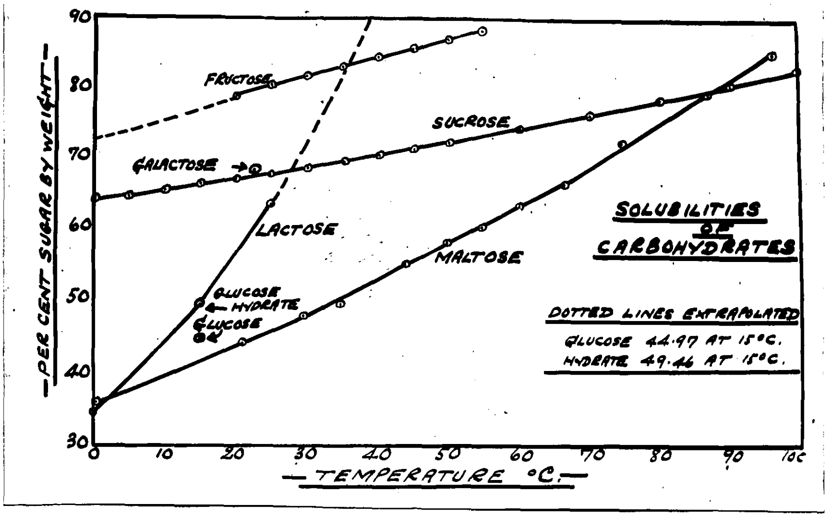

Figure 37 : Solubilities of Sugars

References :-

Galactose :- Dehn, J.A.C.S., 39, 1400, 1917.

Glucose :- Anthon, Dingler, 168, 456, 1863.

Lactose :- Hudson, J.A.C.S., 30, 1767, 1908.

Levulose :- Jackson, Silsbee, and Proffitt, Bur. Standards Sci. Paper No. 519 : Bull. Bur.Stds., 20, 587, 26.

Maltose :- Gillies, Rec.Trav.Chim.Pays Bas,70,43 : 135,24 : Int. Crit. Tables, II, 347, 1927.

Sucrose :- Courtonne, Ann.chim.phys., 5, 12, 569, 1877 : Taylor, J.C.S.,1678, 1947 : Herzfeld, Z. ver. Zuckerind., 181, 1892 : Grut, Z. Zuckerind.Czecho., 61, 356, 1937.

SECTION 5.

Part 5 : Oven Methods for the Determination of Water.

EXPERIMENTAL

1. Scope of the Work ;
2. Factors in oven methods ;
3. General procedure.

SCOPE OF THE WORK ON THE OVEN DRYING OF SUGAR SOLUTIONS.

In the preliminary work on drying sugar solutions in the steam oven it was attempted to establish the following points :-

1. The best type of absorbing medium to use.
2. A comparison of the use of glass and metal dishes of various shapes and sizes.
3. The optimum depth of mixed substance in the dish.
4. The agreement of duplicates, and the reproducibility of results.
5. The optimum amount of absorbing medium to use in relation to the amount of the sample taken.
6. The amount of water necessary for mixing the sample with the absorbing medium, and the effect of this water on decomposition and on drying time.
7. The optimum time of heating.
8. The overall time required for each estimation.
9. The proper preparation of the absorbing medium.
10. The effect of drying at a pre-determined pH value.
11. The influence of external atmospheric conditions on the estimation when repeated day after day.
12. The effect of using different ovens.

A comparison was then made with the vacuum oven method of drying using the data gained above. Comparisons were also made using the distillation method, the Karl Fischer chemical method, and the refractometer method of estimating water.

THE OVEN METHOD OF DETERMINING WATER :-

Thermally sensitive sugars may decompose giving off volatile products, e.g., aldehydes, esters, alcohols, organic acids, ammonia, and carbon dioxide ; this decomposition may proceed simultaneously with absorption of oxygen by the dried material. Most impure sugar products contain acids, gums, protein, and mineral matter which again complicate the drying problem, apart from decomposition of the sugar itself.

The main variables stressed in the literature are Temperature Time, and Drying Surface. When the temperature is lowered to protect the sugar, the time of heating has to be increased, and this extra time in itself may give rise to decomposition of the sugars or impurities present. The time of drying is much shortened by extending the drying surface.

Defects of steam-oven drying :- Uncertain results are mainly due to :-

1. Slow escape of air, the vapour from the samples being incompletely removed. The vapour pressure in the oven is thus higher than in the surrounding atmosphere, and this tends to give low results, with a slow continual rise.

2. The temperature of drying largely controls the rate of drying, both factors being dependent upon the intensity of heating, which may vary considerably in a multi-cellular oven.

Vacuum-oven Drying :- These are usually operated at 15 to 100 mms pressure with a gentle air current passing.

Without the air current, the water vapour escaping from the sample is not carried off so readily, and the results given will not give close agreement.

With the air current the vapour tension is reduced in the oven according to the vacuum. The results obtained are higher, varying with this pressure. The influence of temperature and of humidity are lessened.

Introduction of Samples :- Drying must not be disturbed by introducing fresh samples during the drying period. The number of samples placed in one compartment of an oven must be strictly controlled.

Detailed Consideration of oven drying :-

This will involve a study of the following factors :-

(a) The substance to be dried

(b) The drying dish

(c) The absorbing medium used ; hence drying surface.

(d) Oven conditions and heating details

(e) Time

(f) Desiccator details

(g) Weighing details

(h) General factors

(a) The Substance :-

1. Method of sampling :- Is the sample representative of the bulk?

2. General nature of the sample :-

(a) State of sub-division -Is grinding possible or necessary?

(b) How is the water distributed in the structure of the sample?

(c) Uniformity of the sample.

(d) Can water escape easily from the sample ?

(e) Sample density, for estimation of a convenient weight to take.

3. Behaviour of the sample on heating :-

(a) Tendency to decompose - general resistance to heat and time of heating.

(b) Tendency to oxidise

(c) Liability to formation of surface films occluding water, e.g., surface glazing, or formation of horn-like masses.

(d) Liability to form viscous syrups from which water escapes slowly.

(e) Danger of loss by air-currents or suction (with light materials).

4. Forms in which water is present in the sample :-

(a) Mechanical or adventitious water

(b) Water of constitution

(c) Water of crystallisation

(d) Zeolitic water

(e) Bound water

(b) THE DRYING DISH:-

1. Materials of construction :- Metals :- copper, nickel, aluminium, alloys such as Monel metal or Stainless steel. Non-metals :- glass silica, porcelain.

2. Properties :-

(a) Resistance to heat

(b) Resistance to corrosion by sample, by atmosphere, or by acid fumes

(c) State of surface : polished, dull ; smooth or rough.

(d) Co-efficient of heat transfer, controlling the rate of evaporation obtainable, and the rate of cooling in the desiccator.

(e) Tendency to acquire static charge, and ease of removing this.

(f) Air-tightness, and general convenience in handling.

3. Dimensions :-

(a) Ratio of height to diameter

(b) Shape - round, rectangular, 'dished', etc.

(c) Type of lid, e.g., tight of loose-fitting, with or without knob.

(d) Weight - in general preferably as light as possible.

(e) Flatness of bottom surface - important for heat-transfer.

4. Preparations for weighing :-

Washing, drying, polishing, heating, handling, wiping, etc.

(c) The Absorbing Medium :-

1. Type :- E.g., sand, pumice, kieselguhr or celite, asbestos, paper.

2. Preparation :-

(a) Cleaning and sieving (if necessary).

(b) Treatment by acid or alkali

(c) Washing with water

(d) Ignition to remove water and volatile matter.

(e) Storage.

3. Properties :-

(a) Inertness : there should be no side-reactions between sample and medium.

(b) State of sub-division.

(c) Porosity and weight per cubic foot.

(d) Colour : if white, decomposition of the sample can be seen.

(e) Hygroscopicity when dry.

(f) Surface area exposed : this controls the area of the film of sample

4. Relation to Sample :-

(a) Weight required for optimum drying, i.e., ratio of absorbing medium to test substance.

(b) Thickness of layer in drying dish, controlling resistance to the escape of water.

(c) Amount of water required to mix the absorbing medium and the sample, if the use of water is necessary.

(d) The Oven :- The main requirements are a uniform temperature and adequate ventilation.

1. General :-

(a) Type : size : shape : number of compartments.

(b) Fittings :- doors, shelves, thermostat, lagging, thermometer.

2. Heating, Ventilation, and Temperature Control :-

(a) Mode of heating - gas, steam, electricity, etc.

(b) Adequacy of temperature control - thermostatic regulation within 1°C. is desirable to ensure uniform heating.

(c) Ventilation :- there should be an ample inlet and outlet for air and water vapour : fan ventilation is preferable. The system used should be capable of close regulation.

(d) Steam-heated shelves may be required in large ovens.

(e) The thermometer should be placed so that the bulb comes just over the samples.

(f) The oven should be screened from draughts.

(g) The outside of the oven, particularly the door, should be properly lagged.

3. Relation of Sample to Oven :-

(a) Position of Sample in Oven.

(b) Closeness of contact of sample dish and oven bottom.

(c) Number of samples in the oven at one time.

(d) Fluctuations in the oven conditions due to variations in humidity and temperature, or to the opening of the oven door during drying.

(e) The use of inert gases to minimise decomposition or oxidation.

(f) The absence of conditions tending to cause oxidation.

(g) Continuity of heating, e.g. no samples should be added during a heating period, nor should the oven doors be opened until drying is thought to be complete.

4. The Vacuum Oven :-

(a) Temperature and pressure employed.

(b) The constancy of temperature, and pressure. } These factors will depend on the vacuum pump and the mode of heating.

(c) The degree of superheating in the oven jacket.

(d) Introduction of air during drying - the use of an air-leak.

(e) Pre-drying of the air entering the oven, i.e. air-leak or when breaking vacuum.

(f) Provision of efficient trap between oven and vacuum pump.

5. Placing of dishes :- Different workers recommend varied procedures, such as placing the lid beside the dish in the oven, covering the dish loosely or partially with the lid during drying, placing the lid under the dish, or leaving the lid

outside the oven. The best procedure would appear to be that of placing the lid alongside the dish in the oven.

(e) Time Factors :-

(a) Time for preparation for the estimation - sampling,preparing sample, assembling apparatus, heating oven.

(b) Time required for initial weighings.

(c) Time of heating in the oven, including time taken by sample to attain oven temperature.

(d) Time to cool, and total time in the desiccator.

(e) Time for final weighings.

(f) Total time taken for the estimation.

(g) Exact time when the sample is completely dry.

(h) Rate of Evaporation for the given conditions.

(f) The Desiccator :-

(a) Type, shape, and size of desiccator; material of construction - glass, metal, etc.

(b) Nature and efficiency of the desiccating agent, its type, and its physical state.

(c) Ratio of the volume of the desiccating agent to the total volume of the desiccator.

(d) Total amount of desiccating agent present.

(e) Use of cooling plate or cooling water.

(f) Freshness of the desiccating agent.

(g) Hygroscopicity of the dried samples.

(h) Time in desiccator before weighing -1.to cool : 2. total.

(i) Number of samples in the desiccator at one time.

(j) Risk of loss during opening of desiccator.; method of opening.

(k) Difference between weighing immediately sample is cool, and after say, 24 hours, in the desiccator.

(l) Danger with sulphuric acid of losing SO_3 vapour, especially when using vacuum desiccators.

(m) The use of special modes of desiccation, e.g., evacuation, stirring of desiccator air, etc.

(n) Distance of desiccating agent from the sample.

(o) Position of sam le in the desiccator - above or below desiccating agent.

(p) General convenience of desiccator for carrying and handling.

(g) The Weighing :-

1. The Balance :-

(a) Type :- The balance should be of "short-arm" type. It may be an ordinary analytical balance, or preferably chainomatic, air-damped, or magnetically-damped to give quicker weighing.

(b) Sensitivity :- 0.1 mgm. should be readily detectable with average loads.

(c) Speed :- The period of oscillation should be short ; a period of swing of 5 -10 seconds is satisfactory.

(d) Load :- The load at which the sensitivity becomes forty per cent of its maximum value should be the greatest load allowed.

(e) General :- The balance should be level ; the doors should be kept closed as much as possible ; weights should be placed in the centre of the pans ; a desiccator should be placed in the balance case ; weights should be handled with forceps.

(f) Weights :- Should be calibrated, and checked at least once each year. The same weights should be used in any one experiment.

2. Method of weighing :-

(a) The weight taken may be a round number ; where weighing by difference is necessary it should be made rapidly.

(b) A definite sequence of operations in weighing will make for greater speed, and lessen the chances of error. The choice of the actual method of weighing is also important: for example, the method commonly adopted of making the pointer swing of the loaded balance equal to the pointer swing of the unloaded balance may give rise to considerable error if the zero point changes within a short time.

(c) Tongs may be used in handling dishes to avoid finger-prints,etc

(d) Temperature differences should be avoided: there should be no appreciable change of external humidity of temperature between weighings : the dishes must be adequately cooled.

(e) Constant Weight :- There is considerable difference of opinion as to what is meant by constant weight . This term should be rigidly defined for any given procedure.

(f) Weighing by difference usually gives slightly higher results, and is advisable if the operator cannot weigh quickly.

(g) The time intervals of re-heating to "constant weight",should be strictly prescribed and adhered to.

Further notes on the Balance :-

1. The balance should be on a firm foundation, as free as possible from vibration and shock. It should be perfectly level, and should be in a room at even temperature and placed away from doors, hot pipes, draughts, etc. It should be as dust-free as possible.
2. The balance must give consistent results-that is, it must give the same result in successive weighings of the same body.
3. The balance must be accurate - that is, the beam must be horizontal when the pans are empty and when equal masses are placed on the pans.
4. The balance must be stable, that is, the beam after being displaced from its horizontal position must return to its horizontal position.

(h) General Details :-

1. Method of reporting results :-

(a) The extent of replication desirable should be determined.

(b) There should be a standard procedure governing the agreement of duplicate results.

(c) Analyses should be reported to the second decimal place only when justifiable, bearing in mind that the first decimal place <u>may</u> be accurate, and that the second is retained usually to keep the first place as accurate as possible when using the data in calculation.

(d) For oven drying methods the procedure adopted should be mentioned when reporting results, e.g. "5 hours in steam-oven at 95°C.", or " 6 hours in vacuum oven at 70°C. with pressure 5 cms."

2. Agreement of duplicate results :-

(a) Results should agree within plus or minus 2 per cent to be accepted as duplicates.

3. Type of Method :- This will depend upon the accuracy desired, and factors such as the effect of slow drying versus quick drying on the decomposition of thermally sensitive materials.

In general the vacuum oven operating at temperatures below 100°C. was found to give results much more variable than those by the steam oven without vacuum. This is probably due to the arrangement of the heating element causing a regular convection current system through the water jacket, since certain areas of the oven consistently gave low results.

4. Desiccators :- A desiccator can be dispensed with if the sample is heated in a 'Shield' box with tightly fitting lid surrounding the sample dish. The two are cooled and weighed together.

Two important factors with regard to desiccation are the surface area of the desiccating agent exposed to the sample, and the surface area of the sample exposed to the desiccating agent.

GENERAL PROCEDURE FOR THE DETERMINATION OF WATER AND TOTAL SOLIDS IN SUGAR SOLUTIONS, BY THE OVEN METHODS.

The glass dishes used, squat shape, 60 mms. diameter and 30 mms. deep, with inside-fitting ground-in lids, were carefully selected to ensure that the bottom surface was plane, and that their weights were approximately the same. Each dish was provided with a small glass rod, flat at one end, and sufficiently short to lie flat in the dish. The required amount of freshly-ignited absorbent (sand, celite, pumice, etc.) was placed in the dish, and the weight taken with the lid and rod. The estimated amount of syrup or sugar solution was now run on top of the absorbent, using a small wide pipette, and counting drops to get the approximately correct weight... This operation was carried out as rapidly as possible, and the lids of the dish and of the sample bottle were kept open for the minimum time possible. After accurate weighing, enough water was added to leave the material saturated, but without excess water. The syrup, sand , and water were now thoroughly mixed by means of the rod, which was finally dropped on top of the sand (or other absorbent). The dish was placed in the drying oven with the lid alongside, placing one dish in each compartment of a six compartment cellular type steam-oven, with the ventilators open, or, for vacuum work, placing four dishes together in a semi-circular section vacuum oven (see illustration). At the end of the heating period (e.g. 5 hours) the lid was replaced on the dish while still in the oven, and the sample cooled in a desiccator for 20 minutes, allowing more or less time according to the weights of material present and the nature of the dish (e.g. glass or aluminium). The weighing was made as rapidly as possible on an air-damped balance, using standard weights. The sample was returned to the oven for subsequent periods as desired, cooling and weighing as before.

FIGURE 38 : Aluminium, nickel, and glass dishes of various types as used in moisture determinations by the oven methods.

SECTION 5.

METHODS OF ANALYSIS.

Part 6 : The Rate of Evaporation in the Determination of Water.

INTRODUCTION.

In the constant rate period of evaporation which is the first stage in many drying processes, the rate of evaporation appears to vary as the 0.8 power of the mass velocity of the air (see Marshall and Hougen, T.A.I.Chem.E., p.91, 1942). In the limiting case where a liquid surface is exposed, Powell and Griffiths (T.I.Chem.E., p.175, 1935) have shown that the rate of evaporation is affected by edge-effects which cause irregular turbulence of the air stream by protecting a proportion of the area from the currents of air.

Several formulae have been suggested for the expression of the rate of evaporation from open dishes both in 'still' air and in currents of air. These are generally admitted to be empirical in nature. Thus Thomas and Ferguson (Phil.Mag., 34, 308.1917) state "Evaporation from full circular dishes was not proportional to the radius as Stefan suggested, nor to the square of the radius (or first power of the area) as was commonly assumed, but followed an exactly intermediate law - that of the three-halves power of the radius..." Hinchley developed the well-known "Imperial College" formula $W = 0.02(p_e - p_d)^{1.2}$ where W is the rate of evaporation (kilos per sq. m. per hour at 760 mms. pressure), p_e is the vapour pressure of the water in the pan (mms. Hg), and p_d is the vapour pressure of the water in the air (mms. Hg). This formula has since been modified by Himus (Hinchley, J.S.C.I., 242T, 1922 : Hinchley and Himus, T.I.Chem.E., 2, 57, 1924 : Himus, ibid. 7, 166, 1929).

Powell (ibid., 18, 36, 1940) and Wade, (ibid., 20, 1, 1942) have given modified formulae of a dimensional character.

In a closed compartment of a steam or vacuum oven, the conditions are markedly different from those in open evaporation systems, and the present tests were designed to investigate this difference.

From Hinchley's formula it was calculated that if evaporation takes place at 100°C., with the ambient air at 20°C., the rate of evaporation of water from an open pan with natural convection alone operating, should be 255 gms. per 100 sq. cms. per hour.

The temperature in a single unit steam oven was found never to exceed 98°C. and to reach this temperature the ventilator had to be kept closed. With the ventilator open, the oven temperature fell to 84-88°C. The introduction of a sample caused a drop of about 6°C. in the oven temperature. In most cases the sample dish temperature did not exceed 88°C., with an average of 86°C. On this basis, the rate of evaporation calculated from Hinchley's open pan formula should be 136 gms. per 100 sq. cms. per hour. In the tests made this figure was not approached, but it must be remembered that the rates include here the period of heating up to 86°C., which usually lasted 5-7 minutes. Even allowing for this, the rate would only be increased by about 20 per cent, and would still be well below the Hinchley figure.

Care was taken in the tests to have the copper bottom of the oven well cleaned, so that adequate thermal contact was assured for the dishes.

Of the various factors studied, that of heat maintenance seemed to be most important : the heat necessary to evaporate the liquid must be supplied to the dish. Neglect of this simple fact probably accounts for many discrepancies in results for moisture by

Experiments on the Rate of Evaporation in the Steam and Vacuum Ovens.

1. Effect of dish material
2. " " " diameter
3. Evaporation through sand and through celite
4. Effect of using deep containers
5. Variation of duplicates in different compartments of the oven
6. Evaporation Rate in the vacuum oven - effect of dish material
7. Vacuum oven - effect of insulating the dish
8. Vacuum oven - evaporation through sand
9. Effect of presence of oven shelf
10. Evaporation Rates with silica, porcelain, and clipped watch-glasses
11. Effect of high collar on the dish
12. Replicate tests in different compartments of the oven
13. Effect of having more than one dish per compartment
14. Effect of rate of boiling of the oven water jacket
15. Replicate tests using same dish on different days - Series 1
16. Tests in Single Unit oven - temperatures and conditions
17. Temperature Conditions in a Single Unit oven
18. Collected Results of Replicate Tests in same dish on different days and under different conditions. - Series 2.

EXPERIMENTAL :- 1. Effect of Dish Material :-

Evaporation Rate in Steam-Oven in Glass and Nickel Dishes.

Procedure:- Approx. 20 gms. of water was placed in each dish and weighed accurately. Each dish was given a separate compartment in the steam-oven at about 98°C. In one compartment a nickel and a glass dish were placed together.

Dish Dimensions mms.	Glass (1)	Glass (2)	Nickel Alloy
Diameter	57	58	60
Depth	31	29	16

Evaporation Rate gms. water per 100 sq. cms. per hour	(1)	(2)
Nickel alloy dish alone	56	65
: : : when in with glass dish	44	-
: : : alone on shelf	29	-
Glass dish alone	32	33
: : when in with nickel dish	26	-
: : alone on shelf	23	-

Effect of Dish Diameter.

2.
Evaporation Rates gms. water per 100 sq. cms. per hour.

Glass			Nickel Alloy			Aluminium		
mms. Diameter	Height	Rate	mms. Diameter	Height	Rate	mms. Diameter	Height	Rate
47	23	46	57	19	67	45	13	63
58	31	32	60	16	61	55	16	27
82	13	35	69	20	53	61	24	36
92	12	28	-	-	-	72	18	22

Evaporation Rate gms. per 100 sq. cms. per hour. using 40 ccs. water - 100 minutes heating.

Glass	Nickel Alloy	Aluminium (Basin Shape)
33	64	58
32	61	72

3.

Evaporation Rate through Sand and through Celite.

In this case 20 gms. of sand (or celite) were just covered by water and heated in the steam oven in various dishes.

	Glass	Nickel Alloy	Aluminium (Basin Shape)
Sand	27	48	46
Celite	23	50	35
Water alone	32	56	36

4.

Test using deep containers. Evaporation Rate gms. water per 100 sq. cms. per hr.

		Glass		Aluminium	
		(1)	(2)	(1)	(2)
mms.	Height	42	31	75	18
	Diameter	65	58	70	72
	Rate	40	32	53	22

5.

Variation of Duplicates in Steam-Oven separate compartments. Glass Vessels 60 minutes heating.

Test	Diameter	Depth	Evaporation Rate gms/100sq.cms./hr.
1	58	29	29
2	58	31	29
3	58	30	30
4	60	27	33

6. Evaporation Rate in Vacuum-Oven in Various Dishes
Tests made at 63°C and 70-72 cms/gms/100sq.cms/hr.

	Water Alone	Sand	Celite
Glass	34	30	33
Aluminium (Basin)	48	36	43
Nickel Alloy	61	63	48
Comparison - Steam Oven 98°C			
Glass	32	27	23
Aluminium (Basin)	36	46	35
Nickel Alloy	56	48	50

The surface area of the container bottom and the closeness of contact between it and the bottom of the oven appear to be the important factors in determining the evaporation rate for different materials.

It is clear that the results obtained in the oven method of determining moisture are dependent on the rates of conduction and evaporation.

7. This was demonstrated by placing dishes in the ovens on glass triangles thus keeping the dish clear of the metal surfaces of the ovens.

Evaporation rates gms/100sq.cms/hr.	Steam oven	Normal Rate	Water alone. Vacuum oven	Normal Rate
Glass	14	32	18	34
Aluminium	10	36	11	48
Nickel Alloy	11	56	11	61

8. Evaporation Rate in Vacuum Oven using Sand in same Glass Vessel. 20 gms. and 6 ccs. water - Replicate Tests on Different Days. 63°C and 70-72 cms. vacuum.

Test	Glass Evaporation Rate Gms/100sq.cms/hr	Nickel Alloy
1	27.8	53
2	28.4	62
3	29.8	60

9. **Effect of Oven Shelf:-** A perforated metal shelf put in above the sample did not materially affect the evaporation rate with a glass dish viz. 28.5 found as against the normal 28.6 gms/100 sq.cms/hr.

10. Evaporation Rates with other Materials:- Steam-Oven

		Rate
	Silica Dish	44
	Porcelain	28
	Clipped Watch Glasses	32
Comparison	Glass	32
	Aluminium	36
	Nickel Alloy	56

11. Effect of Collar on Dishes (Nickel Collar on Nickel Alloy Dish)

Steam Oven : Normal Height of dish 2 cms.

Height with collar 15.25 cms.

	(1)	(2)	Normal Rate
Evaporation Rate gms/100 sq.cms./hr	44	48	61

12. Evaporation Rates Gms/100 sq.cms./hr. for Aluminium Capsules in Steam Oven, Separate Compartments.

Dimensions:- 69 mms. diam. x 20 mms. depth.

Dish	Evaporation Rates Steam Oven Test 1	Test 2	Vacuum Oven 61°C. 70 cms.	
1	57	57	76	
2	53	66	64	78
3	58	60	(57 (63	
4	49	65		90
5	60	68		
6	58	65		83
Dish - 102 mms. diam. x 19 mms. depth.				
1	38		46	
2	42		55	

It is possible that a dish of low conductivity is better for thermally sensitive materials, as the tendency towards burning and decomposition may be greater with vessel of high conductivity. Metal dishes are generally more planar than glass ones which often have a dished base so that contact with the bottom of the oven is not complete.

The rate of evaporation depends on the rate at which heat can get to the sample and <u>also</u> on the rate at which water vapour can escape from the sample <u>and</u> from the oven.

Replicate tests on Dish 1 (Steam Oven)

	Rate	Rate	
1	45	57	above
2	64	57	
3	63		

13. Effect of Heating more than one dish in Steam Oven Compartments. Aluminium Capsules 69 mms. diam. x 20 mms. deep.

	Dish	Evaporation Rate Gms/100sq.cms./hr.
Alone	1	54
Together	(2	(44
	(3	(41
Together	(4	(38
	(5	(32
	(6	(31

Note systematic decrease in weight of water evaporated. This follows the order of weighing. This test brings out the error which may result from comparing results from a single sample with results obtained where several samples have been heated together.

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14. Evaporation Rate with Aluminium Capsules, using 20 gms. sand:-

Vacuum Oven Rate - 75

Test in steam-oven with water just boiling - i.e. steam escaping at top but no distilled water being made.

Dish No. 1. Evaporation Rate gms./100sq.cms./hr.

Front Ventilator Shut			Ventilator Open	
(1)	(2)	(3)	(4)	(5)
14	12	11	17	12

Gas turned full on 67

a sample exposed on an ordinary ring water bath gave a rate of 191 gms/100 sq.cms./hr.

The above results show the extreme variation which may occur in evaporation rate in a steam oven, and the large difference on an open water bath shows that the evaporation problem is quite distinct in a closed steam oven.

15. Replicate Tests in Steam Oven on Al. Dish No. 1.

Series 1.

Test No.	Evaporation Rate. Gms./100 sq. cms./hr.	Barometric Pressure.
1	72	760.5
2	73	:
3	74	:
4	76	:
5	78	:
6	66	766
7	69	766
8	69	:
9	78	767.5
10	71	:

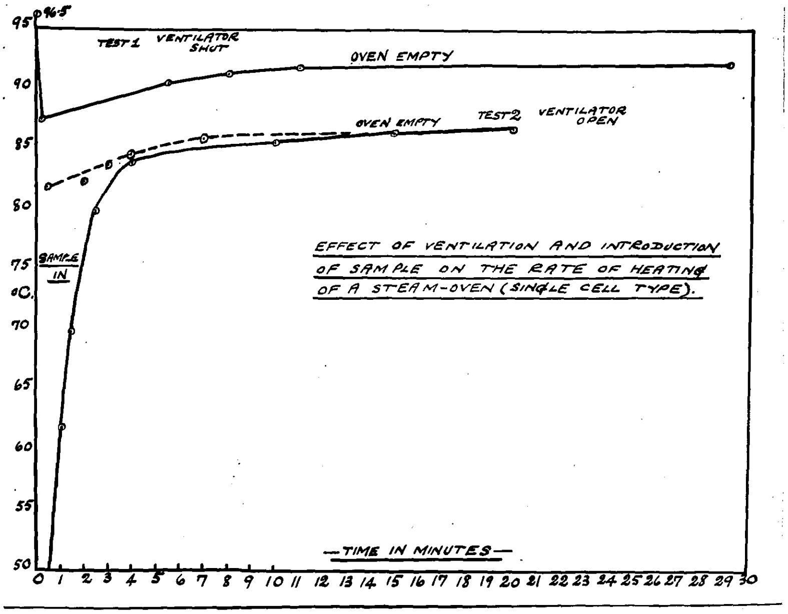


Figure 39.

16.

EVAPORATION RATE

Tests in single unit steam-oven. Aluminium capsules 69 mms. diameter by 20 mms. deep.

Temperatures and Conditions.

No.	(1)	(2)	(3)	(4)
Ventilator	Shut	Open	Shut	Shut
Temp. empty °C.	96	82	97.5	97.0
Fall to (with sample in)°C	93.5	77	92.5	91.5
Temp. °C at end	-	79	94	93.5
Evaporation Rate gms./100sq.cms./hr.	69	72	67	64
Time of Heating mins.	32	30	36	30

No.	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
Ventilator	Shut	Shut	Shut	Shut	Shut	Shut	Shut	Shut	Shut	Shut
Time of Heating mins.	30	30	30	30	30	5	10	15	20	25
Evaporation Rate gms./100sq.cms./hr	62	66	63	70	74	53	68	71	78	74
Barometric Pressure	766.3	766.3	766.3	767.5	767.5			766.5		

Humidity (Atmospheric) - 75 per cent.

17.

Temperature Conditions in Single Unit Oven.

ж Graphed

Test No.	1 ж		2		3		4		5	
Ventilator	Shut		Shut		Shut		Open		Open	
Jacket Temp.	100°C		100°C		100°C		100°C		100°C	
Air Temp. in Oven at start.	96.5		96.5		97.0		84.5		84.5	
Temp. °C After Mins.	Oven	Sample	Oven	Sample	Oven	Sample	Oven	Sample	Oven	Sample
0.5	87.5	-	-	-	89	50	-	-	79.5	51.0
1.0	-	61	-	-	88.5	63	79.5	60.3	79.0	62.5
1.5	-	67.5	-	-	88.5	70	79.8	69.6	79.5	70.8
2.0	-	73	-	-	88.5	75	80.0	75.0	80.0	74.8
2.5	-	7.5.	-	-	89.0	79	80.7	78.8	80.8	78.0
3.0	-	80	88.5	80.5	89.2	82	80.4	83.0	81.2	80.1
3.5	-	81.5	-	-	89.2	83.7	-	-	81.8	82.0
4.0	-	83	-	-	89.2	84.6	82.5	84.7	82.2	82.8
4.5	-	84.4	-	-	89.7	84.3	-	-	82.2	83.5
5.0	-	84.6	-	-	90.0	85.0	83.0	85.8	82.8	84.0
7.0	-	85.0	90.2	86.6	91.2	85.4	84.0	86.2	83.5	84.6
9.0	-	-	91.2	86.7	-	-	-	-	-	-
10.0	-	85.4	-	-	92.0	86.0	84.1	86.1	84.2	84.7
14.0	92.0	-	92.0	87.9	-	-	-	-	-	-
15.0	-	85.7	-	-	92.9	86.5	85.8	87.2	85.2	83.9
17.0	92.0	-	92.0	87.6	-	-	-	-	-	-
20.0	92.1	86.1	-	-	93.2	87.0	85.0	87.6	84.9	84.5
30.0	-	86.3	-	-	93.3	86.8	85.8	87.6	83.4	84.4

Temperature Conditions in Single Unit Oven (Contd.)

* Graphed

	6		7		8		9		10 *	
Ventilator Jacket Temp.	Open 100°C		Open 100°C		Open 100°C		Open 100°C		Open 100°C	
Air Tem. in Oven at start.	84		86.7		88.0		86.5		87.5	
Temp. °C after Mins.	Oven	Sample	Oven	Sample	Oven	Sample	Oven	Sample	Oven	Sample
0.5	78.5	50.0	82.0	51.0	84	49	81	50	82.1	49.8
1.0	79.3	61	82.0	65.0	83.3	61.2	81.1	62	82.2	62.2
1.5	79.3	70.6	82.0	71	83.0	68.8	81.1	70	82.1	70.0
2.0	80.1	75.0	82.2	76	83.2	75.2	81.6	75.8	82.5	75.4
2.5	80.8	78.8	82.0	79.2	84.1	79.0	82.0	79.3	83.2	79.8
3.0	82.0	81.0	82.9	81.7	84.0	81.2	82.3	81.5	83.9	81.3
3.5	82.3	82.4	83.5	83.0	84.2	83.6	83.2	83.0	84.3	82.8
4.0	83.2	83.4	83.8	83.7	84.4	83.4	83.7	83.8	84.7	84.0
4.5	83.3	83.8	84.2	84.3	84.3	83.6	84.5	84.0	85.0	84.3
5.0	83.7	84.1	84.7	84.6	84.3	84.0	84.9	84.9	84.8	84.7
7.0	-	-	84.8	84.9	85.3	84.7	86.0	85.0	86.0	85.5
9.0	-	-	84.9	84.8	85.9	84.6	86.6	85.2	86.0	85.4
10.0	-	-	85.2	85.4	85.4	84.8	86.8	85.2	84.8	85.6
14.0	-	-	-	-	85.6	85.0	87.8	85.5	85.4	85.3
15.0	-	-	-	-	85.0	84.9	87.8	85.1	86.0	85.5
17.0	-	-	-	-	-	-	88.1	85.6	85.8	85.4
20.0	-	-	-	-	-	-	-	-	86.9	86.1
25.0	-	-	-	-	-	-	-	-	86.8	85.8

SERIES 2 :- COLLECTED RESULTS :-

18. Evaporation Rates in the same Aluminium Capsule.

No.	Evaporation Rate gms./100sq.cms./hr	Barometric Pressure	Time of Heating Mins.	Conditions
1	57	750	30	Multiple Steam-oven full on
2	57	763	30	-do-
3	76	763	30	Vacuum Oven
4	45	765	30	Multiple Steam-oven full o
5	64	765	30	-do-
6	63	765	30	-do-
7	54	769	30	-do-
8	14	753	30	-do- just boiling
9	12	753	30	do- -do-
10	11	755	50	-do- -do-
11	17	755	50	-do- -do-
12	12	755	50	-do- -do-
13	191	759	15	On Boiling Water Bath
14	67	765	30	Multiple Steam-oven full on
15	72	761	30	-do-
16	73	761	30	-do-
17	74	761	30	-do-
18	76	761	30	-do-
19	78	761	33	-do-
20	66	766	30	-do-
21	69	766	32	-do-
22	69	766	31	-do-

Evaporation Rates in the same Aluminium Capsule (Contd.)

No.	Evaporation Rate gms./100 sq.cms./hr.	Barometric Pressure	Time of Heating Mins.	Conditions
23	69	766	32	Single Unit Steam Oven
24	72	766	30	-do-
25	78	768	34	Multiple Steam-oven full on
26	71	768	38	-do-
27	67	768	36	Single Unit Steam-oven
28	64	768	30	-do-
29	62	766	30	-do-
30	66	766	30	-do-
31	63	766	30	-do-
32	71	768	30	-do-
33	74	768	30	-do-
34	53	767	5	-do-
35	68	767	10	-do-
36	71	767	15	-do-
37	78	767	20	-do-
38	74	767	25	-do-

CONCLUSIONS AND DISCUSSION OF RESULTS

1. The average rate of evaporation of water from an aluminium capsule 69 mms. diameter and 20 mms. deep was found to be 70 gms. per 100 sq. cms. per hour. The rate was lower with glass, silica, and porcelain dishes.
2. The rate of evaporation of water through sand or celite was not appreciably lower than for water alone.
3. Results were reproducible, allowing for atmospheric conditions.
4. In the vacuum oven the rate of evaporation was on the whole higher than in the steam oven : this appears to depend upon the better withdrawal (by pump) of the water vapour from the vacuum oven.
5. Deep dishes caused a lowering of the rate of evaporation : the velocity of escape is apparently reduced by the 'baffling' effect of the high dish wall.
6. A very marked lowering of the rate of evaporation is observed when more than one sample is heated in the same compartment of the oven.
7. The normal fluctuations of barometric pressure have a small but distinct effect upon the rate of evaporation.
8. The results for oven temperature reveal surprisingly low figures in a normal single unit steam oven. The effect of opening the ventilator is very marked.
9. The rate of evaporation of water in a closed compartment of a steam oven is very much lower than the rate of evaporation from an open pan in'still'air as calculated by Hinchley's formula.
10. The rate of supply of heat to the dish is probably the most important factor in determining water by oven methods.

SECTION 5.

METHODS OF ANALYSIS

Part 7 : The Determination of Water in Golden Syrup.

ABSTRACT

Factors influencing the determination of water in the thermally sensitive material golden syrup have been studied, and several methods have been compared.

An acid-washed kieselguhr has been found suitable as an absorbent for the syrup, yielding more concordant results than sand.

A method is recommended for the estimation of water in such thermally sensitive substamces.

INTRODUCTION.

Golden Syrup is a refinery product made by inverting the sucrose in a low grade product with acid, neutralising with lime and chalk, and adding some of the uninverted product so as to reach a certain ratio between the sucrose and reducing sugars present. The process is completed by filtering,and concentrating the clear liquor in a vacuum pan. The finished syrup should be a light golden-yellow colour and should not crystallise out for at least six months. With such a high proportion of reducing sugars coupled with a very low ash content, golden syrup is very sensitive to heat, and is therefore eminently well suited as a test material in comparing methods for the determination of water in sugar products.

The syrups used in the present work were stored in large airtight jars in the dark. They had the following composition :-

Per Cent	Sample A	B
Sucrose	33.91	32,36
Reducing Sugars	46.50	45.83
Water (Refractometric)	17.50	17.93
Ash (Sulphated)	1.17	1.21
Other Organic Matter (Diffce.)	0.92	2.67
	100 .00	100.00
Unsulphated Ash	0.96	1.02

The composition of the ash of these two samples follows :-

Per Cent	Sample	A	B
Silica		7.7	6.0
CaO		3.1	3.6
MgO		1.4	6.6
Na_2O		9.9	18.3
K_2O		38.1	28.5
SO_3		16.5	1.5
Cl		0.3	18.1
P_2O_5		1.7	1.5
CO_2		18.2	14.2
Fe_2O_3		0.5	0.4
Al_2O_3		0.2	0.3
Unestimated		2.4	1.0
		100.00	100.00

The increased chloride in sample B is possibly due to added salt. Both ashes are alkaline.pointing to the absence of added organic salts. These samples kept well, there being no apparent crystallisation after a year.

The syrups were used to investigate the effect of various types of dishes and absorbents on the moisture per cent obtained, and also the effects of the ratio of absorbent to syrup, and of time of heating. Comparisons were made of the steam and vacuum ovens for heating.

EXPERIMENTAL.

DETERMINATION OF WATER IN GOLDEN SYRUP :-

1. Use of various types of dish and various absorbing media :
2. Influence of ratio of absorbent to syrup -collected results :
3. Effect of thickness of layer of absorbent and syrup :
4. Effect of diameter of dish :
5. Effect of time of heating)- Series 1 and 2 :
6. Optimum ratio of celite to syrup - vacuum oven :
7. Optimum ratio of celite to syrup - steam oven :
8. Use of various organic liquids for mixing syrup and absorbent :
9. Use of sand as absorbent - experiments in steam and in vacuum ovens:
10. Comparison of rate of loss in replicate dishes.

EXPERIMENTAL RESULTS.

ESTIMATION OF WATER IN GOLDEN SYRUP BY STEAM-OVEN DRYING -5 HOURS HEATING USING VARIOUS TYPES OF DISHES AND ABSORBENTS.

No.	Ratio absorbent to 1 of Syrup	% Water Found	Mixing water ccs.	Dish	Absorbent
1	4	4.96	7	Glass	Sand
2	10.8	15.99	7	"	"
3	23.8	16.85	7	"	"
4	11.2	15.99	7	"	"
5	37.7	16.44	20	"	"
6	21.7	16.70	20	"	"
7	25.0	17.03	5	"	"
8	25.0	16.77	10	"	"
9	15.0	17.11	5	"	"
10	15.0	14.71	5	"	"
11	5	16.85	20	"	Celite
12	4	17.12	20	"	"
13	1	16.74	10	"	"
14	2	17.02	10	"	"
15	3	17.10	10	"	"
16	6	17.10	20	"	"
17	4	17.14	10	"	"
18	4	17.02	10	"	"
19	4	17.17	10	"	"
20	4	17.16	10	"	"

ESTIMATION OF WATER IN GOLDEN SYRUP BY STEAM-OVEN DRYING - 5 HOURS HEATING USING VARIOUS TYPES OF DISHES AND ABSORBENTS.

No.	Ratio absorbent to 1 of Syrup	%Water Found	Mixing Water ccs.	Dish	Absorbent
21	4	16.78	10	Glass	Celite
22	4	17.01	10	"	"
23	4	17.32	10	"	"
24	4	17.01	10	"	"
25	4	16.86	15	"	"
26	4	18.42	10	Aluminium	"
27	4	16.97	10	"	"
28	4	17.01	10	"	"
29	25	19.02	10	Glass	Sand
30	25	17.07	10	"	"
31	25	17.26	10	"	"
32	25	17.30	10	"	"
33	25	17.78	10	"	"
34	25	18.41	10	"	"
35	25	16.63	10	Aluminium	"
36	25	16.81	10	"	"
37	25	17.08	10	"	"
38	25	16.81	10	"	"
39	25	16.82	10	"	"
40	25	17.20	10	"	"

INFLUENCE OF THE RATIO OF ABSORBENT TO SUBSTANCE DRIED IN THE STEAM OVEN METHOD FOR WATER IN GOLDEN SYRUP (See figgres 42 & 43)

No.	Ratio	Medium	Apparent per cent moisture after heating			
			5 Hours	10 Hours	15 Hours	20 Hours
1	4:1	Sand	4.96	9.25	11.56	12.86
2	11 : 1	"	15.99	16.69	16.85	18.16
3	23 : 1	"	16.85	16.85	17.61	17.66
4	11 : 1	"	15.99	16.51	16.88	17.14
5	38 : 1	"	16.44	16.49	16.91	17.10
6	22 : 1	"	16.70	16.85	17.14	17.26
7	25 : 1	"	17.03	17.05	17.03	17.71
8	25 : 1	"	16.77	17.04	17.28	17.52
9	15 : 1	"	17.11	16.83	17.27	17.27
10	15 : 1	"	14.71	14.58	15.01	15.05
11	5 : 1	Celite	16.85	17.14	17.93	18.65
12	4 : 1	"	17.12	17.45	18.03	18.58
13	1 : 1	"	16.74	-	-	-
14	2 : 1	"	17.02	-	-	-
15	3 : 1	"	17.10	-	-	-
16	6 : 1	"	17.10	-	-	-
17	4 : 1	"	17.14	-	-	-
18	4 : 1	"	17 02	-	-	-
19	4 : 1	"	17.17	-	-	-
20	4 : 1	"	17.16	-	-	-
21	4 : 1	"	16.78	-	-	-
22	4 : 1	"	17.01	-	-	-

VARIOUS TESTS ON THE DRYING OF GOLDEN SYRUP IN THE STEAM-OVEN

1. Drying in narrow weighing bottles on acid-washed sand absorbent

Dimensions of bottles 30 mms. diameter by 75 mms. high : ratio of sand to syrup 25 : 1. Height of sand layer in bottles, 14 mms. 10 ccs. mixing water used.

Drying time Hours	% Water Found (1)	% Water Found (2)
6	15.53	16.10
7	15.31	16.25

Drying was evidently slowed up by the thick layer of material : this test illustrates the importance of drying in as thin a layer as possible. There is a wide difference in the two results.

---

2. Test with aluminium containers of different diameters

Drying Time Hours	% Water Found 45 mms. Diameter (1)	45 mms. Diameter (2)	55 mms. Diameter (1)	55 mms. Diameter (2)	72 mms. Diameter (1)	72 mms. Diameter (2)
3	16.29	16.44	15.92	16.03	16.21	16.75
4	16.51	16.54	16.94	16.72	16.57	16.93
5	16.63	16.81	17.08	16.81	16.82	17.20
6	16.77	16.90	17.34	17.09	16.92	17.29
7	16.85	16.92	17.44	17.20	17.15	17.38
Approx. Height Sand, mms.	5		4 - 4.5		3	

The sand/syrup ratio was 25 : 1, with 10 ccs. mixing water used.

This test clearly shows the influence of the dish dimensions on the results obtained.

ESTIMATION OF WATER IN GOLDEN SYRUP BY STEAM OVEN DRYING IN GLASS DISHES)- THE EFFECT OF TIME OF HEATING SERIES I.

No.	Time of Heating - Hours 5	10	15	20	Gms. Absorbent	Depth of layer in Dish - mms.
	Per cent water					
1	4.96	9.25	11.56	13.36	20	7
2	15.92	16.69	16.85	18.16	20	6
3	16.35	16.35	17.61	17.66	20	7
4	15.99	16.51	16.33	17.14	15	5
5	16.44	16.49	16.91	17.10	40	12
6	16.70	16.85	17.14	17.26	30	10
7	17.03	17.03	17.05	17.71	14.7	5
8	16.77	17.04	17.28	17.52	36.6	12
9	17.11	16.88	17.27	17.27	9.2	4
10	14.71	14.58	15.01	15.05	14.2	4
11	16.85	17.14	17.93	18.65	3.5	5
12	17.12	17.45	18.08	18.58	4.2	6

(See figure 44.)

SERIES 2 :-

No.	3	Time of Heating - Hours 4	5	6	7	Gms. Absorbent	Depth of Layer in Dish - mms.
		Per Cent Water					
13	16.89	16.89	17.14	17.20	17.18	3.1	5-7
14	16.68	16.90	17.02	17.02	17.13	2.7	"
15	--	16.23	17.01	16.57	16.97	1.8	"
16	--	16.40	16.78	17.17	17.10	3.1	"

SERIES 2 (Continued) :-

No.	Time of Heating - Hours					Gms. Absorbent	Depth of Layer in Dish - mms.
	3	4	5	6	7		
17	16.45	16.97	17.17	17.06	17.17	3.1	5 - 7
18	16.62	16.74	17.16	17.30	17.46	3.3	"
19	--	16.73	17.32	17.32	17.10	2.7	"
20	--	16.42	17.01	17.28	17.08	2.0	"
21	--	16.37	16.86	17.22	17.22	3.3	"
22	--	17.96	18.42	18.35	18.35	2.6	"
23	--	16.47	16.97	17.27	17.27	2.4	"
24	--	16.55	17.01	17.40	17.40	2.3	"
25	--	18.01	19.02	18.69	18.61	21.7	6-7
26	--	16.75	17.07	17.15	17.17	24.0	"
27	--	16.65	17.28	17.26	17.16	19.8	"
28	--	16.61	17.30	17.99	17.41	10.9	"
29	--	16.43	17.78	17.78	17.56	22.1	"
30	--	17.10	18.41	18.05	17.97	17.2	"
31	16.29	16.51	16.63	16.77	16.85	13.5	"
32	16.44	16.54	16.81	16.90	16.92	14.0	"
33	15.92	16.94	17.08	17.34	17.44	14.1	"
34	16.03	16.72	16.81	17.09	17.20	13.6	"
35	16.21	16.57	16.82	16.92	17.15	14.2	"
36	16.75	16.93	17.20	17.29	17.38	14.1	"

Estimation of Water in Golden Syrup in Vacuum Oven using Celite Absorbent in Aluminium Capsules.

Determination of optimum ratio Celite : Syrup.

Vacuum oven at 70°C and 70 cms. vacuum. Aluminium capsules 69 mms. diam. x 20 mms. depth.

Time of Heating Hours	Capsule		% Water			
	1.	2.	3.	4.	5.	6.
1	11.0	10.9	13.3	15.8	15.9	16.2
2	12.6	13.2	16.2	16.3	16.2	16.4
3	13.5	14.3	16.8	16.4	16.2	16.4
4	14.1	15.0	17.1	16.4	16.3	16.5
5	14.3	15.4	17.3	16.6	16.4	16.6
Ratio Syrup to Celite	5:1	4:1	4:1	2:1	1:1	1:2
Multiplier	20	25	100/3	50	100	100
Wt. Syrup (gms.)	5	4	3	2	1	1
Wt. Celite(gms.)	1	1	1	1	1	2
ccs. Water added	3	3	3	3	3	7

In No. 3 there was considerable sticking of syrup to the bottom of the capsule. Nos. 4, 5 and 6 washed clean very easily. The high result in No. 3 is thus probably due to local over-heating of the syrup. From above results it would not seem advisable to exceed a ratio of syrup to celite of 2:1

Estimation of Water in Golden Syrup in Vacuum Oven using Celite Absorbent in Aluminium Capsules.

Determination of optimum ratio Celite : Syrup.

Vacuum Oven at 70°C and 68 cms. vacuum. Aluminium capsules 69 mms. diam. x 20 mms. depth.

Time of Heating Hours	Capsule		% Water			
	1.	2.	3.	4.	5.	6.
1	16.6	16.5	16.6	16.8	16.6	16.6
2	16.8	16.8	16.9	16.9	16.8	16.9
3	16.7	16.7	16.9	16.9	16.8	16.9
4	16.8	16.8	16.9	16.9	16.8	17.0
5	16.8	16.8	16.9	16.9	16.8	17.0
10	16.8	16.8	17.0	17.0	17.0	17.1
Ratio Syrup to Celite	1:1	1:2	2:1	1:1	1:3	1:2
Multiplier	40	40	20	20	40	20
Gms. Syrup	2.5	2.5	5.0	5.0	2.5	5.0
Gms. Celite	2.5	5.0	2.5	5.0	7.5	10.0
ccs. Water added	6	13	6	12	24	26

Atmospheric conditions 69% R.H.: 15°C.: 756 mms. Barometer.

(See figure 41).

Estimation of Water in Golden Syrup in Vacuum Oven using Celite Absorbent in Aluminium Capsules.

Further test on optimum ratio of Celite to Syrup.

Vacuum oven at 70°C and 65-68 cms. First hour's heating at 70°C and 45 cms.

Time of Heating Hours	1.	2.	3.	4.	5.	6.
1	10.7	10.6	-	-	-	-
2	16.8	16.8	16.9	16.7	16.7	16.8
3	16.8	16.8	16.9	16.8	16.8	16.8
4	16.8	16.7	16.9	16.8	16.8	16.9
5	16.7	16.6	16.8	16.7	16.7	16.9

Atmospheric Conditions:- 61% R.H.: 14°C: 758 mms. Barometer.

Ratio Syrup to Celite	1 : 1		1 : 2		1 : 1	
Multiplier	40	40	40	40	20	20
Gms. Syrup	2.5	2.5	2.5	2.5	5.0	5.0
Gms. Celite	2.5	2.5	5.0	5.0	5.0	5.0
cc.s.Water added	6	6	13	13	12	12

Estimation of water in Golden Syrup in Steam-Oven using Celite Absorbent in Aluminium Capsules.

Duplicate of Vacuum-Oven Test, using Steam Oven.

Time of Heating Hours	Capsule			% Water		
	1.	2.	3.	4.	5.	6.
1	15.8	15.8	16.0	16.0		
2	16.3	16.3	16.4	16.4	6.5	
3	16.1	16.1	16.7	16.7	14.7	14.0
4	16.5	16.5	16.9	16.9	14.9	14.7
5	16.6	16.6	16.1	16.2	15.8	15.7
6	15.8	15.6	16.1	16.1	16.4	16.4
7	15.5	15.6	15.9	15.7	16.2	16.2
Ratio Syrup to Celite	1 : 1		1 : 2		1 : 1	
Multiplier	40	40	40	40	20	20
Gms. Syrup	2.5	2.5	2.5	2.5	5.0	5.0
Gms. Celite	2.5	2.5	5.0	5.0	5.0	5.0
ccs. Water Added	6	6	13	13	12	12

Atmospheric Conditions:- 57% R.H.: 12°C: 760 mms. Barometer.

Heating Continuation:

8 Hrs.	-	-	15.9	15.8	-	-
9	15.6	15.5	16.7	16.7	-	-
10	16.4	16.4	16.5	16.5	-	-
11	16.1	16.1	16.3	16.3	-	-

(See figure 40).

Notes on Optimum Celite Ratio Steam-Oven.

On washing out the dishes numbers 5 and 6 were found to have little nodules of syrup on the bottom. Dishes 3 and 4 washed out cleanly but 1 and 2 were coated at the bottom with a thin film of syrup. This would indicate that the ratio of celite to syrup must be over 1:1 i.e. that more celite is required.

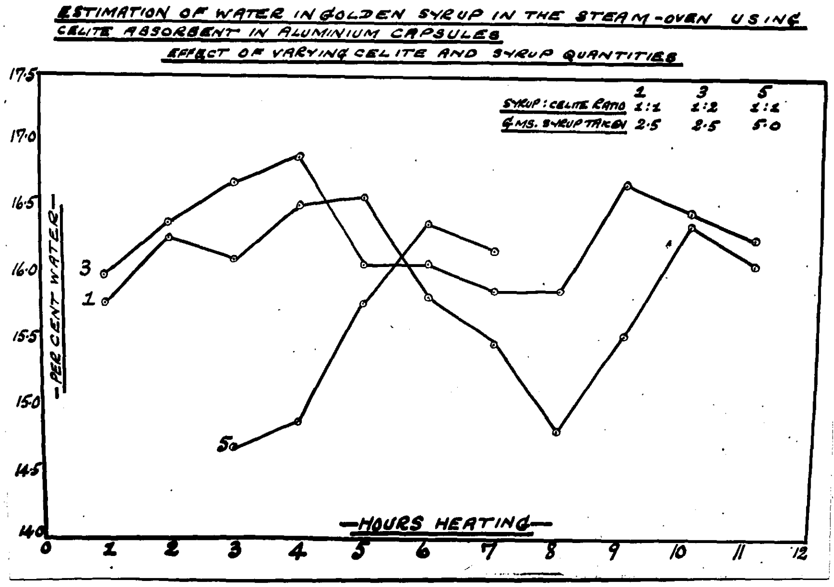


Figure 40.

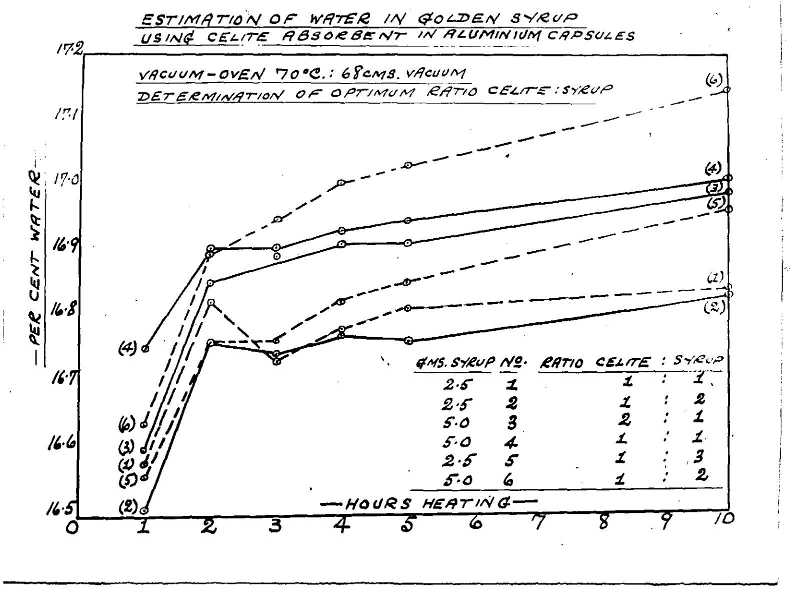


Figure 41.

Estimation of Water in Golden Syrup in Steam-Oven using Celite Absorbent in Aluminium Capsules.

Variation of Syrup - Celite Ratio.

Time of Heating Hours	Capsule			% Water		
	1.	2.	3.	4.	5.	6.
2	15.4	14.8	-	-	-	-
3	15.6	14.9	13.4	-	15.8	15.4
4	14.7	14.2	15.7	15.5	15.6	15.2
5	-	-	-	14.8	-	-
7	16.3	15.7	-	-	-	-
8	-	-	16.3	16.1	16.3	16.0
Ratio Syrup to Celite	1:2	1:3	1:4	1:5	1.25:4	1:2
Multiplier	100	100	100	100	80	100/15
Gms. Syrup	1.0	1.0	1.0	1.0	1.25	1.50
Gms. Celite	2	3	4	5	4	3
ccs. Water added	5	6	10	13	11	7

Atmospheric conditions: 57-60% R.H.: 13-14°C: 752 mms. Barometer.

In this test the samples were weighed out and mixed with the celite at the week end and three days elapsed before they were dried. The close settling and caking of the celite syrup mixture has thus hindered drying and has resulted in very low figures for moisture content.

Estimation of Water in Golden Syrup in Steam Oven using Celite Absorbent in Aluminium Capsules.

Variation of Syrup: Celite Ratio (Repeat of Previous Test.)

Time of Heating Hours	Capsule				% Water	
	1.	2.	3.	4.	5.	6.
2	16.0	15.9	16.1	15.8	15.8	15.5
3	16.4	16.3	16.4	16.2	16.1	15.6
4	15.8	15.7	15.8	15.5	15.7	15.3
5	16.6	16.4	16.7	16.3	16.3	15.7
8	16.3	16.2	16.5	16.2	16.1	15.6

Average of capsules 1 - 5 at 5 hrs. = 16.46%

Ratio Syrup to Celite	1:2	1:3	1:4	1:5	1.25:4	1:2
Multiplier	100	100	100	100	80	100/15
Gms. Syrup	1	1	1	1	1.25	1.5
Gms. Celite	2	3	4	5	4	3
ccs. Water added	5	8	11	13	11	7

Atmospheric conditions:- 65% R.H.: 13°C : 759 mms. Barometer.

Estimation of Water in Golden Syrup using Celite Absorbent in Aluminium Capsules.

Using liquids other than water for mixing sample and celite.

Time of Heating Hours	ACETONE		METHYL ALCOHOL		ETHYL ALCOHOL	
	Steam	Vacuum	Steam	Vacuum	Steam	Vacuum
1	15.5	15.1	19.2	15.4	14.1	13.2
2	15.8	15.4	19.5	15.6	14.5	14.2
3	15.9	14.9	19.6	15.0	14.7	13.2
7	16.5	15.0	20.0	15.4	15.5	14.0
ccs. Solvent added	13		12		12	

Ratio Syrup to Celite	All 1 : 4
Multiplier	All 100
Gms. Syrup	1.0 gms. in each case.
Gms. Celite	4.0 gms. in each case.

Atmospheric conditions:- 63% R.H.: 11.5°C: 749 mms. Barometer.

2nd Series	Time of Heating Hours	ACETONE		METHYL ALCOHOL		ETHYL ALCOHOL	
		Steam	Vacuum	Steam	Vacuum	Steam	Vacuum
New Syrup Sample	2	19.2	19.3	19.6	18.9	19.4	-
	4	19.1	19.2	19.5	18.9	19.3	-
	8	19.3	18.4	19.6	18.2	19.4	-

The general conclusion drawn from these tests was that there is no apparent advantage, in time of drying, to be obtained by the use of solvents such as those above, with B. Pts. below that of water. In general the results are not consistent and show that thorough mixture is not possible with these solvents: in addition danger of loss by spurting is greatly increased.

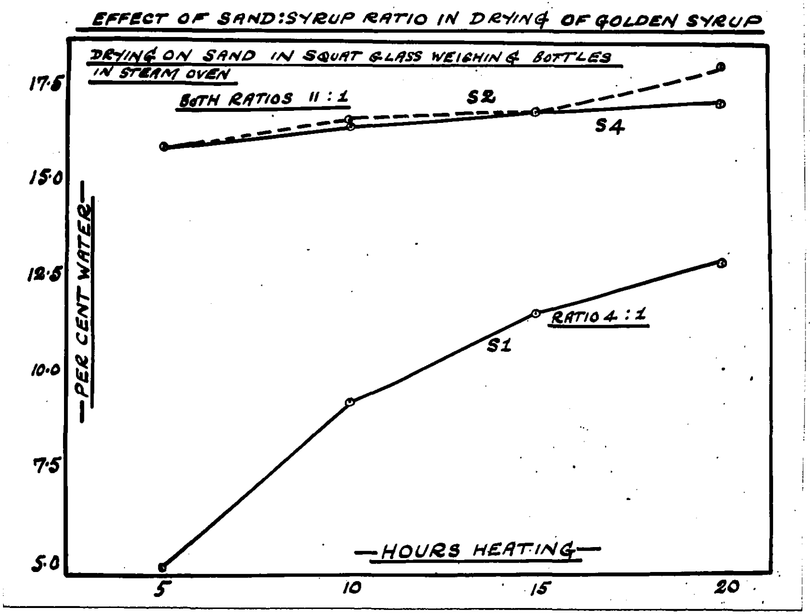


Figure 42.

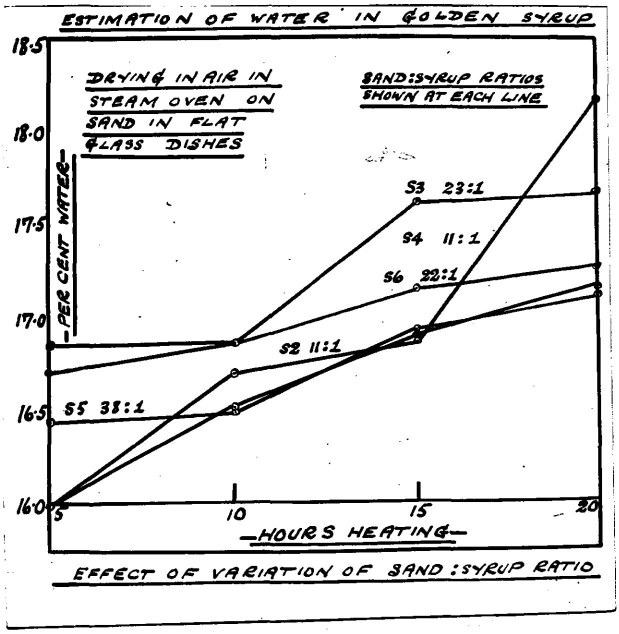


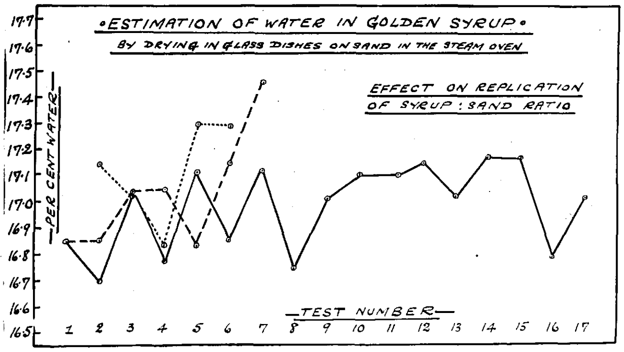
Figure 43.

Estimation of Water in Golden Syrup in Vacuum and Steam Ovens using Aluminium Capsules.

61°C in bath, 70 cms. vacuum. Absorbent 20 gms. sand for each capsule.

Time of Heating Hours	Per Cent Water		
	Steam Oven (1.)	Vacuum Oven (2.)	Vacuum Oven Using 40 gms. Sand (3.)
1	17.7	16.4	15.4
2	17.8	16.7	15.9
3	17.8	17.4	16.6
4	17.9	17.6	16.6
5	17.9	17.6	16.9
6	17.7	17.2 8 hrs.	17.4
6 ccs. water used for mixing in each case.			
Dishes: Diam.	69	102	102
Depth	20	19	19
Wt. Syrup taken	0.76	0.95	1.11

In test (3.) about 1.1 gms. of syrup was placed on 40 gms. of sand as absorbent and mixture was made very thoroughly. This mass of material refused to dry quickly and gave considerable trouble in the desiccator and while weighing due to re-absorption.



Time of Heating

5 Hrs. ————

10 " — — — — —

15 " ....

Figures abstracted from Table on p.

Figure 44.

Estimation of Water in Golden Syrup using Aluminium Capsules in Vacuum Oven

61°C and 70 cms. Dishes 69 mms. diam. x 20 mms. deep.
20 gms. sand as absorbent.

Time of Heating Hours	Per Cent Water				
	No. (1)	(2)	(3)	(4)	(5)
	Dish 2.	3.	4.	5.	6.
1	17.0	17.3	14.5	8.1	14.2
2	17.1	17.5	-	-	-
3	16.8	17.2	-	-	-
4	17.6	18.5	16.6	16.9	16.5
5	-	-	17.2	17.2	17.0
10	-	-	16.4	16.6	16.3
15	-	-	16.6	17.0	16.6
20	-	-	17.3	17.6	17.2
Wt. of Syrup (gms.)	0.65	0.53	0.62	0.64	0.60
Evapn. Rate of Dish (approx.) gms/100 sq.cms./hr.	53	59	62	64	61

There was a tendency for the dishes to lift as air was admitted to the oven; this should therefore be done very slowly.

Discussion :-

The evaporation rate given above is that for water alone from each dish. It is clear that other factors have come in when the syrup was dried, as No. 3 dish gives the quickest rate in the above test. The mixing of the absorbent and sample is probably the important factor in these results apart from the dish itself.

A comparison of the various results found by different methods of estimation is given on the next page.

COMPARISON OF RESULTS BY VARIOUS METHODS FOR THE DETERMINATION OF WATER IN GOLDEN SYRUP.

METHOD		PER CENT WATER	PER CENT SOLIDS
1. Fischer's Titrimetric Method		16.62	83.38
2. Refractometer at 20°C.		17.93	82.07
3. Steam-oven : glass dish, Celite absorbent : 5 hours heating		17.07	82.93
4. Steam-oven : aluminium dish, Celite absorbent : 5 hours heating		17.03	82.97
5. Steam-oven : glass dish, sand absorbent : 5 hours heating		17.35	82.65
	Diam.		
6. Steam-oven : aluminium dish, sand absorbent : 5 hours heating	45 mms.	16.92	83.08
	55 "	16.95	83.05
	72 "	17.01	82.99
7. Vacuum-oven : aluminium dish, Celite absorbent : 5 hours heating, 70°C. 68 cms. vac.		16.89	83.11
8. Vacuum-oven : aluminium dish, sand absorbent : 5 hours heating. 61°C. 71 cms. vac.		17.14	82.86
9. Vacuum-oven : glass dish, sand absorbent : 5 hours heating. 70°C. 70 cms. vac.		17.27	82.73
10. Vacuum-oven : glass dish, Celite absorbent : 5 hours heating. 70°C. 70 cms. vac.		17.18	82.82
11. Desiccator Method	Hours		
(a) with stirring : Celite	2070	16.38	83.62
(b) Circulating Pump : Sand	526	16.03	83.97
(c) Vacuum Desiccation: Sand	520	17.26	82.74
	Hours		
12. Vacuum-oven : glass dish, sand absorbent : 72 cms. vac. 50°C.	3	17.10	82.90
	5	17.05	82.95

THE ESTIMATION OF WATER IN GOLDEN SYRUP BY STEAM-OVEN DRYING

DISCUSSION OF RESULTS :- GENERAL FACTORS

(a) The optimum ratio of absorbing medium to sugar solution

Experiment showed that for sand this ratio must exceed 15 : 1. In the case of celite a ratio above 1 : 1 should be satisfactory; that finally selected was 4 : 1.

(b) The amount of mixing water used

This was found to be important. Very thorough mixing was necessary to get good agreement of duplicates. The amount used should not be so excessive as to lengthen unduly the time of drying. For celite an adequate amount was found to be 2.5 ccs. per gm. of celite, and for sand 1 cc. per 3.0 gms. of sand.

(c) Agreement of duplicates

On the whole, agreement was satisfactory, although occasionally a result appeared which was well outside the usual range.

(d) Dish material

Aluminium dishes were found to have the advantage of rapid heating and cooling, and lack of fragility, this breakage problem being always present when using glass dishes. The rapid heating on the other hand, tends to local decomposition of the sample immediately above the dish bottom.

(e) Optimum time of heating :

This proved to be the most difficult factor of all to assess ; the majority of the results cited show agreement at 5 hours heating for the given conditions, but it is clear that the correct result, (that is, about 17.0 per cent for this oven method on this syrup), is given at a time somewhere between 4 and 6 hours heating, the exact time depending upon such factors as the thickness of the layer in the dish, the amount of water used, the diameter and material of the dishes used, and the actual temperature of the oven on the particular day of the estimation.

(f) Optimum depth of mixture in the drying dish :-

The depth obviously depends on the amounts used, and on the diameter of the dish. The wider the dish the more rapid is the drying with other factors equal. The dish diameter is usually limited by the diameter of the balance pans.

(g) The use of Celite in place of sand :-

More consistent results are obtained with Celite than with sand. The low specific gravity of the Celite may cause error unless precautions are taken to prevent loss by dispersal of the material.

(h) Other factors :-

The oven method requires more time than that necessary for several other methods.

The start of the decomposition period is more easily seen against the nearly white Celite than against the darker sand. Unfortunately part of a sample is often dry while the remainder is still drying ; thus drying is normally quicker at the edges of the dish, and decomposition may commence in these dry portions before the other zones are dry. It is probable that decomposition is very small right up to the completion of drying of a sample.

During certain conditions of the atmosphere it was found difficult to weigh out levulose solution sufficiently quickly to avoid evaporation when using an ordinary Bunge analytical balance. An air-damped Oertling balance was therefore used for most of the work. Using the ordinary balance, rather more than 1 mgm. loss in weight by evaporation was detected on accasion in two minutes of weighing time.

RECOMMENDED OVEN METHOD FOR MOISTURE IN GOLDEN SYRUP :-

The ratio of sand to sugar solution must exceed 15 : 1 : for celite, a ratio of 4 : 1 is satisfactory. Aluminium dishes with close-fitting lids, approximately 70 mms. diameter by 20 mms. deep are suitable: the metal should be about 19 S.W.G. or about 1 mm. thick (0.04 inch). They should preferably have no knob. With celite, up to 5 gms. of syrup can be used in such dishes.

Mixing water should be used in the proportion of 2·5 ccs. per gm. of celite, or 1 cc. per 3 gms. of sand. Very thorough mixing is absolutely essential.

Five hours heating is recommended for either steam or vacuum oven. The vacuum oven should be operated at 70°C. andabout 70 cms. vacuum, with a small air leak. The dishes should be placed in direct contact with the clean metal surface of the oven bottom, and should not be placed on a shelf. If possible each dish should be placed in a separate compartment of the oven. When more than one dish is put in a single compartment, lower results should be expected, and the conditions of heating should be standardised to allow for this.

SECTION 5.

METHODS OF ANALYSIS.

Part 8 :- The determination of Water in Known Solutions of Glucose, Fructose, and Sucrose.

Introduction :

The drying of Levulose Solutions :

The Drying of Glucose Solutions :

The Drying of Sucrose Solutions :

Summary and Conclusions.

The determination of water in glucose, levulose, and sucrose solns.

INTRODUCTION :-

1. Decomposition of levulose and glucose :
2. The work of Matthews and Jackson :
3. Refractometric readings of various sugar solutions :
4. Correction of refractometric solids for reducing sugars :
5. Note on the refractive index of glucose solutions :
6. Examination of kieselguhrs used as absorbents :
7. Technique of the paper roll method for total solids :

THE DRYING OF LEVULOSE SOLUTIONS :-

8. Carr and Sanborn's experiments :
9. Modification of Carr and Sanborn's experiments, using sand, celite, pumice, and paper as absorbents :
10. Shielding experiments - bottom of dish protected from direct heat of vacuum oven bottom :
11. Drying levulose solution at varying pH values : vacuum oven-60°C.
12. Drying levulose solution on sand and celite in the steam oven at approximately 98°C :
13. Drying of levulose solutions - steam and vacuum oven methods contrasted :
14. Drying of levulose solution - control tests wothout buffer solutions in vacuum oven at 70°C. :
15. Drying of levulose solution on paper rolls at varying pH values in vacuum oven at 70°C. :
16. Drying of levulose solution on paper rolls in vacuum oven at 60°C.
17. Drying of levulose solution on sand, celite, and pumice in the vacuum oven at 60°C. :

THE DRYING OF GLUCOSE SOLUTIONS :-

18. Drying of glucose solution in glass and aluminium dishes in the steam oven using celite and sand : contrasted with the drying of sucrose solution under similar conditions :
19. Drying of Glucose solution - control tests in vacuum oven using sand, celite, and paper as absorbents :
20. Drying of glucose solution in the steam oven on paper rolls :
21. Drying of glucose solution in the steam oven on paper rolls at varying pH values :
22. Drying of glucose soln.-vacuum oven on paper rolls with varying pH values at 70°C. :
23. As in No. 22, using celite as absorbent: 70°C. ;

THE DRYING OF SUCROSE SOLUTIONS :-

24. Drying of sucrose soln. -vacuum oven-70°C.-control tests :
25. Drying of sucrose soln.-vac. oven - 70°C.- using paper rolls with varying pH values.

1. The Decomposition of Levulose in solution

Levulose is one of the more reactive sugars, and in aqueous solution is particularly unstable at the extreme ends of the pH scale. Nef has shown that the prolonged action of relatively strong alkali leads to a complete disintegration of the levulose molecule with the possible formation of about 116 products, (Annalen,335,191,1904 : 357,214,1907 : 376,1,1910 : 403,204,1914).

Lobry de Bruyn and van Ekenstein showed that the action of mild alkali leads to the formation of an equilibrium between levulose, dextrose, and mannose, by rearrangement of the common dienol, (Rec. trav. Chim.,14,156,203,1895 : 16,256,1897). This is often referred to as the Lobry de Bruyn rearrangement.

Pictet and Chavan (Helv. Chim. Acta., 9, 809,1926) found that strong acid solutions yielded heterolevulosan as a primary product by dehydration. In the same series of reactions this substance condenses in part to the dimer, diheterolevulosan. More prolonged action of acid solutions results in the formation of levulinic acid,formic acid,oxymethyl furfural, and humus substances of high carbon content von Lippmann,"Die Chemie der Zuckerarten",vol.I.,p.837,1904 (Vieweg und Sohn, Brunswick).

While the inter-conversion of levulose, dextrose, and mannose is a reversible process, true equilibrium is not obtained due to secondary irreversible changes which occur. The transformation can be effected with weak alkalis, with weak bases such as guanidine, and even with neutral sodium phosphate solution. Wolfrom and Lewis (J.A.C.S.,837,1928),found that in saturated calcium hydroxide solu-

solution glucose was converted into a mixture of 63.4 per cent glucose, 30.9 per cent levulose, and 2.4 per cent mannose, together with 3.3 per cent non-sugar substance, probably saccharinic acids.

Stronger alkalis cause more drastic degradation of sugars. Saccharinic acids are formed in the absence of oxidising agents, one part of the sugar molecule being reduced, and another simultaneously oxidised. Twenty-four isomeric acids with six carbon atoms are possible theoretically, and a number of these have been prepared and studied (Kiliani, Ber., 41, 469, 1908 : Nef, Ann., 357, 301, 1907).

Levulose always appears in large quantities in the final molasses in cane sugar manufacture, and this may not all be due to inversion of sucrose, but is often caused by the conversion of dextrose to levulose due to the action of alkalis and salts of alkalis with heat. Likewise under similar conditions levulose may be isomerised and converted into dextrose.

It is clear, therefore, that in sugar solutions containing large amounts of reducing sugars there is considerable scope for decomposition or change, depending upon the pH value of the medium. The work reported in the following pages was an attempt to find the effects of heat and pH value on the decomposition of solutions of glucose, levulose, and sucrose. In figures 45 and 46, the rate of inversion of sucrose is shown (after Sadtler) at 70°C. and 100°C. from pH 4.7 to 7.1 : the two graphs bring out the marked increase in this rate between the temperatures mentioned.

2. THE DECOMPOSITION OF LEVULOSE IN SOLUTION

MATHEWS AND JACKSON : Bureau of Standards Journal of Research, No. 5, p. 619, 1933

These workers investigated the stability of levulose in aqueous solutions of varying pH value. Measurement were made of the initial rate of decomposition of pure levulose over the range of temperatures 4° to 100°C. and from pH 14 to the activity of concentrated HCl on the acid side. The reaction was found to be independent of the concentration of the levulose and of the nature of the buffering solution : the concentration range selected for this work was 2 to 10 per cent levulose. The course of the reaction was followed polarimetrically, and in selected cases with determination of reducing power and of levulose. Velocity constants determined by three independent methods agreed within experimental error.

The primary reaction in alkaline solution is the Lobry de Bruyn rearrangement, and in acid solution is dehydration to hetero-levulosan. The stability of the sugar was found to be maximum at 3.3 pH. Some of the results obtained are appended :-

Time for 1 per cent decomposition of levulose at various pH values.

pH Value	70°C.	100°C.
1	5 hrs. 10 mins.	6.8 mins.
2	47 hrs.	78 "
3	141 "	275 "
4	138 "	280 "
5	56 "	108 "
6	12 "	25 "
7	2 hrs. 6 mins.	4.1 "
8	18.5 "	0.6 "
9	2.7 "	---
10	0.4 "	---

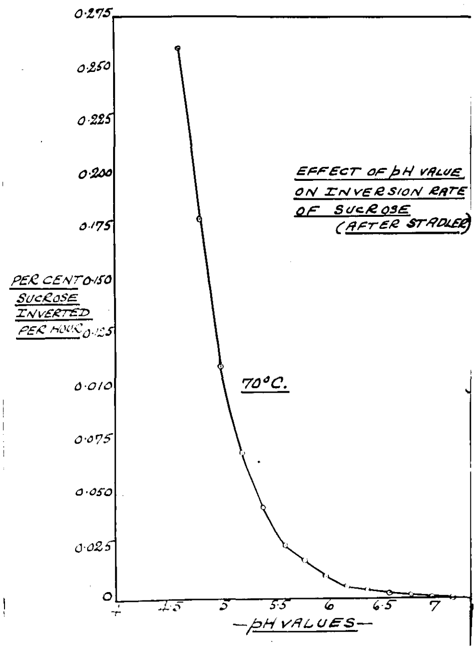


Figure 45.

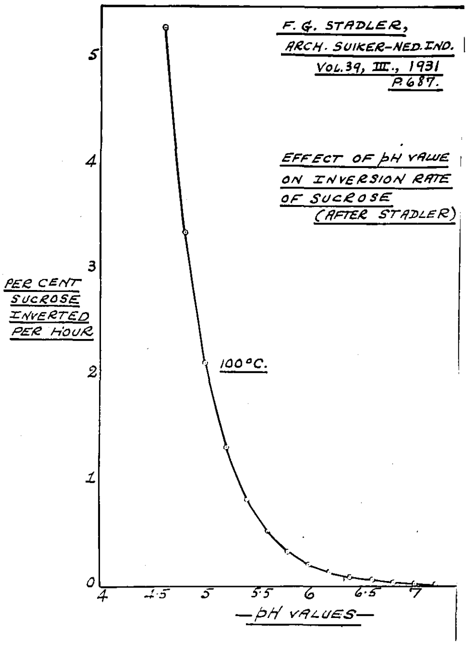


Figure 46.

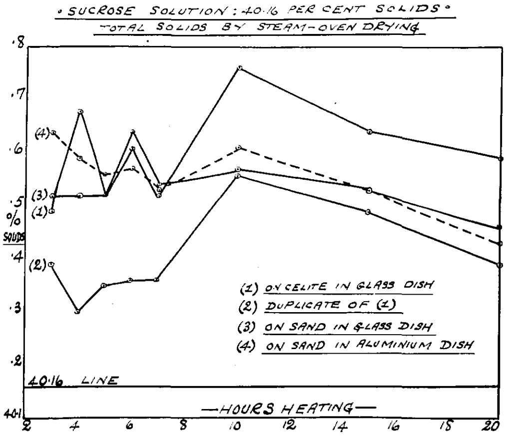


Figure 47.

3. Refractometer Readings of Various Sugar Solutions at 20°C.

No.	Description		% Solids as prepared	Refractometer Reading at 20°C	Refractive Index at 20°C
1	Levulose	1	58.937	57.90	1.4374
2		2	17.029	17.00	1.3592) 4th (place
3		3	17.005	17.00	1.3590) doubtful.
4	Glucose	A	49.96	(40.40)	1.4007
5		B	44.105	43.60	1.4069
6	Sucrose		64.935	64.92	1.4534

From Jackson and Matthews' Levulose table:-

		Prepared Solids	R.I. 20°C	% from J. and M. Table
Levulose	1	58.937	1.4374	59.08
	2	17.029	1.3592)	approx. 17.43%
	3	17.005	1.3590)	

The discrepancy in the lower concentration levulose solutions appears rather large.

The refractometer was checked by the following liquids:-

	R.I. at 20°C
Water	1.3333
Benzene	1.501
Toluene	1.497
Bromo-naphthalene	1.660

4. Correction of Refractometric Total Solids for Reducing Sugars.

De Whalley (I.S.J.,353, 1935) has shown that for materials containing a high percentage of invert sugar a correction should be made of 0.022 for each per cent of invert. This work was done on golden syrup and gave close agreement between refractometer solids corrected for invert and solids obtained by drying in a vacuum oven at 70°C.

When applied to the present work the following results were obtained :- Golden Syrup - refractometric solids at 20°C.

	82.07	
Per cent Reducing Sugars	45.83	
45.83 x 0.022	1.008	
82.07 + 1.008	= 83.08	(True total Solids)

This figure agrees very closely with the results tabulated on page 347.

Levulose :- The results for Levulose solution 1 becomes 57.90 plus 1.27, or 59.17 when corrected. This agrees well with 59.08 obtained from Jackson and Matthews table for Levulose (Browne and Zerban, "Sugar Analysis", p. 1241). The result for the more dilute levulose solutions gives 17.37 in place of 17.43 from the table, but according to the make up of the solutions, neither is correct, and there appears to be some discrepancy in this table at the lower concentrations of levulose.

5. Note on the Refractive Index of Glucose Solutions.

Browne and Zerban "Sugar Analysis", p.103.

Reliable refractive index tables for glucose solutions are not yet available.

Stolle found refractive indices for glucose solutions at 17.5°C. tobe lower than those for sucrose solutions of the same concentrations, but Pulvermacher, working at 25°C., found the reverse, e.g.-

Stolle

	% Sugar	5	15	25
Glucose R.I.	17.5°C.	1.34030	1.35555	1.37169
Sucrose R.I.	17.5°C.	1.34054	1.35594	1.37256

Pulvermacher

	% Sugar	4.36	15.72	24.03
Glucose R.I.	25°C.	1.3401	1.3575	1.3710
Sucrose R.I.	25°C.	1.3388	1.3562	1.3700

This subject requires further investigation, and the work of Stolle and of Pulvermacher on galactose, lactose, maltose, and raffinose also needs revision.

References :-

Stolle - Z. ver deut Zucker Ind., 51, 469, 1901 ;

Pulvermacher - Z. anorg. allgem. Chem., 113, 141, 1920.

6. Examination of Various Samples of Kieselguhr used as Absorbing Media.

Several samples of Johns Manville celite filter aids were examined for moisture, apparent density, and pH value (after boiling under reflux).

			Celite Filter Aids.			
	Analytical Filter-aid	Celite No.501	Hyflo Super-cel.	Lab. Std. Filter-cel.	Std. Super-cel.	Filter-cel.
% Moisture (Loss on 5hrs. heating at 118°C)	1.39	0.22	0.41	0.63	2.44	6.68
pH value after 2 hrs. reflux	4.9	8.3	8.0	6.5	6.5	7.1
Approx. lbs. per cu.ft. (apparent density)	11.6	15.5	18.6	17.7	12.5	15.1

Descriptions

Filter cel:- A natural diatomaceous silica filter aid of the finest pore size.

Standard Super-cel:- A calcined filter aid of approx. twice the flow rate of filter-cel.

Hyflo super-cel:- A chemically calcined pure white filter aid; flow rate approx. twice that of std. super-cel (i.e. with correspondingly greater porosity).

Celite No.501:- Similar to Hyflo super-cel with 40-50% greater flow rate.

Lab.std.filter cel:- Specially prepared for standard laboratory filtration tests to give a uniform rate of filtration.

Celite analytical filter-aid:- Highly purified to give the equivalent of an A.R. chemical for quantitative chemical work.

Analysis of a typical kieselguhr :- Loss on ignition - 0.32 : Silica - 94.42 : Fe_2O_3 - 0.32 : Al_2O_3 - 3.04 : TiO_2 - 0.14 : CaO - 0.40 : MgO - 0.32 : Total Alkalis (as Na_2O)- 0.63 : SO_3 -0.10 : Total - 99.69 per cent.

7. Technique of Paper Roll Method.

1. Preparation of Paper Rolls:-

Postlip English white filter paper sheets were cut into strips 1.75 in. wide and 20 inches long (several sheets can be cut at once). When required for pH experiments the paper was soaked for 10-15 minutes in the appropriate pH solution, and air dried on a string in a neutral atmosphere.

A strip of gauge 43 S.W.G. (approx. 0.004 in. thick), aluminium foil ½ in. wide by 18 inches long and the paper are gauge alumi up together and a paper clip inserted to keep the roll together. The roll is now placed in a clean weighing bottle and heated in the vacuum oven at 70°C for 5-6 hours at 68-70 cms. vacuum.

2. Weighing of Sample:-

Method (a):- The coil is removed from the bottle and the solution weighed into it: 2 ccs. of water are added and the coil replaced. After 5 minutes standing to allow even absorption of the liquid by the coil the bottle is placed in the oven and drying is started.

Method (b):- The coil is kept in the weighing bottle and the sample solution is dropped on to it so that it is all absorbed. The diluting water is added similarly.

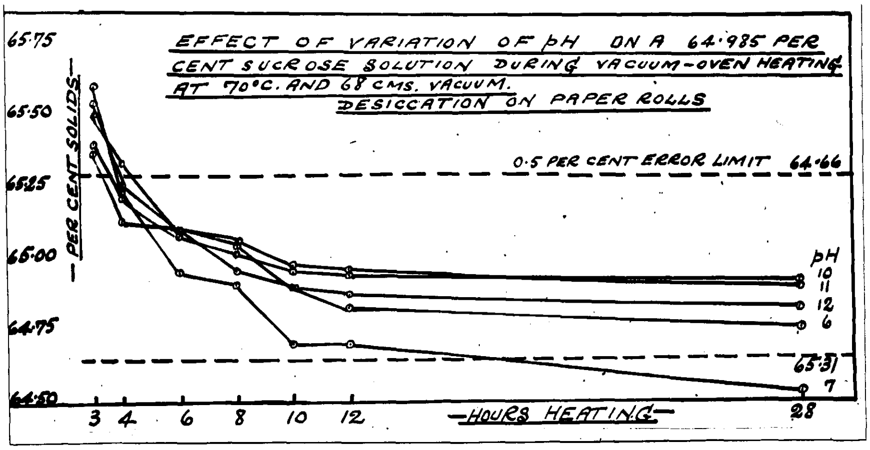


Figure 48.

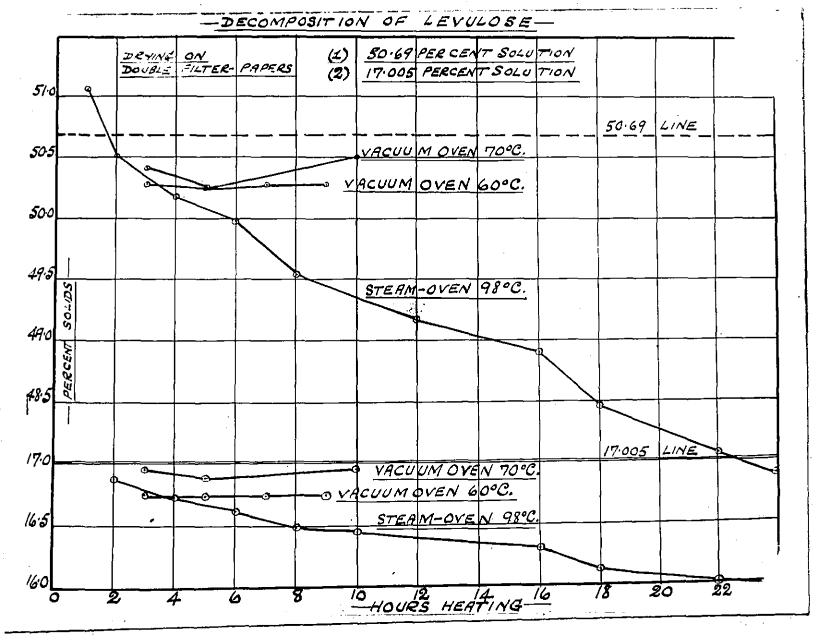


Figure 49.

8.

Repeat of Carr and Sanborn's Experiments with Levulose using a 17.03% Levulose Solution in the vacuum oven at 70°C and 6-8 cms. Pressure.

(See Figure 50).
(Flat glass dishes - celite)

Time of Heating Hours	pH Values and % Solids Found								Carr and Sanborn			
	Blank	2	3	4	5	6	7	8	1	2	3	Mean
4	17.12	16.91	16.79	17.00	17.02	17.04	16.96	16.89	17.12	17.09	17.06	17.09
6	17.08	16.75	16.55	16.81	16.94	16.94	16.87	16.85	-	-	-	-
8	17.08	16.67	16.49	16.81	16.90	16.90	16.83	16.80	17.11	17.09	17.08	17.09
12	17.06	16.56	16.41	16.76	16.66	16.66	16.82	16.80	17.06	17.05	17.06	17.06
17	16.93	15.46	16.19	16.69	16.53	16.53	16.71	16.72	17.09	17.07	17.07	17.08
			Original Solution 17.03%						Original Solution 17.10%			

The experiments recorded at the end of the table under Carr and Sanborn were made by these workers on a solution containing 17.10% levulose, which was dried on pumice stone in flat bottomed dishes at 70°C with 25 inches vacuum. It is seen that constancy in weight was secured after 4 hours, and that no further appreciable loss took place even after 17 hours drying.

It is evident that results with the use of pH buffer solutions are not so satisfactory in the above tests as the results without addition.

Ref. :- Carr and Sanborn, Bull. 47, U.S. Bureau of Chemistry, pp.134-151, 1895

Browne and Zerban, "Sugar Analysis", pp.32-33.

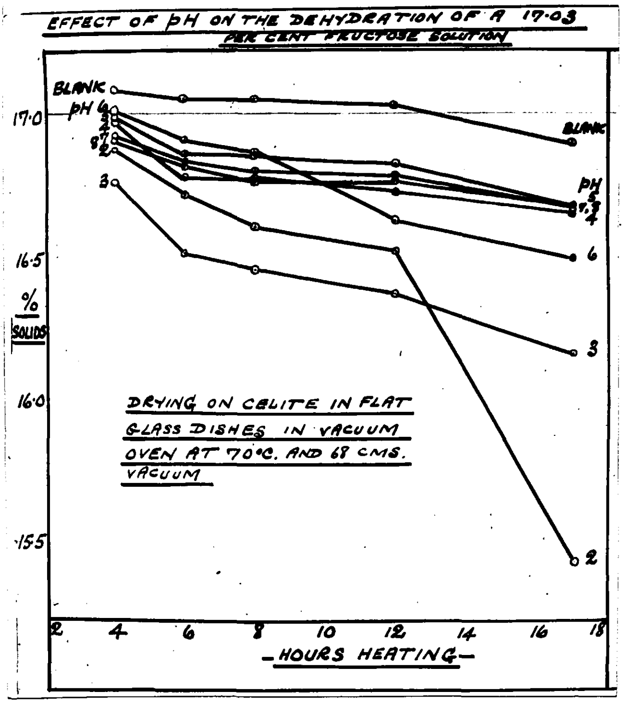


Figure 50.

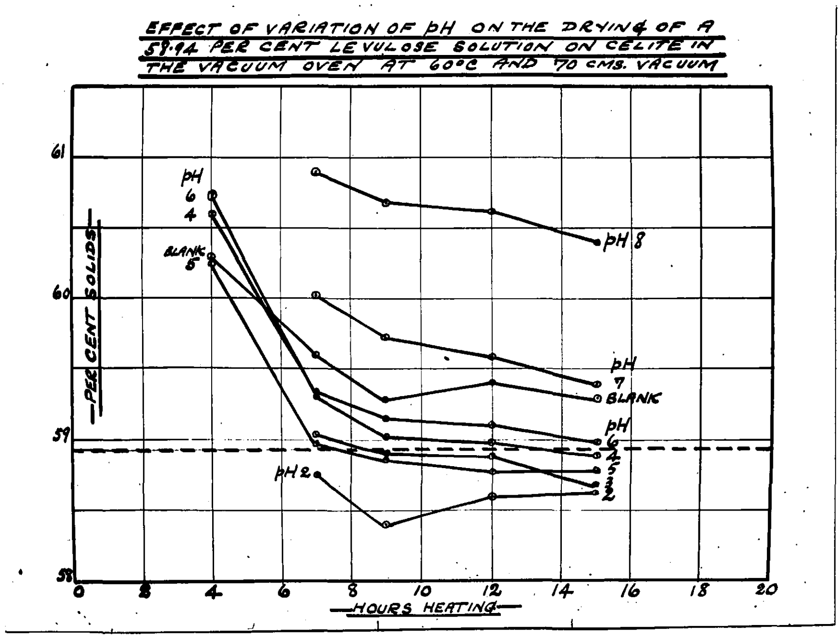


Figure 51.

8. Further Experiments on the Carr and Sanborn Results using 17.03% Levulose Solution.

In the following tests celite, sand, and pumice were used as adsorbing media: approx. 3-3.5 gms. solution was weighed out.

Flat bottomed glass weighing bottles provided with glass rods were used in the vacuum oven at 70°C and 60-65 cms. vacuum.

Mean Results (from triplicate estimations)

Hours of Heating	Celite	30/60 Mesh Sand	8/20 Mesh Pumice
4	16.92	16.98	17.11
6	16.95	16.98	17.06
8	16.92	16.97	17.02
12	16.91	16.96	16.94
17	16.90	16.92	16.90
Gms. Adsorbent used	4	12	12

The 8/20 mesh pumice was prepared by digestion with 2% N_2SO_4 for 24 hours, followed by washing, drying, and ignition. See official method of A.O.A.C. Browne and Zerban, p.28.

9. Carr and Sanborn Shielding Experiment on 17.03% Levulose Solution in Vacuum Oven at 70°C and 65 cms. Vacuum.

In view of the results obtained in the initial repeat of Carr and Sanborn's work with levulose in which the apparent levulose content decreased as time of heating increased, some tests were made in which one sample was placed in direct contact with the oven bottom as usual, while a second sample was shielded from this direct contact by interposing an asbestos mat 2 mms. thick between it and the vacuum oven bottom.

Mean Results (from triplicate estimations)

Hours of Heating	PAPER		CELITE		SAND		PUMICE			
	Glass		Glass		Glass		Glass		Aluminium	
	Shielded	Not Shielded	Shielded	Not Shielded	Shielded	Not Shielded	Shielded	Not Shielded	Shielded	Not Shielded
6	16.47	16.23	17.05	16.99	16.96	17.01	16.98	16.90	17.15	17.01
8	16.48	16.26	17.02	16.97	16.96	16.99	16.93	16.88	17.09	17.01
12	16.44	16.21	16.96	16.92	16.94	16.98	16.91	16.82	17.09	16.98
17	16.42	16.21	16.94	16.89	16.93	16.97	16.88	16.83	17.09	16.88

It is seen that the use of paper gives a result of 16.21 as compared with 16.9-17.1 by the other three adsorbents used. This 16.21 corresponds to levulose with half a molecule of water of crystallisation.

10. Shielding Experiment using paper pulp and Gooch Asbestos - Levulose Solution - 17.01 % Solids

In vacuum oven at 70°C. and 65 cms. vacuum - Aluminium dishes.

Hours Heating	Per cent Solids			
	Paper Pulp		Gooch Asbestos	
	Shielded	Not Shielded	Shielded	Not Shielded
3	16.61	16.58	16.44	16.86
4	16.67	16.52	16.46	16.88
8	16.66	16.63	16.43	16.84

The paper pulp was prepared from Swedish filter paper by maceration with water followed by thorough drying.

11. VARIATION OF pH IN DRYING LEVULOSE SOLUTION

Using 58.9 per cent solution (41.1 per cent water)

On glass dishes in vacuum oven at 60°C. and 68-70 cms. vacuum.

Time of Heating Hours		Per cent water found						on celite.	
	BLANK	pH 2	3	4	5	6	7	8
4	39.7	-	-	39.4	39.8	39.3	-	36.7
7	40.4	41.2	41.0	40.7	41.0	40.6	40.0	39.1
9	40.7	41.6	41.1	41.0	41.1	40.9	40.3	39.3
12	40.6	41.4	41.1	41.0	41.2	40.9	40.4	3914
15	40.3	41.4	41.3	41.1	41.2	41.0	40.6	39.4

See Figure 51.

The results underlined are within reasonable limit from the theoretical percentage of levulose.

12. THE DRYING OF 39.92 per cent levulose solution in the steam oven.

The prepared levulose solution was dried on sand, celite of commercial acid-washed grade, and celite of analytical reagent grade in aluminium dishes, 45 mms. diameter. Temp. c.98°C.

Time of Heating Hours	Per cent ~~water~~ solids found					
	Sand		Commercial Celite		A.R. Celite	
	(1)	(2)	(1)	(2)	(1)	(2)
3	39.55	38.76	38.81	38.76	38.80	36.86
4	39.22	38.49	38.42	38.33	38.45	36.51
5	38.95	38.15	37.91	37.88	38.09	36.10
6	38.73	37.97	37.59	37.53	37.84	35.81
7	38.58	37.35	37.35	37.35	37.64	35.70

Loss per 100 of levulose:-

3	--	-1.29	-1.15	-1.29	-1.18	-6.03
4	-0.13	-1.95	-2.13	-2.35	-2.05	-6.90
5	-0.80	-2.35	-3.40	-3.48	-2.95	-7.93
6	-1.35	-3.25	-4.20	-4.35	-3.58	-8.65
7	-1.73	-3.55	-4.80	-4.80	-4.08	-8.93

The results show that there is better agreement between the duplicates when using commercial celite than when using sand. In all cases there has been considerable loss of solids even after 3 hours heating. The discrepancy between the duplicates for A.R. celite is probably due to the exceedingly light nature of this absorbent.

13.

Decomposition of Levulose.

Steam and vacuum ovens contrasted with weak and concentrated levulose solutions.

Drying on Double Fluted Filter Papers.

Hours Heating	50.69% Solution.		17.005% Solution.	
	Vacuum oven 60°C	Vacuum oven 70°C	Vacuum oven 60°C	Vacuum oven 70°C
3	50.30	50.43	16.76	16.96
5	50.27	50.26	16.74	16.89
7	50.28	-	16.74	-
9	50.28	-	16.74	-
10	-	50.50	-	16.96

Hours Heating	Steam-Oven 98-100°C	
	50.69% Solution	17.005% Solution
1	51.06	20.45
2	50.51	16.88
4	50.19	16.73
6	49.90	16.62
8	49.53	16.48
10	49.37	16.45
12	49.17	16.39
16	48.91	16.32
18	48.47	16.14
22	48.07	16.02
24	47.90	15.97

In this case immediate and progressive decomposition occurred after the material had become dry.

(See Figure 49.)

14. Control Tests on estimation of water in a 58.9% Levulose Solution in the vacuum oven using absorption on Paper Rolls, on Sand, and On Celite at 70°C and 6-8 cms. Pressure.

Time of Heating Hours	Absorbing Agents Untreated. 41.1% Water Present - % Water Found.		
	Sand	Celite	Paper Rolls
3	40.7	40.8	42.5
4	40.8	40.9	42.7
6	40.9	41.0	42.7
8	41.0	41.0	42.8
10	40.8	40.9	42.7
12	40.9	41.0	42.9
28	41.0	41.2	42.9

These results are satisfactory in the sand and celite drying but the paper rolls show a large increase in loss which is too high to be merely experimental error.

Drying of a 58.9% (41.1% water) Levulose Solution on Lab. Std. Filter-Cel with varying pH in vacuum oven at 70°C and 6-8 cms. Pressure.

Time of Heating Hours	% Water Found							
	pH 2	3	4	5	6	7	8	Blank
5	42.0	41.7	41.5	41.3	41.8	40.4	40.6	41.3
11	43.5	43.3	43.0	42.5	42.7	41.6	41.8	42.0
Dish	Glass	Glass	Glass	Glass	Al	Al	Glass	Al

These results were very erratic. The Lab.std. Filter-cel used was rather high in iron - i.e. was apparently not acid-washed.

15.

Estimation of water in a 58.9% Levulose Solution (41.1% water) in the vacuum oven using Paper Rolls impregnated with various pH Buffer Salts. Temperature 70°C at 6-8 cms. Pressure.

Time of Heating Hours.	pH Values											
	1	2	3	4	5	6	7	8	9	10	11	12
3	34.1	-	-	-	41.5	41.3	41.1	41.0	41.4	41.4	41.4	41.5
4	41.6	41.1	41.1	41.1	41.4	41.5	41.3	41.2	41.6	41.7	41.5	41.7
6	42.1	41.5	41.5	41.4	41.5	41.6	41.3	41.3	41.6	41.7	41.5	41.7
8	42.0	41.4	41.4	41.3	41.5	41.5	41.4	41.4	41.6	41.6	41.4	41.7
10	42.3	41.4	41.6	41.4	41.7	41.6	41.5	41.5	41.6	41.7	41.5	41.9
12	42.4	41.6	41.7	41.5	41.7	41.5	41.4	41.4	41.6	41.8	41.5	41.9
28	43.3	42.1	42.5	42.1	41.9	41.8	41.8	41.9	42.0	41.5	41.2	42.3

The general tendency is towards decomposition: in no case have accurate results been obtained throughout the period of heating. The closest results to the known water content are at 7 and 8 pH for 3, 4, and 6 hours heating. Results at 2, 3 and 4 pH for 4 hours heating are good, but deteriorate at once on further heating.

16.

Decomposition of Levulose
Drying on Paper Rolls in Vacuum Oven at 60°C and 65-70 cms. Vacuum: 17.005% Levulose Solution.

Paper rolls 1.75 in. broad by 20 inches long = 35 sq.ins. x 2
= 70 sq.in. surface.

Hours Heating	Paper alone	Paper +Clip	Al Separator no Clip	Al Separator + Clip	Cu Separator no Clip	Zn Separator no Clip
2	16.66	19.34	17.30	18.97	16.74	17.06
4	16.60	16.61	16.64	16.60	16.66	16.65
6	16.58	16.58	16.60	16.57	16.62	16.61
8	16.62	16.60	16.64	16.61	16.68	16.64
12	16.64	16.60	16.63	16.60	16.66	16.63
17	16.64	16.60	16.63	16.60	16.66	16.63

This test demonstrated that the type of separator used and the presence or absence of paper clip or separator did not influence the results obtained.

A test was made under above conditions using 2 Swedish filter papers 11 cms. diameter per dish as adsorbing medium (in tall glass weighing bottles).

Hours Heating	% Solids	
	I	II
4	16.83	16.77
8	16.84	16.97
12	16.84	16.77
16	16.82	16.75
20	16.84	16.74

The two filter papers gave approx. 59 sq. in. surface as compared with 70 sq. in. for the rolls. The filter papers were used without separators.

17. Decomposition of Levulose in vacuum oven at 60°C and 65-70 cms. vacuum: Levulose Solution 17.005%.

Hours Heating	PAPER ROLLS Glass Dishes Duplicate Av.	CELITE Aluminium	CELITE Glass	SAND Aluminium	SAND Glass	PUMICE Aluminium	PUMICE Glass
4	16.36	16.96	16.91	16.90	16.97	17.09	17.00
6	16.36	16.98	16.91	16.92	16.95	17.12	17.01
8	16.37	16.98	16.93	16.88	16.97	17.12	17.03
12	16.34	16.93	16.90	16.88	16.95	17.07	16.97
17	16.30	16.88	16.84	16.81	16.90	16.98	16.90

It was observed that the celite dishes were heated and cooled more quickly than those with sand: pumice being intermediate. This is largely because of varying total mass required for these three adsorbents.

It is clear from above results that paper rolls give low results and pumice the best results. With paper rolls the variation of apparent percentage error is 3.8-4.2, with celite 0.44-0.97, with sand 0.21-0.62 and with pumice 0.03-0.62: over 17 hours heating.

18. Estimation of Water in 40.16% Glucose Solution (of known concentration) 59.8% Water in Steam oven.

Time of Heating Hours	Per cent Water Found. Glass Dishes 1.	2.	3.	Aluminium Dish 1.
3	59.0	60.0	59.7	59.8
4	59.0	59.9	59.6	59.7
5	59.0	59.7	59.7	59.7
6	58.9	59.9	59.7	59.7
7	59.4	59.9	59.7	59.7
10	58.8	59.7	59.7	59.8
15	58.9	59.8	59.7	59.7
20	59.1	60.1	59.9	59.8

Absorbent	
1 & 2-	celite
3-	sand
Al. 1-	sand

The differences are extremely small between 3 hours heating and 20 hours heating. (See Figure 52.)

Estimation of Water in 40.16% Sucrose Solution in Steam Oven.

Time of Heating Hours	Per Cent Water Found. Glass Dishes 1.	2.	3.	Aluminium Dish 1.
3	59.5	59.6	59.5	59.4
4	59.3	59.7	59.5	59.4
5	59.5	59.7	59.5	59.4
6	59.4	59.6	59.4	59.4
7	59.5	59.6	59.5	59.5
10	59.4	59.4	59.2	59.4
15	59.5	59.5	59.4	59.5
20	59.5	59.6	59.4	59.6
	Celite		Sand	

These results are very steady but have in no case reached the 59.8 per cent of water known to be present. (See Figure 47.)

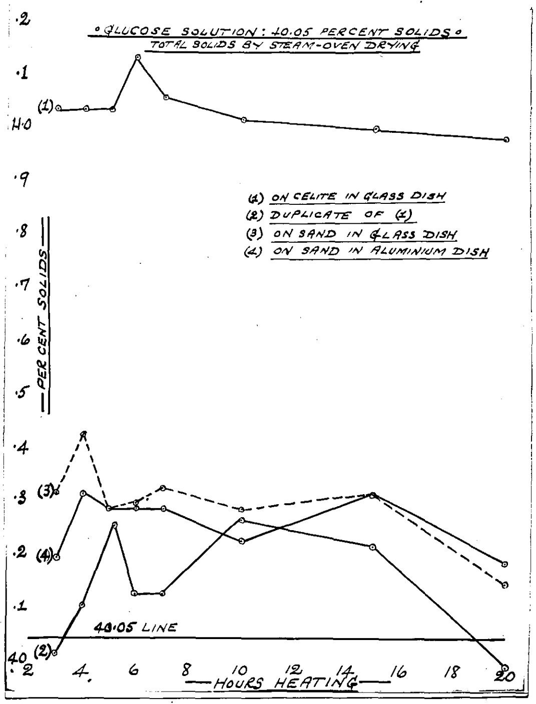


Figure 52.

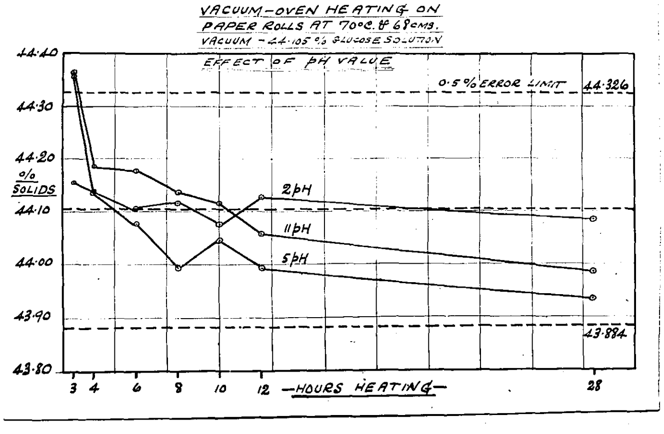


Figure 53.

19. Estimation of Water in a 44.1% Glucose Solution (i.e. 55.9% Water) Control Tests in Vacuum Oven using various absorbents without pH Solutions. 70°C., 65-70cms. vacuum.

Average Results (from duplicates in each case)

Time of Heating Hours	On Sand Aluminium Dishes	On Celite Aluminium Dishes	Paper Narrow Glass Bottles	Paper Wide Glass Bottles
3	55.7	55.9	56.0	56.0
4	55.9	56.0	56.1	56.1
6	56.0	56.2	56.2	56.2
8	56.4	56.1	56.2	56.2
10	56.5	56.1	56.1	56.1
12	55.9	56.1	56.2	56.2
28	55.7	55.9	56.2	56.1

The difficulty with most oven results is here well exemplified - that of knowing WHEN to take the reading as final. There has been uniformity here over 28 hours but the results do not agree with the original solids. The results with paper are low throughout while those using sand and celite descend and then return to the original level e.g. compare results for 3 and 28 hours.

20. Estimation of water in a 49.96 per cent Glucose Solution using Absorption on paper Rolls in Glass dishes in the Steam Oven.

Original water content - 50.04 per cent.

Time of Heating Hours.	Per cent water found 1.	2.
2	5.5	8.5
3	49.8	49.7
4	50.3	50.2
7	50.3	50.2
10	50.4	50.3
12	50.5	50.4
15	50.6	50.5
17	50.7	50.6
21	50.4	50.3
39	50.3	50.2

After 39 hours heating both papers were light cream in colour and light brown at the top edge.

The above results show that glucose is relatively stable to heat at approximately 98°C.

21. Estimation of Water in a 49.96% Glucose Solution using Absorption on Paper Rolls in steam oven in Glass Dishes.

The paper rolls were soaked in selected pH Buffer Solutions and dried.

Time of Heating Hours	% Water Found					
	pH 5.0		pH 6.0		pH 7.0	
	(1)	(2)	(1)	(2)	(1)	(2)
3	50.0	49.3	49.4	49.5	3.8	7.7
4	49.7	49.9	50.3	50.1	40.2	41.4
5	49.8	50.1	50.2	50.1	49.9	49.9
6	49.9	50.1	50.3	50.1	50.1	50.2
7	49.9	50.1	50.3	50.2	50.2	50.3
8	50.0	50.1	50.4	50.2	50.3	50.3
9	50.0	50.3	50.2	50.0	50.3	50.3
14	50.2	50.3	50.2	50.1	50.3	50.4
20	50.4	50.5	50.6	50.3	50.5	50.6
25	50.5	50.6	51.1	50.7	50.8	50.9

It is seen from the above results that there is a time zone during which true results are obtained, this being 5 to 8 hours heating at 5.0 pH and 5 to 6 hours heating at 7 pH.

22. Estimation of water in a 44.1% (55.9% water) Glucose Solution using Absorption on Paper Rolls in Glass Dishes in the Vacuum Oven.

Paper rolls dried after soaking in selected buffer solutions.

Time of Heating Hours	pH Values and % Water Found.											
	1	2	3	4	5	6	7	8	9	10	11	12
3	56.2	55.8	55.5	55.4	55.6	55.9	56.1	56.1	56.8	56.0	55.6	55.8
4	56.4	55.9	55.5	55.4	55.9	56.1	56.2	56.3	57.1	56.3	55.8	56.0
6	56.8	55.9	55.6	55.6	55.9	56.1	56.4	56.3	57.1	56.3	55.8	56.2
8	57.0	55.9	55.6	55.7	56.0	56.2	56.4	56.4	57.2	56.4	55.9	56.3
10	57.1	55.9	55.7	55.7	56.0	56.1	56.4	56.4	57.2	56.4	55.9	56.3
12	57.2	55.9	55.6	55.7	56.0	56.2	56.4	56.4	57.3	56.5	55.9	56.4
28	57.6	55.9	55.7	55.9	56.1	56.2	56.4	56.4	57.3	56.6	56.0	56.6

(See Figures 53, 54, and 55.)

Atmospheric conditions:-

Oven conditions:- 70°C and 68 cms. vacuum.

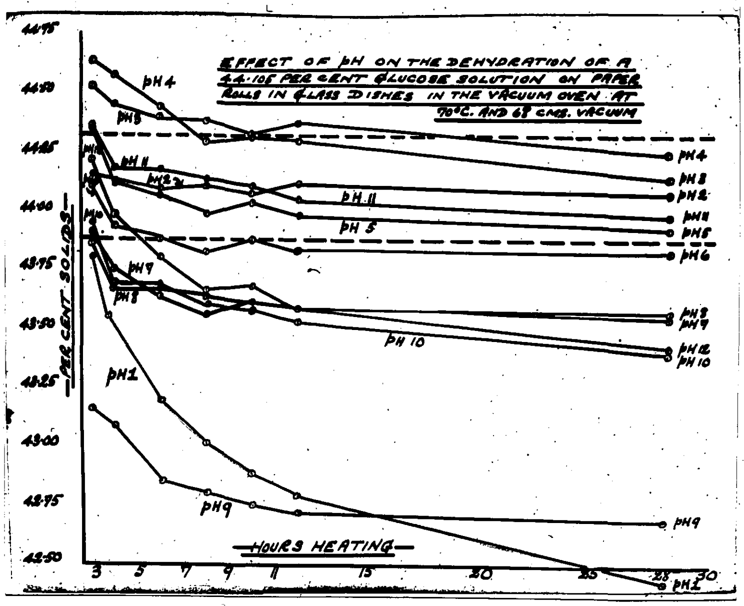


Figure 54.

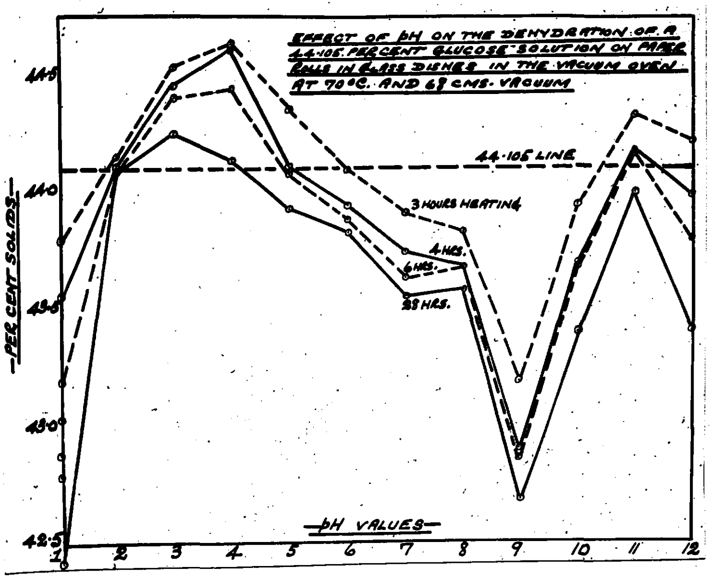


Figure 55.

23. Estimation of Water in a 44.1% (55.9% water) Glucose Solution using Absorption on Celite with addition of pH Buffer Solutions in the Vacuum Oven at 70°C and 68-70 cms. vacuum.

Time of Heating Hours.	pH Values and % Water Found						
	2 pH		5 pH		8 pH	11 pH	
	(1)	(2)	(1)	(2)	(1)	(1)	(2)
3	56.7	57.5	55.5	55.2	55.7	-	-
4	57.0	58.1	55.9	55.6	55.9	55.4	55.0
6	57.1	58.1	56.0	55.8	56.0	55.7	55.2
8	57.2	58.3	56.1	55.9	56.2	55.8	55.4
10	57.0	58.2	56.0	55.8	56.3	55.8	55.4
12	57.0	58.2	56.0	55.8	56.3	55.8	55.4
28	57.0	58.4	56.1	55.9	56.2	56.0	55.6

Mean Results	2 pH	5 pH	8 pH	11 pH
3	57.1	55.4	55.7	-
4	57.6	55.8	55.9	55.2
6	57.6	55.9	56.0	55.5
8	57.8	56.0	56.2	55.6
10	57.6	55.9	56.3	55.6
12	57.6	55.9	56.3	55.6
28	57.7	56.0	56.2	55.8

From above tests the drying at 2 pH appears to be rapid, that at 5 pH and 8 pH of medium speed, and that at 11 pH slow.

24. Control Tests on Estimation of water in a 65% Sucrose Solution (35% water) using absorption on Paper Rolls, on Sand, and on Celite in the vacuum oven at 70°C and 6-8 cms. pressure.

In glass dishes
Absorbing Agents Untreated.

Time of Heating Hours	Per cent Water Sand	Celite	Paper Rolls
3	34.2	35.1	34.7
4	34.7	35.3	34.9
6	34.8	35.1	35.0
8	34.9	35.1	35.0
10	34.9	35.1	35.0
12	34.9	35.1	35.0
28	35.0	35.1	35.0

The results show that sand gives slower drying than celite or paper rolls, either of which gives remarkably constant results for sucrose over as much as 24 hours heating in the vacuum-oven.

Note on Duplication :- Each result reported throughout this work represents the average value of two duplicate tests.

BUFFER SOLUTIONS :- These were made up according to standard formulae with the usual precautions. They were checked by the glass electrode and this check was repeated at intervals. The results after 22 months are here shown :-

KCl/HCl - pH 1.0 read 1.0
" pH 2.0 " 2.0
Na_2HPO_4/citric acid - pH 3.0 read 3.04
" - pH 4.0 " 4.16
" - pH 5.0 " 5.26
KH_2PO_4/Borax - pH 6.0 " 5.91
" - pH 7.0 " 6.805
" - pH 8.0 " 7.805
" - pH 9.0 " 8.81
"

---

25. Estimation of Water in a 65% Sucrose Solution (≡ 35% Water) using absorption on paper rolls in glass weighing bottles in the vacuum - oven at 70°C and 6-8 cms. pressure.

(See Figure 48.)

Time of Heating Hours.	Paper impregnated with various pH Buffer Salts - pH Values.											
	1	2	3	4	5	6	7	8	9	10	11	12
3	34.5	37.0	35.0	35.6	34.1	34.6	34.4	34.7	35.0	34.6	34.5	34.4
4	35.2	37.3	35.4	35.8	34.4	34.9	34.8	35.0	35.3	34.8	34.7	34.7
6	35.8	37.6	35.6	35.9	34.7	34.9	35.0	35.2	35.6	34.9	34.9	34.9
8	36.2	37.9	35.8	36.1	34.8	35.0	35.1	35.3	35.7	35.0	34.9	35.0
10	36.3	37.9	35.8	36.1	35.0	35.1	35.3	35.5	35.7	35.0	35.0	35.1
12	35.6	38.1	35.9	36.1	35.0	35.1	35.3	35.5	35.7	35.0	35.0	35.1
28	37.0	38.3	35.9	36.2	35.2	35.2	35.5	35.7	35.8	35.1	35.1	35.2

Estimation of water in a 65% Sucrose Solution (≡ 35% water) using absorption on Paper Rolls in Glass Weighing Bottles in the vacuun over at 70°C and 6-8 cms. pressure.

Time of Heating Hours.	Paper Impregnated with various pH Buffer Salts - % Water Found.										
	Series 1. pH				Series 2. pH				Series 3 pH		
	6	7	8	9	6	7	8	9	6	7	8
3	34.6	34.4	34.7	35.0	33.9	33.8	33.8	34.4	34.0	33.8	33.6
4	34.9	34.8	35.0	35.3	34.4	34.4	34.3	34.8	34.2	34.2	34.0
6	34.9	35.0	35.2	35.6	34.6	34.6	34.6	34.9	34.3	34.5	34.2
8	34.9	35.1	35.3	35.7	34.8	34.8	34.7	35.0	34.4	34.6	34.3
10	35.1	35.3	35.5	35.7	35.2	35.2	35.2	35.1	34.6	34.7	34.5
12	35.1	35.3	35.5	35.7	-	-	-	-	34.6	34.8	34.6
28	35.2	35.5	35.7	35.8	35.3	35.3	35.2	35.1	35.1	35.1	34.9
	KH_2PO_4 + Borax				NA_2HPO_4 + citric acid			KCl + NaOH	Na_2HPO_4 + citric acid		

It is evident from these results that the sodium phosphate and citric acid buffers are not suitable for this drying process, giving relatively slow drying.

THE DRYING OF LEVULOSE, GLUCOSE, AND SUCROSE SOLUTIONS

SUMMARY AND CONCLUSIONS

LEVULOSE :- 1. Vacuum Oven :-

Levulose solutions can be dried without appreciable loss in the vacuum oven at 70°C. at pH values of 4, 5, or 6 for periods up to 4 hours. Drying at pH values above 7.0 is slower and there appears to be more decomposition of the sugar (Expt. 11). Drying on pumice gave good results : drying on sand and celite gave slightly low results.

For vacuum oven drying, 60°C. is definitely preferable to 70°C., but the optimum time of 4 hours at 70°C. becomes 7-9 hours at 60°C. When drying on paper rolls, there is danger at this lower temperature that water will not be expelled from hydrated forms of the sugars. (e.g. compare results of tests 15 and 17.)

2. Steam Oven :- In all tests made there was considerable loss of solids even after only 3 hours heating at approximately 98°C. (See tests 12 and 13.)

GLUCOSE :- 1. Vacuum Oven :- There was no decomposition apparent after 28 hours heating at 70°C. in the vacuum oven. In tests with regulated pH values, drying at 2, 5, and 11 pH was satisfactory at 70°C., with faster drying in the acid region.

2. Steam Oven :- Results were good : the rate of drying appears to be faster than for levulose. Glucose was relatively stable at 98°C. with an optimum heating period of just over 3 hours.

SUCROSE :- 1. Vacuum Oven :- Drying on celite or paper rolls gave remarkably constant results at 70°C. Sand gave slower drying, reaching the known percentage after 28 hours, compared with 3-6 hours for celite or paper rolls. Drying with buffer solutions gave good results at 5 - 12 pH but not below 5 pH.

2. Steam Oven :- The results obtained were very consistent, but in no instance was the known percentage of water reached (test 18). Sucrose seems to be most reluctant to part with the last trace of water. It is possible that partial inversion occurs, taking up a minute quantity of water and thus increasing the apparent solids.

SECTION 5 .

METHODS OF ANALYSIS.

Part 9 : The Determination of Water in Raw Sugars.

Introduction.

Experimental.

Summary.

INTRODUCTION.

THE DETERMINATION OF WATER IN RAW SUGARS :-

It is well known that moist sugar or sugar products, syrups, and molasses resist drying with great obstinacy. Thus Circular C440 of the U.S. National Bureau of Standards, Washington, 1942, p. 797, states :- "An accurate determination of the moisture in sugar products is frequently a matter of great difficulty, and the proper procedure has not been definitely established."

Sometimes the material is hygroscopic, and at ordinary pressure moisture can only be removed by long heating at high temperature, and it is also known that high temperature exerts a destructive effect on many of the solid sugars. A temperature of 100°C., for example, will cause considerable decomposition of levulose, and will eventually affect such sugars as sucrose and dextrose.

It would therefore appear that the best conditions for drying will be those where low temperature and high vacuum are employed. With liquid products it is usual to mix the sample with dried sand or pumice, which aids drying by exposing a larger surface and preventing the formation of a hard surface crust or film. Asbestos, and rolls of filter-paper have also been used to secure a larger drying area. If levulose is present in other than very small amounts, the drying temperature should not exceed 70°C.

For the determination of moisture in raw sugars Circular C440 recommends the use of polished aluminium dishes of diameter 55 mms. and height 15 mms. with tightly-fitting lids. Approximately 4 gms. of the sugar is dried for 2 hours at a temperature of 100°C., care being taken that the dishes are not in close proximity to the heating elements of the oven. Upon removal from the oven the dish is wiped, covered, placed in a desiccator to cool, and finally weighed.

The methods recommended by the Association of Official Agricultural Chemists for the determination of moisture in sugars are still widely used. The most recent instructions for direct drying specify the drying of 2 - 5 gms. of the prepared sample in a flat dish of nickel, platinum, or aluminium, at the temperature of boiling water for 10 hours, followed by cooling in a desiccator and weighing. A further heating is then given for 1 hour, or a heating until the change in weight after a further period is not more than 2 mgms. For sugars of large grain it is recommended to heat at 105-110°C. to expel the last traces of occluded water.

In vacuum drying, 2 - 5 gms. of the sample is taken in a dish as above, but with a tightly-fitting cover and heated at a temperature not exceeding 70°C. (preferably at 60°C.), under a pressure not exceeding 50 mms. of mercury, for a period of 2 hours. The sample is removed from the oven, covered, cooled in a desiccator, and weighed. Drying is then continued until the change in weight is not more than 2 mgms. between successive weighings at 1 hour intervals. The oven should be 'bled' with a current of dry air during drying to ensure removal of water vapour.

Browne and Zerban ("Sugar Analysis",1941,p.24) state that refined sugars, raw beet sugars, and the superior grades of raw cane sugars can be successfully dehydrated by heating 2 - 5 gms. of the finely powdered sample in a thin layer for 2 - 3 hours in an oven heated by boiling water, and then heating in a special oven for 1 hour at 105 - 110°C. The sample is re-heated at 105-110°C. until successive heatings cause no further loss.

With lower grade sugars it is recommended that the dish be covered during weighing.

Factors investigated in the present work.

Water estimation in raw sugars.

1. Effect of time of heating :- (a) Hourly weighings.
   (b) Continuous heating periods.
2. Effect of weight taken.
3. Effect of dish used :- (a) material : (b) diameter :
   (c) Variation in similar dishes.
4. Study of replication.
5. Effect of oven temperature.
6. Comparison of steam and vacuum ovens.
7. Effect of position in the oven.
8. Effect of atmospheric conditions - temperature, humidity, pressure.
9. The effect of the heating in various ovens on the reducing sugars present.
10. The use of the Spencer oven for raw sugar moisture estimations, with special regard to the high temperature used in this oven.
11. The effect of grain size in the sugar on its moisture content.
12. A study of the rate of evaporation in a steam oven.

ANALYSES OF RAW SUGARS USED IN MOISTURE TESTS.

ORIGIN	BARBADOS	BRITISH WEST INDIES	CUBA		NATAL		SANTO DOMINGO
			I.	II.	I.	II.	
SUCROSE	96.36	96.72	96.25	96.93	98.93	97.90	97.19
REDUCING SUGARS	1.26	1.39	1.49	0.95	0.21	0.57	1.33
ASH	0.54	0.49	0.53	0.56	0.33	0.59	0.41
Water	0.72	0.69	0.73	0.59	0.27	0.52	0.50
OTHER ORGANIC MATTER	1.12	0.71	1.00	0.97	0.73	0.42	0.57
RATIO $\frac{\text{ASH}}{\text{RED. SUGARS}}$	0.43	0.35	0.35	0.59	1.57	1.03	0.31
pH VALUE (Glass Electrode)	5.97	5.85	5.86	5.93	6.05	5.80	6.08

ESTIMATION OF WATER IN RAW SUGARS.

In the experimental section which follows, various raw sugars were tested in the steam oven at 98-99°C., and in the vacuum oven.

The first tests made sought to establish the extent of the variation in moisture content recorded with time, and from sample to 1 sample. Aluminium dishes were used, 45 mms. in diameter, with tight lids.

Experiment (1) :- Five gms. of the raw sugar were weighed into each dish, using six dishes. One dish was weighed each hour for three hours, and then pairs of dishes were weighed after 4, 5, and 6 hours.

Sugar	Time of Heating Hours	Apparent Moisture %	Time of Heating Hours	Replicates	Apparent Moisture %
West	1	0.70	4	0.75	
	2	0.70		0.75	0.75
Indian	3	0.70	5	0.72	
	4	0.73		0.73	0.73
(Weighings	5	0.73	6	0.74	
each hour)	6	0.72		0.72	0.73
Experiment (2) :- No weighings for first two hours					
West	2	0.71		0.76	
	3	0.72	5	0.76	0.76
Indian	4	0.73		0.76	
	5	0.76		0.79	
5 gm. samples	6	0.79	6	0.80	0.79
				0.78	
Experiment (3) :- Weighings each hour					
Cuban					
	1	0.46		0.50	
	2	0.43	4	0.45	0.48
5 gm. samples	3	0.47		0.43	
	4	0.52	5	0.50	0.49
	5	0.51		0.52	
	6	0.52	6	0.52	0.52

Notes on experiments 1 - 3 :- In Experiment (1) the oven door was opened each hour, and cold samples were later returned to the oven : this was a disturbing factor. On the whole the results were remarkably uniform. All samples were in one compartment of the oven.

In Experiment (2) the first test was repeated with no weighings until two hours heating had been given to all the samples : this treatment gave higher results.

Experiment (3) was conducted as in test (1) using a different sugar. Apparent moisture figures here tended to increase as the time of heating was increased : there is a notable discrepancy between the duplicates after 4 hours heating.

Experiment (4) :- The samples were placed in duplicate pairs in separate compartments of the steam oven and were not disturbed until the full time of heating had elapsed.

Sugar	Time of Heating Hours	Apparent Moisture %	Time of Cooling in Desiccator minutes	Mean Apparent Moisture %
West Indian	4	0.744 0.746	20	0.745
	5	0.714 0.728	20	0.721
	6	0.772 0.792	20	0.782

Experiment (5) :- Using 10 gms. sugar and larger aluminium dishes (55 x 14 mms.)

West Indian	4	(5) 0.734 (6) 0.758	20	0.746
	5	(3) 0.743 (4) 0.753	20	0.748
	6	(1) 0.783 (2) 0.764	20	0.774
	8	(5) 0.752 (6) 0.774	20	0.763

Experiment (5) continued :-

Sugar	Time of Heating Hours	Apparent Moisture %	Time of Cooling in Desiccator Minutes	Mean Apparent Moisture %
West Indian	9	(3) 0.752 (4) 0.762	20	0.757
	10	(1) 0.770 (2) 0.790	20	0.780

Experiment (6) :- As in Expt. (4), extending time of heating

Sugar	Time of Heating Hours	Apparent Moisture %	Time of Cooling in Desiccator Minutes	Mean Apparent Moisture %
West Indian	4	(1) 0.738 (2) 0.728 (3) 0.730 (4) 0.732	20	0.732
	6	(5) 0.606 * (6) 0.706	20	0.656
	8	(1) 0.768 (2) 0.764	20	0.766
	9	(3) 0.764 (4) 0.758	20	0.761
	10	(5) 0.634 * (6) 0.730	20	0.682
	12	(1) 0.784 (2) 0.784	20	0.784
	13	(3) 0.782 (4) 0.778	20	0.780
	14	(5) 0.654 * (6) 0.746	20	0.700

The sample marked " * " above had a low result to start with, and this did not improve as the heating continued : it is therefore doubtful if it should be included in the average results.

SUMMARY OF RESULTS FOR PER CENT MOISTURE IN WEST INDIAN SUGAR : EXPERIMENTS 1-6. (OMITTING No. 3).

Time of Heating Hours			Experiment			
	1	2	4	5	6	Mean Result
1	0.70	--	--	--	--	0.70
2	0.73	0.71	--	--	--	0.72
3	0.70	0.72	--	--	--	0.71
4	0.73	0.73	0.75	0.75	0.73	0.74
5	0.73	0.76	0.72	0.75	0.73	0.74
6	0.72	0.79	0.78	0.77	0.71	0.75
8	--	--	--	0.76	0.77	0.77
9	--	--	--	0.76	0.76	0.76
10	--	--	--	0.78	0.73	0.76
12	--	--	--	0.78	--	0.78
13	--	--	--	--	0.78	0.78
14	--	--	--	--	0.75	0.75
						Range 0.70-0.79
Factor Investigated.	Weighings each hour	Weighed after 2 hours	Continuous heating periods	Continuous heating periods	Extended heating	Grand Average:- 0.75
Gms. taken	5	5	5	10	5	
Dish diameter mms.	45	45	45	55	45	

THE EFFECT OF HEATING ON THE REDUCING SUGAR CONTENT OF RAW SUGARS : DETERMINATION OF WATER IN DISHES OF VARYING DIAMETER.

Expt.7 :- The raw sugar used was from San Domingo : tests were made in duplicate in aluminium dishes of various diameters, pairs being placed in separate compartments of a cellular steam oven at 99.5°C. The atmospheric temperature 24.7°C., and thenpressure 766 mms. Ten grams sugar were taken in each dish, the reducing sugars being estimated before and after heating.

Time of Heating Hours	Apparent per cent moisture					
	Duplicates	Mean	Duplicates	Mean	Duplicates	Mean
1	0.50 0.47	0.49	0.48 0.44	0.46	0.46 0.49	0.48
2	0.51 0.50	0.51	0.50 0.46	0.48	0.48 0.50	0.49
3	0.51 0.48	0.50	0.45 0.42	0.44	0.47 0.50	0.49
4	0.56 0.53	0.55	0.50 0.46	0.48	0.51 0.53	0.52

Dish dimensions mms.	Series 2	Series 3	Series 1
Height	20	19	13
Diameter	69	102	45
Bottom surface area : sq.cms.	37.4	81.7	15.9
Depth of sugar in dish : mms.	5	3	8

After the heating period, the sugar in each dish was made up to 1 litre and the reducing sugars estimated.

Series	Dish Diameter mms.	Total Hours Heating	Mean Apparent Moisture %	Reducing Sugars %	Decrease in Reducing Sugars %
1	45	4	0.52	1.32	0.14
2	69	4.5	0.55	1.29	0.17
3	102	4.5	0.48	1.26	0.20

Per cent reducing sugars in original sugar :- 1.46

THE EFFECT ON THE REDUCING SUGAR CONTENT OF RAW SUGARS OF 1 AND 2 HOURS HEATING : SIX REPLICATES IN ALUMINIUM DISHES IN THE STEAM-OVEN.

Experiment 8 :-

In this test the conditions were maintained as in the previous experiment, using six 69 x 20 mms. aluminium dishes, and placing each pair of dishes in a separate compartment of the steam-oven. Reducing-sugars were estimated in the residues.

No.	Gms. Weighed	Apparent Moisture %	Av. Moisture %	Reducing Sugars %	Mean % Reducing Sugars	Decrease in Reducing Sugars %
1	10 1 hr. in oven	0.45	0.47	1.36	1.36	0.10
2	10	0.49		1.35		
3	10	0.47		1.36		
4	10 2 hrs. in oven	0.50	0.53	1.32	1.32	0.14
5	10	0.50		1.33		
6	10	0.59		1.31		

Per cent reducing sugars in original sugar :- 1.46.

THE EFFECT ON THE REDUCING SUGAR CONTENT OF RAW SUGAR OF / 3,4, AND 5 HOURS HEATING IN THE STEAM - OVEN.

Expt. 9:-This test was conducted as in the previous experiment, using six 69 x 20 mms. dishes, and placing each pair of dishes in a separate compartment of the steam-oven. Reducing sugars were estimated in the residues. Ten gms. of sugar were weighed in each dish.

No.	Hours Heating	Apparent % Moisture	Average % Moisture	% Reducing Sugars	Mean % Reducing Sugars	Decrease in % Reducing Sugars
1	3	0.46		1.33		
2		0.46	0.46	1.31	1.32	0.08
3	4	0.49		1.28		
4		0.50	0.50	1.28	1.28	0.12
5	5	0.52		1.28		
6		0.53	0.53	1.26	1.27	0.13

Per cent reducing sugars in original sugar :- 1.40

Experiment 10 :- As in previous test, using aluminium dishes of larger diameter : 10 gms. sugar in dishes 102 mm. diam. x 19 mm. deep each dish placed in a separate compartment of the steam-oven.

No.	Hours Heating	Apparent % Moisture	Average % Moisture	% Reducing Sugars	Mean % Reducing Sugars	Decrease in % Reducing Sugars
1	0·5	0.45		1.40		
2	0·5	0.44	0.45	1.40	1.40	0.02

Per cent reducing sugars in original sugar :- 1.42

LOSS OF REDUCING SUGARS DURING THE ESTIMATION OF WATER IN SAN DOMINGO RAW SUGAR BY STEAM-OVEN DRYING

A SUMMARY OF EXPERIMENTS 7-10.

Aluminium dishes used with 10 gms. sugar.

No.	Hours Heating	Apparent Moisture per cent	Reducing Sugars per cent	Loss of Reducing Sugars	Decrease Reducing Sugars per hour	Dish Diam. mms.	No. of Replicates
1	0.5	0.44	1.40	0.03	--	102	2
2	1	0.47	1.36	0.07	0.07	69	3
3	2	0.53	1.32	0.11	0.04	69	3
4	3	0.46	1.32	0.11	--	69	2
5	4	0.49	1.28	0.15	0.04	69	2
6	5	0.53	1.27	0.16	0.01	69	2
7	4	0.52	1.32	0.11	0.03	45	2
8	4.5	0.54	1.29	0.14	0.03	69	2
9	4.5	0.48	1.26	0.17	0.04	102	2
	Original Sugar		1.43				

The reducing sugars were estimated by Lane and Eynon's method using methylene blue, removing calcium salts as oxalate.

DETERMINATION OF WATER IN CUBAN RAW SUGAR IN A SMALL STEAM-OVEN

Experiment 11 :- In this case a small steam-oven 6.5 inches cube internally was used. The temperature of the water in the jacket was 99.5°C., the room temperature 17°C., and the barometric pressure 751 mms. The internal temperature was taken - on the shelf, 93°C., and on a thermometer suspended over the sample, 92.5°C.

Four replicates were weighed using 2 gms. sugar ; two in aluminium dishes 69 mms. diameter by 20 mms. deep, and two in similar dishes 45 mms. diameter by 12 mms. deep.

Hours Heating	Dishes	Apparent per cent moisture					
		69 mms. diameter			45 mms. diameter		
		1	2	average	1	2	Average
1		0.47	0.45	0.46	0.42	0.53	--
2		0.50	0.50	0.50	0.49	0.54	0.52
3		0.51	0.54	0.53	0.51	0.56	0.54

The dishes to the right hand side of the bath showed greater loss, but there is little difference in the actual drying rate. The dishes were placed on the oven bottom ; not on the shelf.

Experiment 12 :- As in No. 11, using a Natal raw sugar

Room temperature, 17.5°C., Barom. pressure, 752 mms. 2 gms. sugar.

Hours Heating	Dishes	Apparent per cent moisture					
		69 mms. diameter			45 mms. diameter		
		1	2	Average	1	2	Average
2		0.48	0.50	0.49	0.49	0.47	0.48

DETERMINATION OF MOISTURE IN RAW SUGAR USING THE VACUUM OVEN

Experiment 13 :- Cuban raw sugar was used, weighing 5 gms. in triplicate in aluminium capsules of 45 mms. and 69 mms. diameter respectively with a temperature of 70°C. and 68 cms. vacuum.

Series (1) :-

Hours Heating	Apparent moisture per cent Dish diameter 45 mms. 1	2	3	Mean	69 mms. 1	2	3	Mean
1	0.43	0.44	0.42	0.43	0.29	0.38	0.39	0.35
2	0.44	0.45	0.44	0.44	0.34	0.41	0.42	0.39
3	0.45	0.45	0.44	0.45	0.37	0.45	0.44	0.42
4	0.45	0.46	0.45	0.45	0.37	0.44	0.44	0.42
9	0.49	0.49	0.48	0.49	0.45	0.51	0.51	0.49

Series (2) :-

1	0.45	0.46	0.48	0.46	0.47	0.44	0.44	0.45
2	0.50	0.49	0.51	0.50	0.50	0.48	0.46	0.48
3	0.53	0.50	0.52	0.52	0.50	0.47	0.46	0.48
4	0.54	0.51	0.53	0.53	0.52	0.49	0.47	0.49
9	0.57	0.53	0.55	0.55	0.57	0.52	0.51	0.53

In series (2) the oven was taken to 75°C., inadvertently, for about 20 minutes while the samples were in. It was cooled then to 66°C. re-heated to 70°C., and the samples replaced. This mishap is reflected in the higher average figures obtained in this series for the apparent moisture content.

DETERMINATION OF MOISTURE IN RAW SUGARS IN THE VACUUM OVEN

THE EFFECT OF DISH SIZE AND MATERIAL.

Experiment 14 :- Tests were made using various dishes of glass, nickel, and aluminium. Five gms. of Cuban raw sugar were weighed in each case : the oven was maintained at 70°C. and 68 cms. vacuum.

Hours Heating	Glass Weighing Bottles			Watch Glasses			Nickel Dishes			Aluminium Basin
	(1)	(2)	Mean	(1)	(2)	Mean	(1)	(2)	Mean	
1	0.51	0.48	0.50	0.31	0.36	0.34	0.46	0.48	0.47	0.43
2	0.53	0.49	0.51	0.35	0.36	0.36	0.47	0.50	0.49	0.50
3	0.54	0.49	0.52	0.35	0.36	0.36	0.49	0.51	0.50	0.50
4	0.56	0.51	0.54	0.34	0.39	0.37	0.57	0.53	0.55	0.52
9	0.55	0.51	0.54	0.37	0.35	0.36	0.58	0.53	0.56	0.52

Flat Aluminium Dishes :- Diameter shown in mms.

Hours Heating	45 mms. diameter				69 mms. diameter				102 mms. Diameter		
	1.	2.	3.	Mean	1.	2.	3.	Mean	1.	2.	Mean
1	0.43	0.46	0.48	0.46	0.35	0.45	0.39	0.40	0.39	0.40	0.40
2	0.44	0.50	0.50	0.48	0.39	0.48	0.43	0.43	0.41	0.44	0.43
3	0.45	0.52	0.51	0.49	0.42	0.48	0.43	0.44	0.46	0.47	0.47
4	0.45	0.53	0.50	0.49	0.42	0.49	0.42	0.44	0.40	0.41	0.41
9	0.49	0.55	0.53	0.49	0.49	0.53	0.45	0.49	0.46	0.46	0.47

DETERMINATION OF MOISTURE IN RAW SUGARS IN THE VACUUM OVEN

THE EFFECT OF OVEN TEMPERATURE.

Five gms. of Cuban raw sugar (new sample) in aluminium dishes 69 mms. diameter. Six replicates in each test.

Experiment 15 :-

Hours Heating	Oven Temperature 40°C.						Oven Temperature 50°C.					
	1	2	3	4	5	6	1	2	3	4	5	6
1	0.39	0.41	0.43	0.43	0.41	0.45	0.38	0.38	0.41	0.42	0.34	0.29
2	0.44	0.46	0.47	0.46	0.44	0.49	0.44	0.44	0.47	0.46	0.39	0.33
3	0.40	0.43	0.45	0.44	0.43	0.47	0.43	0.43	0.47	0.47	0.39	0.34
4	0.48	0.49	0.50	0.49	0.47	0.52	0.44	0.44	0.47	0.49	0.40	0.33
9	0.48	0.49	0.50	0.50	0.48	0.52	0.54	0.52	0.53	0.54	0.44	0.33

	Oven Temperature 60°C.						Oven Temperature 70°C.					
	1	2	3	4	5	6	1	2	3	4	5	6
1	0.50	0.45	0.49	0.38	0.52	0.50	0.43	0.48	0.37	0.41	0.46	0.48
2	0.47	0.45	0.48	0.36	0.52	0.50	0.50	0.53	0.42	0.46	0.50	0.53
3	0.50	0.48	0.53	0.39	0.54	0.52	0.53	0.57	0.59	0.48	0.52	0.53
4	0.50	0.49	0.52	0.40	0.54	0.53	0.49	0.52	0.55	0.44	0.49	0.52
9	0.50	0.49	0.53	0.38	0.54	0.52	0.57	0.61	0.63	0.52	0.55	0.58

Experiment 15 (continued) :-

Mean Results for the effect of oven temperature in the vacuum oven determination of moisture in Cuban raw sugar :-

Hours Heating	Oven Temperature			
	40°C.	50°C.	60°C.	70°C.
1	0.42	0.37	0.47	0.44
2	0.46	0.42	0.46	0.49
3	0.44	0.42	0.49	0.54
4	0.49	0.43	0.46	0.50
9	0.50	0.48	0.49	0.58

Total Range :- 0.37 - 0.58

Atmospheric Conditions during the above tests :-

Test	Room Temperature Dry Bulb °C.	% Relative Humidity	Barometric Pressure mms.
40°C.	15.5	74	769
50°C.	16	81	743
60°C.	17	62	750
70°C.	19	69	765

THE EFFECT OF THE POSITION OF THE SAMPLE IN THE VACUUM OVEN ON THE APPARENT MOISTURE CONTENT OF RAW SUGAR.

Experiment 16 :- Six replicates were placed in standard positions in the vacuum oven at 70°C. and 68 cms. vacuum, using 5 gms. of Cuban raw sugar in each aluminium capsule.

These tests extended over 5 days with the oven and atmospheric conditions noted below.

Hours Heating	Mean apparent per cent moisture.						
	1	2	3	4	5	6	Average
1	0.50	0.48	0.43	0.48	0.47	0.48	0.47
2	0.54	0.53	0.49	0.51	0.50	0.51	0.51
3	0.54	0.53	0.52	0.52	0.50	0.51	0.52
4	0.54	0.52	0.52	0.53	0.51	0.52	0.52
9	0.60	0.56	0.55	0.55	0.53	0.54	0.56
Average	0.54	0.52	0.50	0.52	0.50	0.51	

Range of mean results :- 0.43 - 0.60

Atmospheric and oven conditions :-

Day	Atmos. Temp. °C. Dry Bulb	Wet Bulb	% Rel Humid -ity	Barom. Press. mms. Hg	Oven Jacket Temp. °C.	Temp. Inside oven °C.	Vacuum mms. Hg.
1	18,0	14.5	68.5	765	70	69	680
2	19.5	16.5	74.2	759.5	70	69	680
3	19.0	16.5	76.0	763.7	70	69	680
4	19.5	17.0	82.0	769.3	70	69	680
5	20.0	17.0	82.5	765.0	70	69	680

Experiment 16 (continued) :-

RANGES OF RESULTS.

Hour	Test 1		Test 2		Test 3		Test 4		Test 5	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
1	0.37	0.49	0.43	0.51	0.43	0.50	0.47	0.55	0.49	0.54
2	0.42	0.53	0.47	0.57	0.49	0.58	0.48	0.55	0.50	0.55
3	0.48	0.59	0.45	0.55	0.47	0.56	0.50	0.55	0.50	0.56
4	0.44	0.55	0.47	0.57	0.47	0.53	0.51	0.57	0.53	0.62
9	0.52	0.63	0.49	0.61	0.49	0.62	0.47	0.53	0.55	0.65

Extremes :- 0.37 (1st. Hour) to 0.65 (9th. Hour).

Probable Mean Value :- 0.52 (see previous table).

Experiment 17 :- Estimation of Moisture in Cuban raw sugar in the Vacuum oven with Continuous Periods of Heating.

The oven was at 70°C. and 68 cms. vacuum : 5 gms. of sugar weighed in each of six aluminium capsules, 69 mms. diameter

Hours Heating	REPLICATES						Average
	1	2	3	4	5	6	
2	0.52	0.61	0.61	0.55	0.58	0.62	0.58
3	0.58	0.61	0.59	0.57	0.59	0.54	0.58
4	0.50	0.54	0.56	0.50	0.56	0.58	0.54
5	0.55	0.56	0.60	0.56	0.58	0.59	0.57

The average results obtained in this test are rather similar to those obtained in Experiment 16. In general the vacuum oven appears to give slightly lower results than the steam oven.

DETERMINATION OF APPARENT MOISTURE CONTENT OF RAW SUGARS

THE VARIATION IN INDIVIDUAL CAPSULES.

Experiment 17 :- Aluminium Capsules 69 mms. diameter were used, weighing 5 gm. samples of a Cuban raw sugar in each of six dishes. The vacuum oven was maintained at 70°C. and 68 cms.vacuum.

Hours Heating			Capsule Number				
	1	2	3	4	5	6	Average
1	0.46	0.49	0.48	0.47	0.47	0.49	0.48
2	0.49	0.52	0.52	0.51	0.51	0.53	0.51
3	0.50	0.53	0.55	0.50	0.51	0.53	0.52
4	0.49	0.53	0.55	0.50	0.52	0.53	0.52
9	0.53	0.55	0.58	0.54	0.55	0.55	0.55

(Per cent apparent moisture)

Mean Results for five series of tests:- six replicates in each:-

Series	Hours Heating and per cent apparent moisture				
	1	2	3	4	9
1	0.44	0.49	0.54	0.50	0.58
2	0.46	0.51	0.49	0.52	0.54
3	0.46	0.52	0.51	0.48	0.56
4	0.51	0.52	0.53	0.54	0.50
5	0.52	0.53	0.53	0.56	0.57
Average	0.48	0.51	0.52	0.52	0.55
Range	0.44-0.52	0.49-0.53	0.49-0.54	0.48-0.56	0.50-0.58
Total Range	0.44 - 0.58				

With 5 weighings for each replicate, this gave a total of 150 results

DETERMINATION OF MOISTURE IN RAW CUBAN SUGAR IN THE STEAM OVEN AT 99.5°C. IN ALUMINIUM CAPSULES.

Experiment 18 :- Six 5 gm. portions of the sugar weighed in 45 mms. diameter aluminium capsules : all samples in one compartment of the oven.

Hours Heating	SERIES 1 1	2	REPLICATES 3	4	5	6	Average
1	0.59	0.61	0.64	0.65	0.69	0.60	0.63
2	0.64	0.65	0.68	0.70	0.73	0.62	0.67
3	0.61	0.63	0.66	0.67	0.71	0.62	0.65
4	0.62	0.64	0.68	0.69	0.72	0.64	0.67
9	0.63	0.66	0.69	0.70	0.74	0.65	0.68
	SERIES 2 :-						
1	0.61	0.64	0.60	0.63	0.63	0.62	0.62
2	0.63	0.67	0.63	0.65	0.65	0.64	0.65
3	0.67	0.71	0.66	0.68	0.68	0.67	0.68
4	0.69	0.73	0.69	0.71	0.71	0.69	0.70
9	0.71	0.75	0.70	0.72	0.72	0.71	0.72

Joint average for Series 1 and Series 2 (Steam-Oven) :-

1	0.63
2	0.66
3	0.67
4	0.69
9	0.70

The probable Mean value is 0.67 : this compares with a Mean value of 0.52 for the vacuum oven.

THE DETERMINATION OF MOISTURE IN CUBAN RAW SUGAR IN THE VACUUM OVEN USING 10 GM. SAMPLES

Experiment 19 :- The oven was maintained at 70°C., and 68 cms. vacuum. Six replicates were weighed in aluminium capsules 69 mms. in diameter.

Hours Heating	REPLICATES						
	1	2	3	4	5	6	Average
1	0.55	0.55	0.50	0.48	0.52	0.47	0.51
2	0.55	0.54	0.51	0.48	0.52	0.48	0.51
3	0.58	0.58	0.54	0.50	0.55	0.51	0.54
4	0.58	0.58	0.54	0.51	0.56	0.51	0.55
9	0.58	0.58	0.55	0.51	0.57	0.52	0.55

COMPARISON OF AVERAGE RESULTS FOR 5 AND 10 GMS. SAMPLES IN THE VACUUM OVEN, AND 5 GMS. SAMPLES IN THE STEAM OVEN .

Hours Heating	Vacuum Oven 5 gms. Samples					Average* of 5 Tests (5 gms.)	Steam Oven 5 Gms.
	40°C.	50°C.	60°C.	70°C.	10 gms. Samples		
1	0.42	0.37	0.47	0.44	0.51	0.48	0.63
2	0.46	0.42	0.46	0.49	0.51	0.51	0.66
3	0.44	0.42	0.49	0.54	0.54	0.52	0.67
4	0.49	0.43	0.46	0.50	0.55	0.52	0.69
9	0.50	0.48	0.49	0.58	0.55	0.55	0.70

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* This average includes the results for 5 gms. sugar with continuous periods of heating (Experiment 17).

REPLICATE DETERMINATIONS OF MOISTURE IN CUBAN RAW SUGAR IN THE STEAM OVEN USING 5 GMS. IN DUPLICATE AND 2 HOURS HEATING PERIOD.

Experiment 20 :- The dishes used were aluminium capsules 45 mms. in diameter : They were placed always in the same relative positions in the middle bottom compartment of a cellular steam oven for 2 hours Each replicate test was made on a different day or at a different time on the same day.

Test No.	Per cent moisture 1	2	Average	% Rel. Humidity	Atmospheric Temp. °C.	Barometric Pressure mms. Hg	Replicates on one Day for Comparison 2 Hours Heating	
1	0.67	0.62	0.65	76	20	750	0.64	
2	0.60	0.61	0.61	82	17	762	0.65	
3	0.60	0.61	0.61	80	18	754	0.68	
4	0.56	0.61	0.59	77	17	756	0.70	**Series**
5	0.62	0.59	0.61	77	17	756	0.73	
6	0.65	0.65	0.65	71	18	751	0.62	(1)
7	0.53	0.57	0.55	80	16	743	Av. 0.67	
8	0.60	0.59	0.60	80	16	743	0.63	
9	0.62	0.61	0.62	74	16	756	0.67	
10	0.67	0.66	0.67	74	16	756	0.63	**Series**
11	0.58	0.59	0.59	71	15	766	0.65	
12	0.58	0.65	0.62	65	16	771	0.65	(2)
13	0.62	0.61	0.62	65	16	771	0.64	
14	0.62	0.62	0.62	71	14	773	Av. 0.65	
15	0.56	0.57	0.57	67	15	775	0.52	
16	0.63	0.63	0.63	82	16	759	0.61	**Series**
17	0.60	0.59	0.60	60	17	760	0.61	
18	0.64	0.61	0.63	60	15	764	0.55	(3)
19	0.60	0.62	0.61	74	16	758	0.58	
							0.62	
							Av. 0.58	

RANGE :- Min. 0.53 Max. 0.67 Humidity Variation. 60 - 82 %

Temperature Variation :- 14 - 20°C. **Barom. Pressure Variation** 743 - 775

Note :- Series (1) and (2) above were not in continuous heating periods : Series (3) was in continuous periods of 2 hours.

DETERMINATION OF MOISTURE IN CUBAN RAW SUGAR.

VARIATION OF :- (a) Weight Taken : (b) Type of Dish used :
(c) Temperature : (d) Type of Oven used .

No.	METHOD	TEMP. °C.	GMS. TAKEN	DISH	PER CENT LOSS 2	3	4 hours
1.	Electric Oven	65	10	Aluminium, 69 mms.diam.	0.39	0.40	0.42
2.	"	65	5	" " "	0.38	0.40	0.41
3.	Steam Oven	98	10	" " "	0.41	0.43	0.46
4.	"	98	5	" " "	0.40	0.45	0.47
5.	Vacuum Oven	70	10	" " "	0.28	0.32	0.34
6.	"	70	5	" " "	0.30	0.35	0.36

No.	METHOD	TEMP. °C.	GMS. TAKEN	Dish	Per Cent Loss 4 Hours.
7.	Steam Oven	98	5	Watch-glass	0.37
8.	"	98	10	Al.69mms.diam. (Sugar ground)	0.37
9.	"	98	20	Large Nickel Dish	0.44
10.	"	98	10	Aluminium Basin	0.43
11.	Vacuum Oven	70	10	Al.69 mms. diam.) Sugar ground	0.32
12.	"	70	10	" " ")	0.34
13.	"	70	5	Watch-glass	0.34
14.	"	70	20	Large Al. Dish, 105 mms. Diameter.	0.35

SUMMARY OF CONCLUSIONS ON THE OVEN METHOD FOR THE ESTIMATION OF WATER IN RAW SUGARS.

Effect of Time of Heating :- Weighing at intervals of one hour gives lower results than weighing only after a continuous period exceeding 2 hours.

There is an overall tendency towards higher apparent loss as the time of heating is increased.

The vacuum oven gives uniformly lower loss figures than the steam oven, but there is virtually the same order of increasing loss with increasing time.

Effect of the weight taken :- The error due to multiplication may become important. Thus 2 gms. taken means multiplication by 50 ; 5 gms, by 20 , and 10 gms. by 10. It is not often practicable to use more than say 20 gms. of the sugar per estimation.

It is clear that too small a weight should be avoided, and for practical convenience and rapidity a weight of not less than 5 gms, nor more than 20 gms. would seem to be desirable for this method.

Effect of dish material :- Glass dishes appear to give somewhat higher results than aluminium capsules. Nickel dishes gave the same results as glass dishes in these tests. The 'dished' aluminium basin with only a small area in contact with the oven bottom gave a result intermediate between nickel and glass. The convex surface of a watch glass similarly prevents sufficient transfer of heat to give evaporation of the water in a reasonable time.

Effect of Dish Diameter :- Using aluminium dishes, the smaller diameter dishes tend to give higher results than those of larger diameter

Variation of results with similar dishes :- With a set of six dishes of identical dimensions it was found that there was little difference in the results given by any one dish, or between the results given by the six dishes. The actual position in the oven seemed to be a much more significant factor.

Study of Replication :- A general conclusion from this part of the work is that the apparent moisture percentage obtained is largely conditioned by the time of heating. The range in one test was from 0.37 per cent in the first hour to 0.65 per cent in the ninth hour, with a probable mean value of 0.52 per cent moisture after 150 separate weighings. Contributing factors which disturb exact replication include the temperature of the oven, the position of the sample in the oven, the type of dish used, the atmospheric conditions during the test, and the type of oven used.

Effect of Oven Temperature):- Temperatures of 40°, 50°, 60°, and 70°C. were used in the vacuum oven, and did not appear to influence the results appreciably. In the ordinary oven, with a higher range of temperature, this factor was much more important, and a departure of a few degrees from 100°C. had considerable effect on the moisture content found.

Contrast of the steam oven with the vacuum oven :- A Cuban raw sugar gave an apparent water content of 0.67 per cent at 98°C. compared with 0.52 per cent water in the vacuum oven at 70°C.

Effect of position in the oven :- This was of definite importance. Variations were recorded between dishes placed on the oven bottom, the oven shelf, and in positions close to the oven walls.

Effect of atmospheric conditions :- It seems probable that the Atmospheric conditions of pressure, temperature, and humidity were at least partly responsible for many of the variations found in the day by day replication of raw sugar moisture in the same sample. This effect has often been used as an argument against the use of the oven method.

Effect of Heating on the reducing sugars :- The results found show a decrease in the reducing sugar content on heating raw sugars in the steam oven, even after only 30 minutes heating.

It is possible that three actions are proceeding simultaneously during this heating, viz :- Inversion of sucrose ; increase in weight by oxidation ; and decrease in weight by actual decomposition of reducing sugars.

SECTION 5.

METHODS OF ANALYSIS.

PART 10 : Determination of Water in the Spencer Oven.

Introduction - The Spencer Oven :
The Drying of a known Levulose Solution :
Application to Raw Sugars :
Effect on the Reducing Sugars in Raw Sugars.

DETERMINATION OF WATER USING THE SPENCER OVEN.

ABSTRACT.

In this oven, in which electrically heated air is drawn through the sample being dried, four series of tests were made.

1. Known Levulose solution:- A temperature of 53°C. was too low. At 66°C. drying was satisfactory, and required 4 hours. Temperatures above 75°C. were unsuitable and should not be used.

2. Spencer and Steam Oven Comparison on Raw Sugars :- In the steam oven 0.84 per cent water was found, compared with 0.72 at 70°C., 0.73 at 77°C, and 0.75 per cent water at 91°C. in the Spencer oven.

3. Moisture in different sizes of Raw Sugar crystals :- The differences found were not significantly great.

4. Effect of Spencer Oven heating on Reducing Sugars :- Using a Cuban raw sugar, heating above 115°C. for over 20 minutes caused a progressive decrease in the reducing sugar content.

General Conclusion :-

The Spencer Oven can yield comparable results in routine testing, but it cannot be regarded as an accurate means of determining water in thermally sensitive substances.

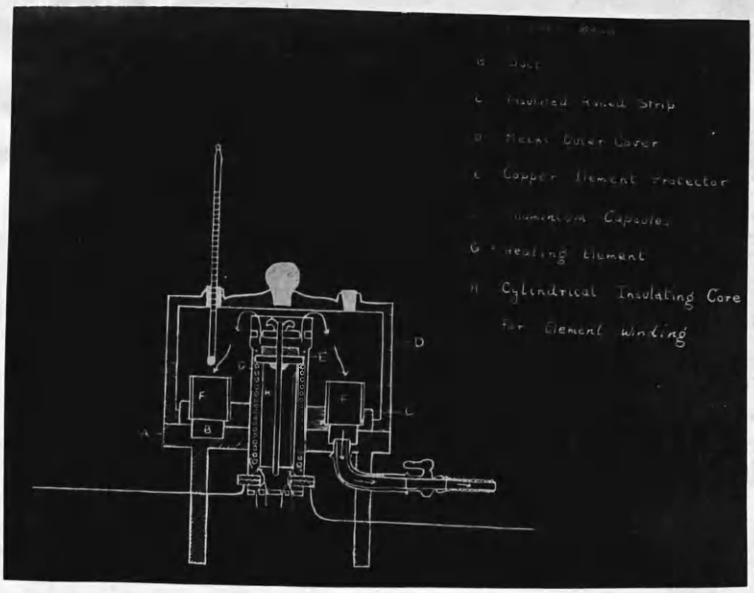
-----oOo-----

THE SPENCER OVEN FOR THE DETERMINATION OF MOISTURE IN SUGARS MOLASSES, SYRUPS, JUICES, Etc.

The Spencer oven is a device for passing a large volume of air over a heating element and then through a capsule containing the material to be dried. The temperature is regulated by a rheostat. The capsules are made of aluminium and have a metal mesh bottom of Monel metal to permit air to pass. Solid sugars are weighed directly into the capsules. (See Spencer's Cane Sugar Hand Book, 7th. Ed., p. 263, 1929).

With liquid products the material is absorbed on asbestos. Several precautions are hecessary to ensure concordant results :- The asbestos should be freshly ignited and fluffy, only one test should be made at a time and not more than 4 ccs. of the liquid used. The oven should be brought to temperature of operation (about 110°C.) before inserting the sample : liquids other than thin juices should be diluted 1 : 1 before weighing.

PROCEDURE :- The capsule is loosely filled with fluffy freshly - ignited asbestos and heated in the oven at 110°C. for a few minutes, cooled, and weighed. The liquid is then slowly added from a weighing bottle fitted with a dropping pipette, taking care that it is absorbed by the asbestos. (The drops should be kept to the middle of the asbestos : if there is any sign of liquid on the bottom gauze, start again.) The capsule is then placed in the oven (at 110°C.), and suction applied for 20 minutes, keeping the temperature at 110°C. ; it is now cooled and weighed. It has been found that the air will not pass evenly through two or more capsules, so one sample only should be tested at a time.



Spencer Electric Oven.

Figure 56

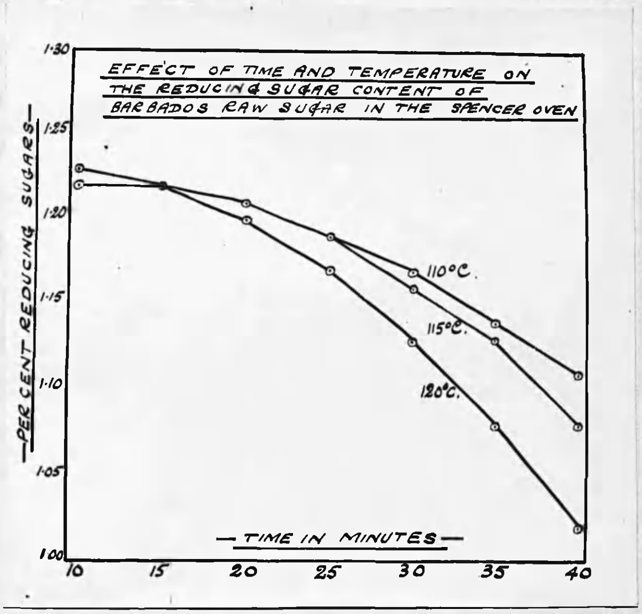


Figure 57

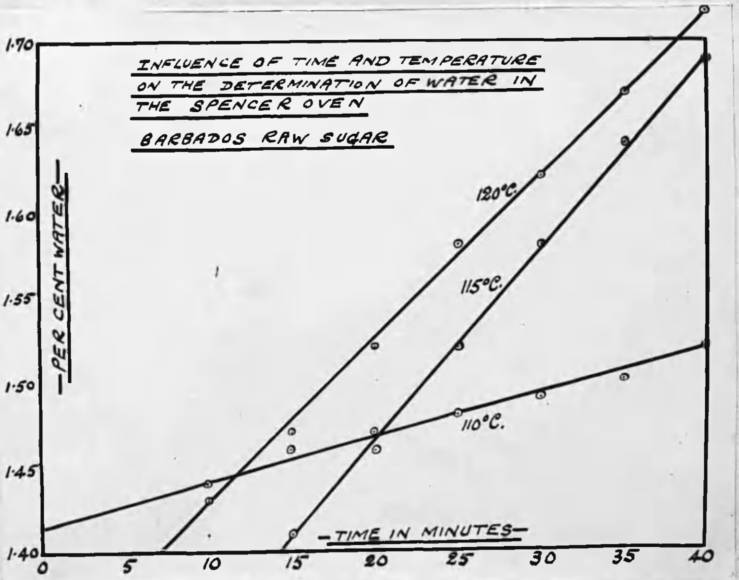


Figure 58

The Drying of a Levulose Solution in the Spencer Oven.

The levulose solution used contained 61.73 per cent water and 38.27 per cent levulose. It was absorbed on either Gooch asbestos or 16/20 mesh pumice in the usual Spencer Oven capsules.

No.	Average Temp. °C.	Hours Heating	Apparent Per Cent Water				
			1.	2.	3.	4.	Average
1	73-78	3.5	61.95	61.69	-	-	61.82
2	73-78	1.33	61.18	61.07	-	-	61.13
3	77	2.5	61.37	61.27	-	-	61.32
4	77	4.0	61.59	61.57	-	-	61.58
5	75	6.0	61.64	61.60	-	-	61.62
6	77	7.0	61.77	61.72	-	-	61.75
7	77	9.0	61.74	61.72	-	-	61.73
8	77	11.0	61.78	61.74	-	-	61.76
9	76	13.0	61.82	61.76	-	-	61.79
10	76	16.0	61.77	61.74	-	-	61.76
1	53	2.0	61.12	61.12	61.14	61.05	61.11
2	54	4.0	61.13	61.11	61.14	61.07	61.11
3	52	8.0	61.23	61.20	61.21	61.19	61.21
4	54	10.0	61.28	61.26	61.29	61.26	61.27
5	53	14.0	61.34	61.31	61.34	61.30	61.32
6	52	19.0	61.16	61.12	61.16	61.06	61.13
7	53	26.0	61.19	61.17	61.20	61.14	61.18
1	65	2.0	61.56	61.58	61.61	61.59	61.59
2	67	3.0	61.67	61.69	61.73	61.73	61.71
3	68	5.0	61.71	61.74	61.77	61.74	61.74
4	64	16.0	61.72	61.72	61.75	61.77	61.74
Weight levulose			3.0274	3.0740	3.0446	2.9953	-
" asbestos			3.7979	3.8540	3.2051	3.8149	-

Drying of Levulose Solution in the Spencer Oven.

At the drying temperature of 66°C. drying appeared to be complete in about 4 hours,and there was little change after 16 hours from the figure reached in 5 hours. The dishes which had a degree or two higher temperature were highest in apparent per cent water.

At 53°C. the temperature appears to be too low for the levulose to part with its last traces of water.

Examination of the residues left in the capsules indicated that the solution remained in the top half of the asbestos absorbent,leaving the bottom part of the packing unused-i.e., about 3 gms. of the levulose was absorbed in about 3 gms. of the asbestos.

At 90-95°C. there was a distinct odour of burnt sugar in the air ; this is too high a temperature.

At a temperature of 82.5°C. the correct result was obtained in 90 minutes, while at 83.7°C. the correct result was exceeded in 65 minutes. It seems probable that it is not wise to dry a sensitive sugar like levulose above 75°C. in the Spencer Oven.

Temperatures :- The Spencer Oven was fitted with four thermometers and temperatures taken during the final experiment : some specimen results are here shown :-

At start Oven empty	Temperatures °C., after Minutes									Thermometer Number
	1	3	5	9	10	12	15	17	20	
87.5	81.5	80.5	81	81	81	82	83	83	83	1
87.0	82.0	80.5	81	81	81	82	82	82	83	2
87.0	82.0	81.0	81	82	82	83	83	84	84	3
85.0	82.0	81.0	81	82	82	82	82	84	84	4

Drying of Levulose Solution in the Spencer Oven (continued):-

No.	Average Temp. °C.	Hours Heating	Apparent Per Cent Water				
			1.	2.	3.	4.	Average
1	85	1	61.72	61.82	61.85	61.77	61.79
2	87	2	61.83	61.86	61.88	61.85	61.86
3	89	3	61.88	61.93	61.96	61.92	61.92
Average Temperatures			86	85	86	87	-
1	80	1.5	61.77	61.74	61.74	61.77	61.76
2	85	2.5	61.76	61.72	61.76	61.77	61.75
3	78	3.5	61.79	61.72	61.77	61.77	61.77
4	95	4.5	62.03	61.96	62.01	62.00	62.00
Average Temperatures			80	78.5	82.5	81.0	-
		Mins.					
1	78	20	39.86	33.95	40.19	42.87	39.22
2	82	40	59.43	54.64	59.20	61.19	58.62
3	82	60	61.51	61.46	61.51	61.54	61.51
4	84	80	61.62	61.62	61.64	61.63	61.63
5	87	120	61.67	61.68	61.72	61.69	61.69
6	85	140	61.72	61.73	61.79	61.76	61.75
7	88	160	61.73	61.73	61.77	61.75	61.75
8	88	100	61.60	61.61	61.65	61.64	61.63

SUMMARY OF RESULTS.

Average Temperature	Time to get Approx. correct Result, Hrs.	Best Result Obtained (Levulose Solution 61.73 % Water)
75-77	7	61.77 and 61.72
53	14	61.34 (followed by less).
66	3	61.71 and 61.74
85	1	61.79 (Temperature too high).
80	1.5	61.76

Comparison of Steam Oven and Spencer Oven for Raw sugar Moistures.

These tests were made using a Barbados Raw Sugar:

Spencer Oven:- Test 1. Av. Temp. 70°C., four samples in oven at once, 5 gms. sugar in each capsule.

Hrs. Heat-ing	Apparent Per Cent Moisture 1.	2.	3.	4.	Mean
1	0.70	0.69	0.72	0.71	0.71
2	0.75	0.69	0.72	0.72	0.72
3	0.74	0.70	0.70	0.72	0.72
4	0.72	0.71	0.73	0.70	0.72

Test 2a:- Started with four capsules at 73°C., and removed one each half-hour. **Test 2b :-** Repeated 2a at 88°C. start. All on 5 gms.

	Hrs. Heat-ing	Av. Temp. °C.	Vessels in Oven	Apparent Per cent water
2a.	0.5	73	4	0.69
	1.0	77	3	0.69
	1.5	77	2	0.73
	2.0	78	1	0.73
2b.	0.5	88	4	0.75
	1.0	88	3	0.77
	1.5	91	2	0.75
	2.0	95	1	0.71

Test 3 :- Same sugar in Steam-Oven at 99°C.

No.	Gms. Taken	Hours Heating	Apparent Per Cent Water
1.	10	5	0.80
2.	10	5	0.82
3.	5	2	0.83
4.	5	4	0.91
5.	10	2	0.80
6.	10	4	0.87

The effect of temperature, and the effect of the number of samples in the oven at one time are clearly seen from these tests.

Determination of Moisture in different sizes of crystals in various Raw Sugars in the Spencer Oven.

Screen Analysis of Sugars used :-

Source of Sugar	Colour	Per Cent Retained on Mesh 10	20	30	40	50
1. San Domingo	Dark	1.54	83.41	14.79	0.24	0.02
2. " "	Light	5.72	89.72	4.56	-	-
3. " "	Medium	0.01	65.57	32.90	1.42	0.10
4. Natal	-	0.23	53.53	45.35	-	-

RESULTS:

Sugar	Temperatures °C. Start	Middle	End	°C. Temp. Range	Per Cent Moisture Normal Sugar	Portion Retained on 10	20	30 mesh
1.	88	87	90	85-90.5	0.034	-	0.024	0.034
2.	85	87	89	85-89	0.041	0.059	0.040	0.026
3	87	88	90	87-90.5	0.039	-	0.042	0.041
4.	85	87	89	85-89	0.027	-	0.025	0.024

The tests here recorded were carried out to see if there was any marked difference with small crystals where the surface of the molasses film on the crystals would be necessarily less in area, and where in consequence less water might be expected to be present

The most notable difference is on 30 mesh with No.2 sugar, but this result is in direct contradiction to the result expected. In any case the differences are not significantly great.

THE EFFECT OF THE SPENCER OVEN HEATING ON THE REDUCING SUGARS IN CUBAN RAW CANE SUGAR.

Five grams of the sugar were taken for each test and the time factor was varied for temperatures of 110, 115, and 120°C. Reducing sugars were estimated by the Lane and Eynon method, and a control test was run in the steam and vacuum ovens.

No.	Temp. of Heating °C.	Time of Heating Minutes.	Reducing Sugars %	Apparent Moisture %	Decrease in Reducing Sugars %
1	120	40	1.02	1.72	0.22
2	"	35	1.08	1.67	0.16
3	"	30	1.13	1.62	0.11
4	"	25	1.17	1.57	0.07
5	"	20	1.20	1.52	0.04
6	"	15	1.22	1.47	0.02
7	"	10	1.22	1.44	0.02
8	115	40	1.08	1.69	0.16
9	"	35	1.13	1.64	0.11
10	"	30	1.16	1.58	0.08
11	"	25	1.19	1.52	0.05
12	"	20	1.21	1.46	0.03
13	"	15	1.22	1.41	0.02
14	"	10	1.22	1.41	0.02
15	110	40	1.11	1.52	0.13
16	"	35	1.14	1.50	0.10
17	"	30	1.17	1.49	0.07
18	"	25	1.19	1.48	0.05
19	"	20	1.21	1.47	0.03
20	"	15	1.22	1.46	0.02
21	"	10	1.23	1.44	0.01

CONTROL TESTS ON CUBAN RAW SUGAR IN STEAM AND VACUUM OVENS.

OVEN	TEMP. OF HEATING °C.	TIME OF HEATING HOURS.	REDUCING SUGARS %	APPARENT MOISTURE %
ORIGINAL SUGAR	---	---	1.24	---
Vacuum	60	4	1.24	1.40
"	70	4	1.24	1.48
Steam	98	4	1.16	1.49

CONCLUSIONS :- This work shows that heating above 115°C. for over 20 minutes causes higher apparent moisture percentage to be recorded when using the Spencer oven system. There is at the same time a progressive decrease in the reducing sugar content.

It does not seem that there is appreciable inversion of sucrose under these conditions ; in fact, sucrose is probably stable in normal circumstances at this temperature unless the medium is of low pH value.

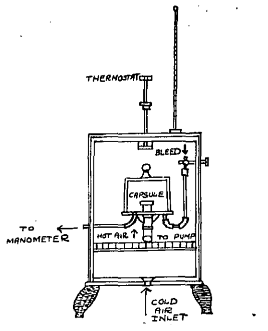
The Spencer oven cannot be regarded as an accurate means of determining water in thermally-sensitive substances, but it will yield comparable results for routine testing when the oven is carefully controlled and standardised. The apparent increase in moisture in a raw sugar would be reflected as an increase in the Safety Factor of the sugar ($S.F. - \frac{\text{Moisture}}{100 - \text{Poln.}}$), where the maximum allowable ratio is 0.33. The Factor would appear fictitiously high. Not much harm would result as a carefully watched sugar of apparently high safety factor would in reality be quite safe.

THE DRYING OF SUGARS UNDER VACUUM

A NOTE ON THE SERBIA DRYING OVEN

G. R. SERBIA (Sugar, Aug. 1943, p. 19) has described a simple and inexpensive oven for determining moisture in sugars.

It is a combination of the Spencer oven method of drying in a current of heated air and the Official vacuum oven method. A thermostatically controlled electric drying oven supplies the heated air at the temperature required. The circulation of air within the oven is arranged so that it passes over the heating elements, the thermometer and the thermostat, and thence goes through the sugar sample contained in a perforated capsule. The capsule is itself placed in an airtight chamber with an easily removable cover. A manometer connection is provided and the rate of flow of air can be regulated from outside to give the desired pressure. It is possible to dry 10 gram samples of sugar in 30 minutes at 75°C. with a vacuum of 25" after which the loss is less than 1 mgm. per hour. At higher vacua, lower temperatures can be used and the operation is completed in very much less time than that prescribed in the official methods.



SERBIA'S DRYING OVEN

Figure 58 a.

SECTION 5.

METHODS OF ANALYSIS.

Part 11 : The Determination of Water by Desiccation Methods.

Introduction :

The Drying Agent :

Discussion of Factors influencing the Method:

Experimental :

Summary of Results.

The Determination of Water by Desiccation :- Introduction:-

Oliver Lyle, ("Technology for Sugar Refinery Workers", Chapman and Hall, London, 1941, p. 304), states that :- " It is most unlikely that faulty estimation of water accounts for our unknown loss, but the fact remains that the estimation of water in raw sugars, molasses, and golden syrup is one of the parts of our analysis in which we can put least faith, and is the one estimation that can put all our loss figures entirely wrong."

There is a natural tendency in most experimental work on sugar moisture determination to test the complex substance being investigated-e.g. golden syrup, starch, or glucose syrup, although its true water content is not and cannot be directly known.

On the other hand it is difficult, if not impossible to prepare a synthetic material which will contain all the constituents of the natural material in their correct ratios.

The chief problem with most methods of determining water is in knowing when to stop - that is - the time at which the percentage recorded is the true amount of water present in the sample under test.

A further difficulty is that different methods used for the estimation do not usually give comparable results, for instance, one method may give both the 'mechanical' and the combined water, while another method may give only the 'mechanical' water.

The importance of adequate and correct sampling must also be emphasised ; no analysis can be any better than the sample.

C.B.Morison (1926) states that the method of vacuum desiccation at room temperature shows marked variations in the amounts of water absorbed, this being due principally to the difficulty of maintaining constant pressure in the desiccator and constant composition in the drying agent. He also noted that these tests are time consuming, and require careful attention.

Snyder and Sullivan (1924) do not consider this method any more accurate than other methods, mainly because of the uncertainty of gauging the exact end-point of the estimation. They found that flour itself is a good desiccating agent when dry, and will then absorb water from many reagents used for drying. In addition, particles of flour are often lost while evacuating the desiccator. Phosphorus pentoxide was found to give lower final results than sulphuric acid owing to the impervious glaze which soon forms on the surface of the solid reagent.

Coleman and Snider (1935) take the contrary view that this method can reasonably be assumed to represent more nearly the true water content of a material than results by any other method largely on account of the absence of heating. De Whalley's views have already been mentioned in this connection.

Rice (1927) states that desiccation at room temperature will remove water of crystallisation from some but not from all substances likely to occur in final sugar syrups. Such syrups reached constant weight in 48 hours in a Hempel desiccator with sulphuric acid at 2.5 cms. pressure, and no further loss was found after 10 days.

Desiccators showing stirring arrangements and Safety Box.

Figure 59.

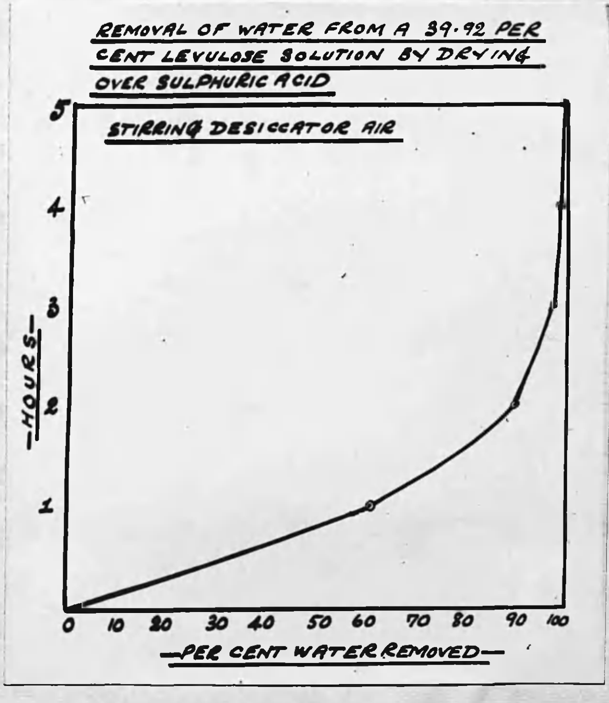


Figure 60.

DESICCATION AT ROOM TEMPERATURE -

THE DRYING AGENT

Yoe (Chem News, 130,340,1925) stated :- A satisfactory desiccating agent should have the qualities of high capacity and high activity, and should show little change in efficiency with change of temperature. It should be capable of easy and repeated re-activation and be cheap and obtainable in large amounts.

Other desirable qualities include absence of channelling through use, absence of volume change through water absorption, freedom from stickiness, and non-reactivity with the substance being dried.

Booth and McIntyre (I.E.C., Anal. Ed., p. 12, 1930) pointed out that the use of desiccators in the analytical laboratory is frequently faulty, and often led the chemist to form erroneous ideas in regard to its efficiency - In view of the moisture always inadvertently admitted, no matter how rapidly the desiccator is opened and closed, it is useless to use a desiccant of the highest drying power such as P_2O_5, since the object cooling in the desiccator will ordinarily be removed for weighing before the space can be dried completely...... Generally the air in the laboratory is nearly saturated with moisture.....

The authors considered sulphuric acid to be satisfactory, apart from the danger of spilling, for use in ordinary analytical work, and advocated hydroxide-free calcium chloride as a neutral desiccant.

Bower (Bur. Stands. Jl. Res., 12,241,1934) studied the comparative efficiencies of various dehydrating agents used for drying gases. His results show the various dehydrating efficiencies to fall into

His results show the various dehydrating efficiencies to fall into

four groups, in which the agents are arranged in order of efficiency (most efficient first). The group headings show the mgms. water left per litre of air after drying at 30.5°C. with the desiccants mentioned :-

GROUP 1 :- Residual water 0.00065 to 0.005 mgms.

Barium Oxide : Anhydrous Magnesium Perchlorate : Calcium Oxide : Calcium Sulphate.

GROUP 2 :- Residual water 0.01 to 0.02 mgms.

Potassium Hydroxide (sticks).

GROUP 3 :- Residual water 0.02 to 0.03 mgms.

Silica Gel : Magnesium Perchlorate trihydrate.

GROUP 4 :- Residual water 0.1 to 0.3 mgms.

Calcium chloride (anhydride) : Sodium Hydroxide (sticks) : Barium Perchlorate (anhydrous) : Zinc Chloride (sticks) : Calcium chloride (technical anhydrous) : Calcium chloride (granular) : Copper Sulphate (anhydrous).

It is clear that the only real dehydrating agents are to be found in the first three groups, those in group four being more correctly called dehumidifiers. The efficiency of calcium oxide will be greatly reduced if it contains even small amounts of silicates or aluminates which glaze its surface during the burning.

THE MODE OF ACTION OF DESICCATING AGENTS.

The removal of water from a system by a drying agent is generally accomplished either by fixation of the water by chemical reaction with the agent, or by removal of the water by physical surface adsorption. Some drying agents combine these two mechanisms, drying both by chemical combination and by contact adsorption. When new chemical compounds are formed the capacity of the drying agent for water is dependent upon the number of co-ordinate valencies which come into play.

Drying agents which react through primary valence bonds include P_2O_5 and metallic sodium or potassium. With P_2O_5 metaphosphoric acid HPO_3 is formed as a first product of the reaction with water, and finally orthophosphoric acid H_3PO_4. This type of reagent forms the largest group. The primary valence type shows the greatest number of perfect drying efficiencies, but as a rule they are not regenerative, and while exceedingly fast have often low capacity. The physical and chemical properties of the product are often undesirable in this class also. Bower (loc.cit.) divides drying agents into five classes with efficiencies depending upon physical and chemical reactions of the following types :-

Class 1 :- $A(H_2O)y + xH_2O = A(H_2O)x + y(\text{solid})$: example:-

Calcium chloride monohydrate

$CaCl_2.H_2O + H_2O = CaCl_2.2H_2O$.

Class 2 :- $A(\text{solid}) + H_2O$ = Saturated solution, e.g., common salt.

Class 3 :- $A(\text{liquid}) + H_2O$ = Solution, e.g., Sulphuric acid.

Class 4 :- Adsorption drying agents, e.g., Silica-gel.

Class 5 :- $M + (H_2O)x = M(OH)x + x/2\ H_2$, where M = metal :

Examples :- metals and metal alloys such as the alkali and alkaline metals and their amalgams.

Thus class 1 gives solid reaction products, class 2 gives saturated solutions, class 3 gives solutions of low vapour pressure, class 4 hold water by capillary attraction, and class 5 absorb water through its decomposition to form hydrogen.

CO-ORDINATION DRYING AGENTS AND PRIMARY VALENCY REACTANTS.

Drying agents which form new chemical compounds in removing water from a system can be classified by the Werner system of co-ordination types. The co-ordination numbers are usually 2,4, or 6,1 : 3 and 5 are less common.

The water molecules and the parent substance are joined by secondary valence bonds, and the combination is generally less intense as the number involved decreases.

The capacity of reagents of this type for water is dependent upon the number of co-ordinate valencies at work. Thes desiccants are usually less efficient than the primary valence reactants. Phosphorus pentoxide and the alkali metals are examples of the primary valence type of desiccant, and anhydrous magnesium perchlorate is the most efficient of the co-ordinate valence desiccants.

INTENSIVE DRYING.

The principal investigations of water catalysis due to Baker, (J.C.S.,91,1862,1907 : 101,2239,1912 : 121,568,1922), involved the study of intensive drying, with a technique based on heating glass apparatus nearly to fusion in a vacuum, and the use of P_2O_5 as drying agent over a period of several years. Many attacks have been made on Baker's results, with which we are not concerned here, but the experiments emphasise the difficulty of removing the last traces of water from a system. Smits has given a theory of dynamic allotropy, where water catalyses the changes between two molecular species in the undried liquid.

THE DRYING OF SUGAR SOLUTIONS AT ROOM TEMPERATURE.

EXPERIMENTAL

Solutions of sucrose, glucose, and levulose were dried at room temperature, (a) in a static atmosphere, (b) in a stirred atmosphere, using concentrated sulphuric acid as drying agent.

Celite or sand were used as dispersing and absorbing media. Similar tests were made using golden syrup, and vacuum drying was also tried with this material, both at room temperature and within the temperature range 36-50°C.

The moisture content of a raw sugar was estimated at room temperature with stirring : this was intended to serve as a contrast to the estimations made on solutions as above.

A detailed description of the various factors encountered, and of the precautions found necessary, is given on the following pages.

THE DRYING OF SUGAR SOLUTIONS AT ROOM TEMPERATURE

1. Use of single desiccators :- It was quickly found that each sample must have a desiccator to itself. Thus, for example, with two samples in one desiccator it was found that the first sample taken out differed by 0.0004 gm. from the previous weighing (loss). The second sample which had suffered exposure during the opening of the first weighing, was found to be 0.0039 gm. heavier, a gain of nearly 4 milligrams, apparently due to the double exposure.

2. 'Dished' Containers :- The 'dished aluminium containers used in one series of tests were found to be unsuitable for two reasons, firstly the uneven thickness of the sample layer caused uneven drying, and secondly there was very poor contact with the oven surface when these dishes were used for oven drying : this also applies to the use of watch glasses which are frequently recommended for moisture determinations.

3. Mixing water used:- The amount of water added had to be varied to suit the nature of the absorbing medium, the nature of the sugar dried, and the amounts of the sugar and absorbing medium weighed.

4. Use of stirring :- In tests involving stirring it was found necessary to have a shield over the sample to prevent glass or rubber dust from the stirrer falling into the sample. Care was also required to ensure that there was no blowing away of the sample as it became dry : this was more likely to happen where celite was used as absorbent. Regulation of the stirrer speed was thus important, with adjustment as the motor warmed up.

5. Static charge :- In one or two tests loss was caused by static charge induced by wiping the dishes, e.g. in one case particles of celite flew to the lid after its inner surface had been wiped. This charge must therefore be guarded against by the usual precautions of micro-analysis when wiping the dishes.

6. Time factor in weighing and manipulation :- Approximately 15 minutes was required for the complete weighing of one sample, that is, for the weighing of dish, lid, and rod alone, then plus absorbent, and finally with the sugar solution, or three weighings in all. It took about 5 minutes more to pipette the mixing water and mix it with the sample.

7. Precautions with Celite :- This material, especially the analytical reagent grade, is very light and 'fluffy' and therefore liable to loss by blowing away unless care is taken. This loss is most likely when the mixing water is added. The commercial grade of celite (acid-washed) was preferred as absorbent since it was not so light. On the whole there was better agreement among the replicates when celite was absorbent than when sand was used. It is possible that the greater surface of the celite may render it more liable to absorb moisture while weighing, although no trouble was actually encountered from this in the course of this work. Static charge was much more noticeable with ignited sand than with celite or pumice.

8. Advantages of Celite :- (a) No preparation is required except ignition : (b) larger surface exposed than with sand or pumice : (c) the weight is less :(d) it dries adequately at almost any ratio of celite to syrup : (e) it is almost white, hence decomposition is

shown up:(f) less ignition is required than with sand. Its main disadvantage is the risk of loss in air currents.

9. Amount of sugar solution or syrup to be weighed :- Since 1 mgm. makes relatively a large difference in the moisture content when small amounts of syrup are weighed, an amount equivalent to 0.5 gm. solids is the minimum which should be taken.

10. The mixing of the sample with the absorbent using water :- Most of the discordant results obtained in the earlier part of the work could be traced to incomplete mixing of the sample with the absorbent. Enough water must be added to ensure thorough mixture, without swamping the sample. It is possible that failure here is a frequent source of error in the determination of total solids.

NOTES APPLICABLE TO OVEN DRYING :-

1. Decomposition of levulose :- Levulose appears to start decomposing immediately the last trace of water has been evaporated. It is also more liable to loss by evaporation while weighing, for instance, a loss of 1 mgm. in 2 minutes was found while weighing a 39 per cent levulose solution.

2. Metal dishes are generally more uniform than glass ones, which often have a concave base, so that there is not complete contact of the bottom of the dish with the metal of the oven.

3. The rate of evaporation depends on the rate at which heat can get to the sample, and also on the rate at which water-vapour can escape from the oven. There may be danger however in having too good a rate of heat transfer, as the tendency to burn and decompose will be greater. A plane glass dish has some advantage with heat-sensitive materials.

LIST OF EXPERIMENTS ON DRYING OF SUGAR SOLUTIONS BY DESICCATION AT LOW TEMPERATURES.

No.	SUGAR SOLN.	DESICCANT	METHOD
1	Levulose on Celite 4 : 1	Sulphuric acid	Static: 2 in one desiccator
2	" 3 : 1	" "	" "
3	Sucrose on Celite 2.8:1	" "	" "
4	Glucose Soln. on Celite 2.8:1	" "	" : in separate desiccators
5	Levulose on Celite 2.8:1	" "	Vacuum desiccation
6	Levulose on Celite 2.8:1	" "	With Stirring
7	As in No.6	" "	" "
8	As inNo. 6 using sand	" "	With Stirring
9	As in No. 6	" "	" "
10	Sucrose on Celite	" "	With Stirring
11	Glucose on Celite	" "	" "
12	As in No. 11	" "	" "
13	Raw Sugar	" "	" "(no Celite)
14	Golden Syrup on Celite	" "	" "
15	Sucrose on Celite	" "	" "
16	Golden Syrup	" "	With Stirring and vacuum
17	Golden Syrup on Sand 44 : 1	" "	Circulating Pump & Vacuum Stirring
18	Golden Syrup on Sand 30 : 1	" "	Static Drying
19	Golden Syrup on Sand 23 : 1	" "	Vacuum Desiccation
20	Golden Syrup on Sand 44 : 1	" "	" "
21	G.S.on sand	-- --	Vac.oven at 36-50°C.
22	G.S.on sand	-- --	" " 50°C.

CIRCULATING PUMP

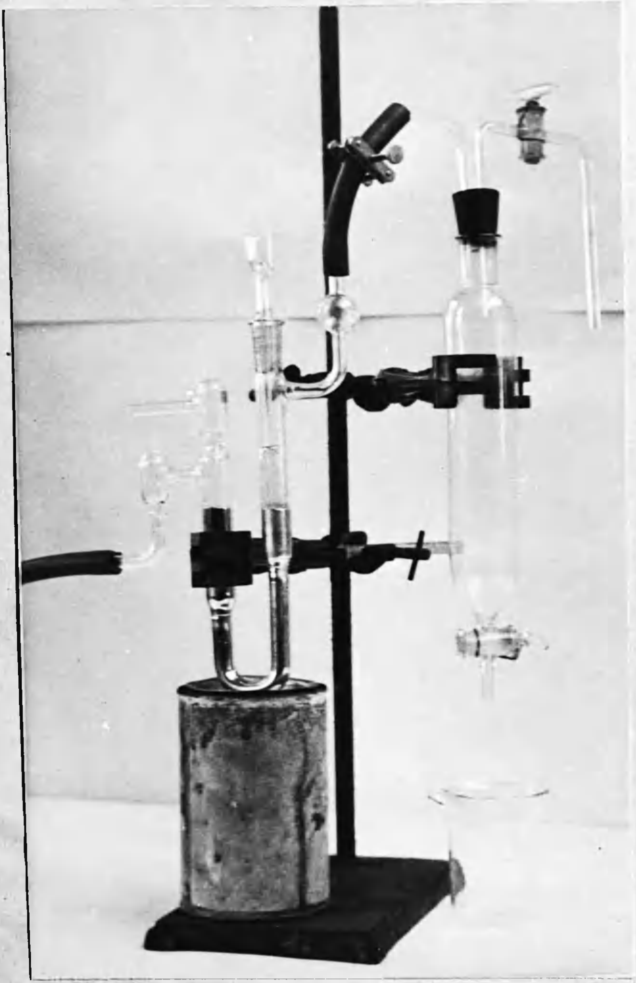


Figure 61

"STIRRING" DESICCATOR

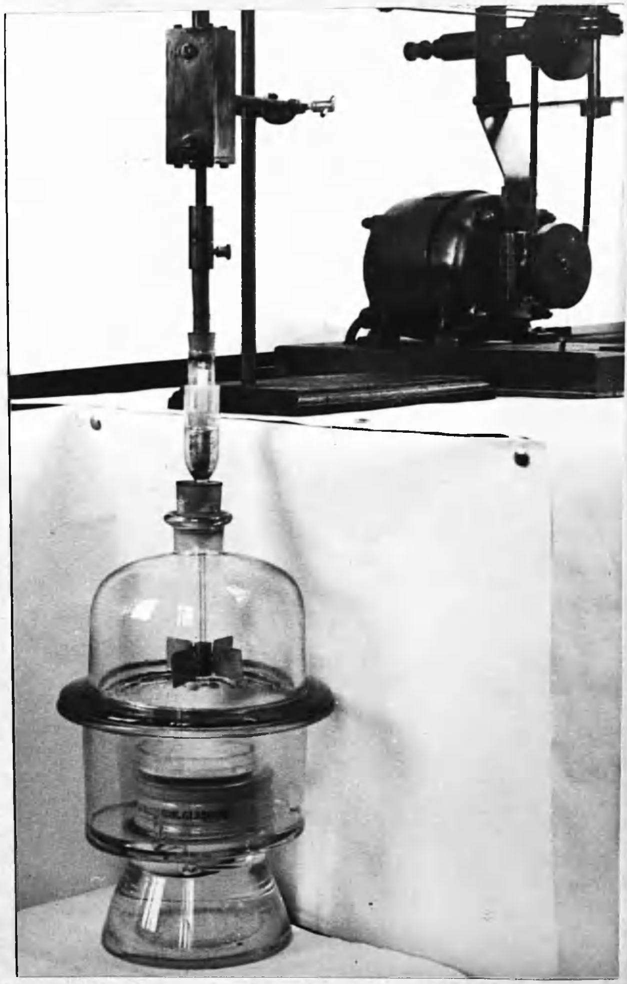


Figure 62.

EXPERIMENT D1 :6

DRYING BY DESICCATION OF 59.92% LEVULOSE SOLUTION.

CONDITIONS.

ARRANGEMENT	Two samples in one desiccator = static desiccation.
DESICCANT	1500 ccs. 1.84 sp. gr. fresh H_2SO_4 followed in 1 case by KOH drying (454 gms.)
ABSORBING MEDIUM	Ignited celite 2.5 gms. per sample.
DISHES	Glass petri dishes 82 mms. diam. x 13 mms. deep.
SAMPLE SURFACE EXPOSED	52.8 sq. cms.
H_2SO_4 SURFACE EXPOSED	268.8 sq. cms.
RATIO ABSORBENT : SUGAR SOLIDS	Approx. 4 : 1
RATIO WATER TO DESICCANT	Approx. 1 : 76
DISTANCE SAMPLE TO DESICCANT	Approx. 25 mms.
RATIO OF SURFACE EXPOSED SAMPLE : DESICCANT	Approx. 1 : 5.1

RESULTS :- The experiment was continued over nearly 33 days and there was about 0.5 per cent of water still retained in the sample (1) after that time. It is evident that the static drying of a sugar solution at room temperature is very slow.

EXPERIMENT D1 :-

Drying of Levulose Solution.

	(1)	(2)
Wt. of Levulose Solution	1.5085	1.5680
Wt. of water present in Levulose Solution	0.9061	0.9421
Water added	9.000	9.000
Water total present	9.9061	9.9421

No.	Time Hours	Water Lost gms.		Water Left gms.	
		(1)	(2)	(1)	(2)
1	67	6.5527	6.2655	3.3534	3.6766
2	94	8.5035	8.9867	0.9194	1.4386
3	116	9.8867	9.9282	0.0194	0.0139
4	139	9.8939	9.9368	0.0122	0.0053
5	163	9.8957	0.9395	0.0104	0.0026
6	236	9.8955	9.9381	0.0106	0.0040
7	239	9.8967	9.9403	0.0094	0.0018
8	261	9.8965	9.9410	0.0096	0.0011
9a	265	1500 ccs.	Fresh H_2SO_4		
9	285	9.8956	9.9425	0.0107	-0.0004
10	312	9.8951	9.9430	0.0112	-0.0009
11	406	9.8947	9.9435	0.0116	-0.0013
12	431	9.8949	9.9342	0.0114	+0.0079
13	450	9.8947	discarded	0.0116	-
14	475	9.8971	-	0.0092	-
14a	No. 1 transferred to desiccator with fresh KOH				
15	548	9.8979	-	0.0084	-
16	618	9.9004	-	0.0057	-
17	642	9.9005	-	0.0056	-
18	717	9.8989	-	0.0072	-
19	788	9.8992 discarded	-	0.0069	-

EXPERIMENT D1 :- (continued) - RESULTS

No.	Drying Time Hours	% Water and % Total Solids (1)	(2)	Difference from known Total Solids (1)	(2)
3	116	H_2O 58.78 T.S. 41.22	59.20 40.80	+ 1.30	+ 0.88
4	139	59.27 40.73	59.75 40.25	+ 0.81	+ 0.33
5	163	59.37 40.63	59.92 40.08	+ 0.71	+ 0.16
6	236	59.39 40.61	59.82 40.18	+ 0.69	+ 0.26
7	239	59.44 40.56	59.96 40.04	+ 0.64	+ 0.12
8	261	59.43 40.57	60.02 39.98	+ 0.65	+ 0.06
9a	265	1500 ccs. Fresh H_2SO_4			
9	295	59.36 40.64	60.12 39.88	+ 0.72	- 0.04
10	312	59.32 40.68	60.15 39.85	+ 0.76	- 0.07
11	406	59.29 40.71	60.17 39.83	+ 0.79	- 0.09
12	431	59.30 40.70	59.58 40.42	+ 0.78	+ 0.50
13	450	59.29 40.71	discarded	+ 0.79	-
14a	No. 1 transferred to desiccator with fresh KOH				
14	475	59.48 40.52	-	+ 0.60	-
15	548	59.51 40.49	-	+ 0.57	-
16	618	59.68 40.32	-	+ 0.40	-
17	642	59.67 40.33	-	+ 0.41	-
18	717	59.58 40.42	-	+ 0.50	-
19	788	59.61 40.39	-	+ 0.47	-

EXPERIMENT D2 :-

DRYING BY DESICCATION OF 39.92% LEVULOSE SOLUTION.

CONDITIONS.

ARRANGEMENT	Two samples in one desiccator static desiccation.	
DESICCANT	1500 ccs. fresh 1.84 sp. gr. sulphuric acid.	
ABSORBING MEDIUM	Ignited celite 1.5 gms. per sample.	
DISHES	Glass petri dishes 82 mms. diam. x 13 mms. deep.	
SAMPLE SURFACE EXPOSED	52.8 sq. cms.	
H_2SO_4 SURFACE EXPOSED	268.8 sq. cms.	
	(1)	(2)
RATIO ABSORBENT : SUGAR SOLN.	1.21 : 1	1.18 : 1
To SUGAR SOLIDS	Approx. 3 : 1	
DISTANCE SAMPLE TO DESICCANT	Approx. 50 mms.	
RATIO WATER TO DESICCANT	Approx. 1 : 316.	
RATIO OF SURFACE EXPOSED SAMPLE : DESICCANT	Approx. 1 : 5	

In this experiment the amount of absorbent used was halved and in consequence the amount of water required for mixing was reduced from 9 ccs. to 4 ccs. The result of this test was satisfactory, and it is clear that the water to be dried out should be kept to the minimum.

EXPERIMENT D2 :- RESULTS

Drying of 39.92% Levulose Solution as in D1 but less water added.

		(1)		(2)
Gms. Wt. of Levulose Solution taken		1.2427		1.2667
Wt. of water present	solids 0.4963	0.7464	solids .5058	0.7609
Wt. of water added		4.0000		4.0000
Total gms. water present		4.7464		4.7609

No.	Drying Time Hours	Water Lost gms.		Water Left gms.		% Water and % Total solids		Difference from known total solids	
		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1	19	2.2645	2.2933	2.4819	2.4676	-	-	-	-
2	92	4.7407	4.7542	0.0057	0.0067	59.58 40.42	59.54 40.46	+ 0.50	+0.54
3	119	4.7430	4.7549	0.0034	0.0060	59.80 40.20	59.60 40.40	+0.28	+0.48
4	141	4.7435	4.7575	0.0029	0.0034	59.84 40.16	59.80 40.20	+0.24	+0.23
5	165	4.7443	4.7583	0.0021	0.0026	59.91 40.09	59.07 40.03	+0.17	+0.11
6	191	4.7450	4.7590	0.0014	0.0019	59.96 40.04	59.91 40.09	+0.12	+0.17
7	287	4.7458	4.7584	0.0006	0.0025	60.03 39.97	59.87 40.13	+0.05	+0.21
8	312	discarded	4.7545	-	0.0064	-	59.57 40.43	-	+0.51
9	429	-	4.7632	-	0.0023	-	60.24 39.76	-	-0.16
10	500	-	4.7613	-	0.0004	-	60.10 39.90	-	-0.02

EXPERIMENT D3 :-

DRYING BY DESICCATION OF 40.155% SUCROSE SOLUTION.

CONDITIONS.

ARRANGEMENT	Two samples in one desiccator; static desiccation.		
DESICCANT	750 ccs. fresh 1.84 sp. gr. Sulphuric Acid.		
ABSORBING MEDIUM	Ignited Celite 1.5 gms. per sample.		
DISHES	Dished aluminium capsules 72 mms. diam. x 18 mms. deep.		
SAMPLE SURFACE EXPOSED	40.7 sq. cms.		
H_2SO_4 SURFACE EXPOSED	188.7 sq. cms.		
		(1)	(2)
RATIO ABSORBENT : SUGAR SOLN.		1.15 : 1	1.06 : 1
TO SUGAR SOLIDS	Approx.	2.86 : 1	2.78 : 1
DISTANCE SAMPLE TO DESICCANT	Approx. 50 mms.		
		(1)	(2)
RATIO WATER TO DESICCANT	Approx.	1 : 157	1 : 154
RATIO OF SURFACE EXPOSED SAMPLE : DESICCANT	1 : 4.63		

In this experiment, the drying of a sucrose solution at room temperature was found to be extremely slow. After 36 days there was 0.545 gm. of water left in one sample ; while the other had come very near to the known water content in about 19 days. This difference seems to be caused by variation in the thoroughness of mixing.

EXPERIMENT D3 :- RESULTS

Drying by Desiccation of 40.155% Sucrose Solution.

		(1)		(2)
Gms. Sucrose Solution Taken		1.3080		1.4148
Wt. of Water Present	Solids 0.5250	0.7830	Solids 0.5580	0.8568
Wt. of Water Added		4.0000		4.0000
Total gms. Water Present.		4.7830		4.8568

No.	Drying Time Hours	Water Lost gms.		Water Left gms.		% Water and % Total Solids		Difference from known total solids	
		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1	68	3.8217	4.5450	0.9613	0.3118	-	38.52 61.48	-	-
2	95	4.7657	4.8200	0.0173	0.0368	58.56 41.44	57.95 42.05	+1.285	+1.895
3	118	4.7740	4.8255	0.0090	0.0313	59.19 40.81	58.35 41.65	+0.655	+1.495
4	141	4.7750	4.8295	0.0080	0.0273	59.27 40.73	58.64 41.36	+0.575	+1.205
5	168	4.7755	4.8305	0.0075	0.0263	59.30 40.70	58.70 41.30	+0.545	+1.145
6	264	4.7788	4.8315	0.0042	0.0253	59.55 40.45	58.78 41.22	+0.295	+1.065
7	289	4.7788	4.8305	0.0042	0.0263	59.55 40.45	58.70 41.30	+0.295	+1.145
8	308	4.7800	4.8325	0.0030	0.0243	59.64 40.36	58.84 41.16	+0.205	+1.005
		Both transferred to Desiccator with fresh KOH							
9	381	4.7780	4.8338	0.0050	0.0230	59.50 40.50	58.92 41.08	+0.345	+0.925
10	451	4.7840	4.8355	0.0010	0.0213	59.95 40.05	59.06 40.94	+0.105	+0.785
11	475	-	4.8372	-	0.0196	-	59.17 40.83	-	+0.675

Contd.

EXPERIMENT D3 :- RESULTS (continued).

No.	Drying Time Hours	Water Lost gms.		Water Left gms.		% Water and % Total Solids		Difference from known total solids	
		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
12	549	-	4.8365	-	0.0203	-	59.13 40.87	-	+0.715
13	611	-	4.8382	-	0.0186	-	59.24 40.76	-	+0.605
14	635	-	4.8390	-	0.0178	-	59.30 40.70	-	+0.545
15	710	-	4.8407	-	0.0161	-	59.53 40.47	-	+0.315
16	755	-	4.8395	-	0.0173	-	59.34 40.66	-	+0.505
17	778	-	4.8400	-	0.0168	-	59.37 40.63	-	+0.475
18	850	-	4.8400	-	0.0168	-	59.37 40.63	-	+0.475
19	870	-	4.8390	-	0.0178	-	59.30 40.70	-	+0.545

NOTE REGARDING EXPERIMENT D7 AND D10

In these experiments there was loss by blowing away of the Celite in the air current caused by the fan in the desiccator,and the tests were abandoned.

This is obviously a danger when a process of dynamic absorption is adopted, and the rate of stirring must therefore be carefully regulated.

Experiment D 4 :- DRYING BY DESICCATION

CONDITIONS.

ARRANGEMENT :- Static desiccation : two samples in separate desiccators.

DESICCANT :- Sulphuric acid, 1.84 sp. gr., 750 ccs. fresh acid per desiccator

ABSORBING MEDIUM :- Ignited Celite : 1.5 gms. per sample

DISHES :- Glass Petri dishes : nos.	(5)	(6)
mm. Diameter	92	82
mm. Depth	12	12
SAMPLE SURFACE EXPOSED : - Sq. cms.	66.5	52.8

SURFACE OF SULPHURIC ACID EXPOSED :- 188.7 sq.cms. per desiccator

	(5)	(6)
RATIO OF ABSORBENT TO SUGAR SOLN. :-	1.11 : 1	1.1 : 1
" " " " " SOLIDS :-	2.76 : 1	2.74 : 1

DISTANCE FROM SAMPLE TO DESICCANT : Approx. 50 mm.

	(5)	(6)
RATIO OF WATER TO DESICCANT :- Approx.	1 : 156	1 : 156
RATIO OF SURFACE EXPOSED : SAMPLE TO DESICCANT :-	1 : 2.8	1 : 3.6

The samples were finally transferred to desiccators each containing 1 lb. of fresh KOH pellets.

EXPERIMENT D4 :- DRYING BY DESICCATION OF 40.16 PER CENT GLUCOSE SOLUTION.

	(1)	(2)
Gms. Glucose solution taken	1.3505	1.3585
Weight of water present, gms.	0.8081	0.8129
" " solids " "	0.5424	0.5456
Weight of water added, gms.	4.0000	4.0000
Total gms. water present	4.8081	4.8129

No.	Drying Time Hours	Water left Gms. (1)	Water left Gms. (2)	Per cent water (1)	Per cent water (2)	Per cent Solids (1)	Per cent Solids (2)	Difference from known solids (1)	Difference from known solids (2)
1.	21	1.3790	1.0486	---	---	---	---	---	---
2.	43	0.0236	0.0197	58.09	58.39	41.91	41.61	+1.75	+1.45
3.	68	0.0123	0.0125	58.92	58.92	41.08	41.08	+0.84	+0.84
4.	94	0.0101	0.0112	59.09	59.02	40.91	40.98	+0.75	+0.82
5.	191	0.0081	0.0094	59.24	59.16	40.76	40.84	+0.60	+0.68
6.	216	0.0084	0.0089	59.21	59.20	40.79	40.80	+0.63	+0.64
7.	235	0.0071	0.0082	59.30	59.26	40.70	40.74	+0.54	+0.58
	Transferred to fresh KOH desiccators :								
8.	307	0.0076	0.0137	59.28	58.83	40.72	41.17	+0.56	+1.01
9.	377	0.0071	0.0096	59.30	59.14	40.70	40.86	+0.54	+0.70
10.	403	0.0056	0.0123	59.43	58.93	40.57	41.07	+0.41	+0.91
11.	475	0.0055	0.0089	59.43	59.20	40.57	40.80	+0.41	+0.64
12.	547	0.0106	0.0079	59.06	59.27	40.94	40.73	+0.78	+0.57
13.	569	0.0051	0.0071	59.46	59.32	40.54	40.68	+0.38	+0.52
14.	644	0.0051	0.0072	59.46	59.32	40.54	40.68	+0.38	+0.52

In this experiment there was a marked increase in water content when the samples were transferred to the fresh desiccators ; the known amount of water was not reached in either duplicate. The test extended over nearly 27 days.

EXPERIMENT D5 :- DRYING BY DESICCATION OF A 39.92 PER CENT SOLUTION OF LEVULOSE, USING VACUUM.

ARRANGEMENT :- One dish in Desiccator, above desiccant :

DESICCANT :- Sulphuric acid : 750 ccs., 1.84 sp.gr.:

ABSORBING MEDIUM :- Ignited Celite ; 1.5 gms.:

DISH :- Glass Petri dish ; 92.mm. diam. by 12 mm. deep :

DESICCATOR :- 15.5 cm. diam. Dome type : sample 25 mm. from desiccant:

PRESSURE IN DESICCATOR :- 15 cm. Hg.

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 66.48 sq.cm. to 188.7 sq. i.e. approx. 1 to 3 :

RATIO CELITE TO SUGAR TOTAL SOLIDS :- 2.83 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx.1 to 175 :

Levulose solution taken, gms.:- 1.3303 containing 0.7993 gm. water and 0.5310 gm. solids : 3.5 gms. water added,making 4.2993 gms.total water.

RESULTS

No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from known Total Solids
1	4	1.6435	2.6558	---	---	---
2	25	4.2835	0.0158	57.55	42.45	+ 2.53
3	29	4.2910	0.0083	59.46	40.54	+0.62
4	123	4.2965	0.0028	59.87	40.13	+0.21
5	148	4.2965	0.0028	59.87	40.13	+0.21
6	167	4.2988	0.0005	60.03	39.97	+0.05
7	192	4.2975	0.0018	59.95	40.05	+0.13

In this test the use of vacuum brought a result which was very near the known amount of water present : a week was required.

EXPERIMENT D6 :- DRYING BY DESICCATION OF A 39.92 PER CENT SOLUTION OF LEVULOSE WITH STIRRING OF THE DESICCATOR AIR.

ARRANGEMENT :- See Figures 59 and 62 : fan in desiccator :

DESICCANT :- Sulphuric acid : 750 ccs., 1.84 sp. gr.;

ABSORBING MEDIUM :- Ignited Celite : 1.5 gms. :

DISH :- Glass Petri dish ; 92 mm. diam. by 12 mm. deep :

SECOND DESICCATOR :- Dome type, 15.5 cm. diam. containing 500 gms. P_2O_5.

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 66.48 sq. cm. to 188.7 sq. cm., i.e. approx. 1 to 3 :

RATIO CELITE TO SUGAR TOTAL SOLIDS :- 2.82 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 to 175 : sample 25 mm. from desiccant :

FAN :- Approx. 50 mm. from sample : 270 r.p.m.

Levulose solution taken, gms. :- 1.3363 containing 0.8029 gm. water and 0.5334 gm. solids : 3.5 gms. water added, making 4.3029 gms. total water.

RESULTS

No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from known Total Solids
1	155 mins.	3.8471 (89.4%)	0.4558	25.96	74.04	---
2	94.5 hrs.	4.2967	0.0062	59.61	40.39	+ 0.47
3	118.5 "	4.2971	0.0058	59.65	40.35	+ 0.43
4	Transferred to second desiccator : P_2O_5, without stirring :					
	166	4.2998	0.0031	59.82	40.18	+ 0.26
5	308	4.3013	0.0016	59.95	40.05	+ 0.13
6	332	4.3025	0.0004	60.10	39.90	− 0.02

Note the rapid removal of 89.4 per cent of the total water present (in 155 minutes), due to the stirring of the desiccator air.

EXPERIMENT D8 :)- DRYING BY DESICCATION OF A 39.92 PER CENT SOLUTION OF LEVULOSE WITH STIRRING OF THE DESICCATOR AIR.

ARRANGEMENT :- See Figures 59 and 62 : fan in desiccator :

DESICCANT :- Fresh sulphuric acid : 750 ccs. : 1.84 sp. gr. :

ABSORBING MEDIUM :- Ignited sand : 9 gms. :

DISH :- Glass Petri dish : 82 mm. diam. by 13 mm. deep :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 52.8 sq. cm. to 188.7 sq. cm., i.e. approx 3.6 to 1 of sample :

RATIO SAND TO SUGAR TOTAL SOLIDS :- 16.85 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 to 268 : sample 25 mm. from desiccant :

FAN :- approx 50 mm. from sample : 270 r.p.m.

Levulose solution taken, gms. :- 1.3383 gms. containing 0.8041 gm. water and 0.5342 gm. solids : 2.0 gms. water added, making 2.8041 gms. total water.

No.	Time Hours	Water lost, gms.	Water left, gms.	RESULTS. Per cent Water	Per cent Solids	Difference	Per cent water removed total	in hour
1.	1	1.6998	1.1043	---	---	---	60.61	60.61
2.	2	2.5198	0.2843	39.02	60.98	+21.06	89.86	29.25
3.	3	2.7373	0.0668	55.09	44.91	+ 4.99	97.16	7.30
4.	4	2.7525	0.0516	56.22	43.78	+ 3.86	98.17	1.01
5.	5	2.7578	0.0463	56.62	43.38	+ 3.46	98.58	0.41
6.	72	2.7798	0.0243	58.25	41.75	+ 1.83	---	---
7.	96	2.7838	0.0203	58.56	41.44	+1.52	---	---
8.	118	2.7865	0.0176	58.76	41.24	+ 1.32	---	---
9.	144	2.7873	0.0168	58.83	41.17	+ 1.25	---	---
10.	218	2.7889	0.0152	58.93	41.07	+ 1.15	---	---
11.	240	2.7943	0.0098	59.34	40.66	+ 0.74	---	---
12.	262	2.7950	0.0091	59.40	40.60	+ 0.68	---	---
13.	334	2.7955	0.0086	59.44	40.56	+ 0.64	---	---
14.	379	2.7958	0.0083	59.46	40.54	+0.62	---	---
15.	527	2.7926	0.0115	59.21	40.79	+ 0.87	---	---
16.	599	2.7926	0.0115	59.21	40.79	+ 0.87	---	---
17.	692	2.7930	0.0111	59.26	40.74	+0.82	---	---
18.	788	2.7933	0.0108	59.28	40.72	+0.80	---	---
19.	2423	2.7958	0.0083	59.46	40.54	+0.62	---	---

The difference column shows the difference from the known total solids.

EXPERIMENT D9 :)- DRYING BY DESICCATION OF A 39.92 PER CENT SOLUTION OF LEVULOSE WITH STIRRING OF THE DESICCATOR AIR.

ARRANGEMENT :- See Figures 59 and 62 : fan in desiccator :

DESICCANT :- Sulphuric acid, once used : 750 ccs. : 1.84 sp.gr. :

ABSORBING MEDIUM :- Ignited Celite : 1.5 gms. :

DISH :- Glass Petri dish : 92 mm. diam. by 12 mm. deep :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 66.48 sq. cms. to 188.7 sq. cm., i.e., approx. 1 to 3 :

RATIO CELITE TO SUGAR TOTAL SOLIDS :- 2.78 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 to 178 : sample 25 mm. from desiccant :

FAN :- approx. 50 mm. from sample : 200 r.p.m.

Levulose solution taken :- 1.3467 gms. containing 0.8089 gm. water, and 0.5378 gm. solids : 3.5 gms. water added, making 4.3089 gms. total water.

No.	Drying Time Hours	Water lost gms.	RESULTS Water left gms.	RESULTS Per cent Water	Per cent Total Solids	Difference from known Total Solids
1	4.5	4.3007	0.0082	59.44	40.56	+ 0.64
2	22.0	4.3069	0.0020	59.89	40.11	+ 0.19
3	26.0	4.3059	0.0030	59.82	40.18	+ 0.26
4	46.5	4.3069	0.0020	59.89	40.11	+ 0.19

The results of experiments D8 and D9 show that there is a great acceleration of the rate of removal of water from the samples by the stirring of the desiccator air. There is risk in this stirring that the light Celite may be blown from the dish ; for this reason the spedd of the fan was reduced to 200 r.p.m. from 270 r.p.m.

EXPERIMENT D11 :- DRYING BY DESICCATION OF A 40.156 PER CENT SOLUTION OF GLUCOSE WITH STIRRING OF DESICCATOR AIR.

ARRANGEMENT :- Stirring of desiccator air for the first 7 hours only : fan in desiccator as in Figures 59 and 62 :

DESICCANT :- Fresh sulphuric acid : 750 ccs. : 1.84 sp. gr. :

ABSORBING MEDIUM :- Ignited Celite : 1.5 gms. :

DISH :- Glass Petri dish : 82 mm. diam. by 13 mm. deep :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 52.8 sq. cm. to 188.7 sq. cm., i.e., approx. 1 to 3.6 ;

RATIO CELITE TO SUGAR TOTAL SOLIDS :)- 2.84 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 to 175 : sample 25 mm. from desiccant :

FAN :- approx. 50 mm. from sample : 20 r.p.m.

Glucose solution :- 1.3285 gms. taken, containing 0.7948 gm. water and 0.5337 gm. solids : 3.5 gms. water added, making 4.2948 gms. total water

			RESULTS			
No.	Drying Time Hours	Water lost gms.	Water left gms.	per cent Water	Per cent Total Solids	Difference from known Total Solids
1	7	2.1760	2.1188	---	---	---
2	22	4.2800	0.0148	58.70	41.30	+ 1.144
3	48	4.2855	0.0093	59.13	40.87	+0.714
4	71	4.2825	0.0123	58.89	41.11	+0.954
5	146	4.2855	0.0093	59.13	40.87	+0.714
6	191	4.2860	0.0088	59.16	40.84	+0.684
7	315	4.2873	0.0075	59.27	40.73	+0.574
8	387	4.2880	0.0068	59.30	40.70	+0.544
9	481	4.2866	0.0082	59.20	40.80	+0.644
10	577	4.2878	0.0070	59.29	40.71	+0.554
11	2212	4.2873	0.0075	59.27	40.73	+0.574

It is clear from the above results that there is a very slow interchange of water between the sample and the desiccant in the latter stages of drying . This sample did not dry down to its expected total solids.

EXPERIMENT D12 :- DRYING BY DESICCATION OF A 40.156 PER CENT SOLUTION OF GLUCOSE WITH STIRRING OF THE DESICCATOR AIR.

ARRANGEMENT :- Stirring of desiccator air for the first 5 hours only. Fan in desiccator as in Figures 59 and 62 :

DESICCANT :- Fresh sulphuric acid : 750 ccs. : 1.84 sp. gr. :

ABSORBING MEDIUM :- Ignited Celite : 1.5 gms. :

DISH :- Glass Petri dish : 92 mm. diam. by 12 mm. deep :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 66.48 sq. cm. to 188.7 sq. cm., i.e., approx. 1 to 3 :

RATIO CELITE TO SUGAR TOTAL SOLIDS :- 2.88 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 to 175 : sample 25 mm. from desiccant.

SECOND DESICCATOR:- The samples were transferred to a KOH desiccator containing 500 gms. fresh KOH pellets after 5 hours :

FAN :- approx 50 mm. from sample : 140 r.p.m.

Glucose Solution :- 1.2968 gms. taken, containing 0.7760 gm. water and 0.5208 gm. solids: 3.5 gm. water added making 4.2760 gm. total water.

RESULTS

No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from known Total Solids
1	5	4.2575	0.0185	58.41	41.59	+1.434
2	25	4.2611	0.0149	58.69	41.31	+1.154
3	48	4.2630	0.0130	58.83	41.17	+1.014
4	123	4.2642	0.0118	58.92	41.08	+0.924
5	168	4.2652	0.0108	59.00	41.00	+0.844
6	195	4.2605	0.0155	58.64	41.36	+1.204
7	289	4.2640	0.0120	58.91	41.09	+0.934
8	361	4.2652	0.0105	59.00	41.00	+0.844
9	455	4.2655	0.0095	59.03	40.97	+0.814
10	551	4.2665	0.0095	59.10	40.90	+0.744
11	2187	4.2695	0.0065	59.33	40.67	+0.514

In this experiment there was considerable regaining of weight after some of the time periods.

EXPERIMENT D13 :- DRYING BY DESICCATION - DETERMINATION OF PER CENT MOISTURE IN A BRITISH WEST INDIAN RAW SUGAR.

ARRANGEMENT :- Stirring of desiccator air : no absorbing medium used:

DESICCANT :- Fresh sulphuric acid : 750 ccs. : 1.84 sp. gr.

	No. (1)	No.(2)
DISH :- Glass Petri dishes :-		
Diameter,mm.	92	82
Depth, mm.	12	13
SAMPLE SURFACE EXPOSED :- Sq.cm.	66.48	52.81
SULPHURIC SURFACE EXPOSED:- " "	188.7	188.7
RATIO OF SURFACE EXPOSED SAMPLE TO DESICCANT :-	1 : 3	1 : 3.6
RATIO WATER TO DESICCANT :-	1 : 1316	1 : 1363
FAN :- 50 mm. from sample:- r.p.m.	140	200
DISTANCE SAMPLE TO DESICCANT:-	approx. 25 mm.	

B. W. I. SUGAR :- 5 gms. weighed into each dish: no water added :

	1.	RESULTS		2.		
No.	Drying Time Hours	Loss in weight Gms.	per cent Water	Drying Time Hours	Loss in weight Gms.	per cent Water
1	3	0.0192	0.384	4	0.0195	0.390
2	7	0.0202	0.404	7	0.0202	0.404
3	24.5	0.0222	0.444	76	0.0235	0.470
4	100	0.0215	0.430	122	0.0247	0.494
5	146	0.0240	0.480	150	0.0247	0.494
6	174	0.0240	0.480	244	0.0247	0.494
7	270	0.0240	0.480	317	0.0247	0.494
8	342	0.0244	0.488	338	0.0250	0.500
9	366	0.0238	0.476	410	0.0248	0.496
10	435	0.0246	0.492	506	0.0259	0.518
11	531	0.0250	0.500	2142	0.0275	0.550
12	2167	0.0285	0.570	-	-	-

This sugar showed 0.802 per cent moisture by vacuum oven drying at 70°C. No attempt was made to grind the sugar. The absorptive power of sulphuric acid of this strength is apparently not enough to withdraw the occluded moisture from the sugar crystals. The tests lasted 90 days.

EXPERIMENT D14 :- DRYING BY DESICCATION OF GOLDEN SYRUP WITH STIRRING OF THE DESICCATOR AIR.

ARRANGEMENT :- Fan in desiccator as in Figures 59 and 62 :

DESICCANT :- Fresh sulphuric acid : 750 ccs.: 1.84 sp.gr. :

ABSORBING MEDIUM :- Ignited Celite : 1.5 gms. :

DISH :- Glass Petri dish : 82 mm. diam. by 13 mm. deep :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 52.8 sq. cm. to 188.7 sq. cm., i.e., approx. 1 to 3.6 :

RATIO CELITE TO TOTAL SUGAR SOLIDS :- 2.45 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 to 182 : sample 25 mm. from desiccant :

FAN :- approx. 50 mm. from sample : 200 r.p.m.

Golden Syrup :- 0.7375 gm. taken, containing 0.1254 gm. water and 0.6121 gm. solids (at 17.00 per cent water in syrup) : 4 gms. water added, making 4.1254 gms. total water present.

			RESULTS			
No.	Drying Time Hours	Water lost gms.	Water left gms.	per cent Water	per cent Total Solids	Difference from known Total Solids
1	7 stirring	4.1023	0.0231	13.87	86.13	+ 3.13
2	24 static	4.1110	0.0144	15.05	84.95	+ 1.95
3	31 stirring	4.1113	0.0141	15.09	84.91	+ 1.91
4	48 static to end	4.1126	0.0128	15.26	84.74	+ 1.74
5	77	4.1130	0.0124	15.32	84.68	+ 1.68
6	173	4.1153	0.0101	15.63	84.37	+1.37
7	245	4.1158	0.0096	15.70	84.30	+1.30
8	338	4.1170	0.0084	15.86	84.14	+1.14
9	434	4.1182	0.0072	16.03	83.97	+0.97
10	2070	4.1208	0.0046	16.38	83.62	+0.62

It is probable that the low result here is due to the inability of the desiccant to abstract the moisture in the interior of the dried syrup due possibly to the viscous films at the surface.

EXPERIMENT D15 :- DRYING BY DESICCATION OF A 40.155 PER CENT SUCROSE SOLUTION WITH STIRRING OF DESICCATOR AIR.

ARRANGEMENT :- Fan in desiccator as in Figures 59 and 62 : two sampl in separate desiccators :

DESICCANT :- Fresh sulphuric acid : 750 ccs. in each desiccator : 1.84 sp. gr.

	No. (1)	No. (2)
DISHES :- Glass Petri dishes :-		
Diameter, mm.	92	82
Depth, mm.	12	13
SAMPLE SURFACE EXPOSED, SQ. CM. :-	66.48	52.8
SULPHURIC SURFACE EXPOSED, SQ. CM. :-	188.7	188.7
RATIO OF SURFACE EXPOSED SAMPLE TO DESICCANT :-	1 : 2.8	1 : 3.6
RATIO WATER TO DESICCANT :-	1 : 175	1 : 175
FAN :- 50 mm. from samples :- r.p.m.	200	200
DISTANCE SAMPLE TO DESICCANT :- approx. 25 mm.		
RATIO CELITE TO SUGAR TOTAL SOLIDS :-	2.87 : 1	2.71 : 1

		No. (1)	No. (2)
Sucrose Solution :-	Gms. taken	1.3040	1.3798
	Water present, gms.	0.7805	0.8256
3.5 gms. water added	Total solids, gms.	0.5235	0.5542
to each sample	Total water, gms.	4.2805	4.3256

RESULTS

		(1)				(2)			
No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Water lost gms.	Water left gms.	Per cent Water	Per cent T.Solids
1	7 BOTH WITH STIRRING	4.2568	0.0237	58.05	41.95	2.0248	2.3008	---	---
2	14	4.2685	0.0120	58.95	41.05	4.2950	0.0306	57.61	42.39
3	48 STATIC	4.2703	0.0102	59.06	40.94	4.3100	0.0156	58.69	41.31
4	55	4.2720	0.0085	59.21	40.79	---	---	---	---
5	124	4.2735	0.0070	59.33	40.67	4.3158	0.0098	59.12	40.88
6	196	4.2747	0.0058	59.41	40.59	4.3168	0.0088	59.19	40.81
7	220	4.2738	0.0067	59.34	40.66	4.3163	0.0093	59.16	40.84
8	290	4.2745	0.0060	59.40	40.60	4.3173	0.0083	59.23	40.77
9	386	4.2740	0.0065	59.36	40.64	4.3162	0.0094	59.14	40.86
10	2022	4.2748	0.0057	59.41	40.59	---	---	---	---

The nearest approach to the known total solids still left 0.435 per cent of water in the sample.

EXPERIMENT D16 :- DRYING BY DESICCATION OF GOLDEN SYRUP USING BOTH STIRRING AND VACUUM TO AID DRYING.

ARRANGEMENT :- Fan in vacuum desiccator with mercury gland seal as shown in Figures 59 and 62 :

DESICCANT :- Sulphuric acid : 1000 ccs. : 1.84 sp. gr. :

DISH :- Glass Petri dish : 92 mm. diam. by 12 mm. deep :

ABSORBING MEDIUM :- Ignited Celite : 1.5 gms. :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 66.48 sq. cm. to 188.7 sq. cm., i.e., approx 1 to 3 :

RATIO CELITE TO SUGAR TOTAL SOLIDS :- 3.28 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx 1 to 191 : sample 25 mm. from desiccant :

Fan :- Approx. 50 mm. from sample : 200 r.p.m. :

Vacuum :- 60 - 61 cm. mercury.

Golden Syrup :- 0.5518 gm. taken, containing 0.0938 gm. water, and 0.4580 gm. solids (allowing 17.00 per cent water in the syrup). Water added - 5.2505, giving a total of 5.3443 gms. water present.

RESULTS

No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from average Total Solids
1	1	1.1168	4.2275	-	-	-
2	2	2.3755	2.9688	-	-	-
3	3	3.5106	1.8337	-	-	-
4	4	4.3088	1.0355	-	-	-
5	5	5.0638	0.2805	-	-	-
6	6	5.3098	0.0345	10.75	89.25	+6.25
7	7	5.3121	0.0322	11.16	88.84	+5.84
8	8	5.3210	0.0233	12.77	87.23	+4.23

One of the difficulties with golden syrup is the large amount of water necessary to mix the syrup thoroughly with the Celite. Most of the work of the sulphuric acid is done in removing this added water. It is probable that the difficulty of penetrating the surface film of the syrup at room temperature makes this method unsuitable for viscous syrups such as this.

EXPERIMENT D17 :- DRYING BY DESICCATION OF GOLDEN SYRUP USING AN AIR CIRCULATING SYSTEM (SEE FIGURE 62).

ARRANGEMENT :- The air circulating system was connected to the desiccator containing the sample, and air was circulated in closed circuit at the rate of approximately 420 ccs. per minute.

The fan was kept going at the same time. The desiccant was 1000 ccs. fresh sulphuric acid with surface exposed of 188.7 sq. cm. The dish was a glass Petri dish 82mm. diameter by 13 mm. deep, and the absorbing medium was 20 gms, of ignited sand. Ratio water to sulphuric was 1 : 161, and the ratio of absorbent to sugar was 44 : 1.

The combination of fan stirring (200 r.p.m.) and circulating pump was in operation for the first 51 hours of this test.

Golden Syrup :- 0.5480 gm. taken containing 0.0932 gm. water and 0.4543 gm solids : 6.1315 gm. water added : total water 6.2247 gms.

RESULTS

No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from estimated Total Solids
1	1	0.3389	5.8858	-	-	-
2	2	0.6850	5.5397	-	-	-
3	26	0.7000	5.5247	-	-	-
4	27	1.7357	4.4890	-	-	-
5	28	2.8405	3.3842	-	-	-
6	29	4.1870	2.0377	-	-	-
7	30	5.0449	1.1798	-	-	-
8	31	5.6740	0.5507	-	-	-
9	49	6.1948	0.0299	11.55	88.45	+ 5.45
10	50	6.1935	0.0314	11.32	88.68	+ 5.68
11	51	6.1893	0.0354	10.54	89.46	+ 6.46
12 Days	5	6.2002	0.0245	12.54	87.46	+ 4.46
13 "	6	6.2013	0.0234	12.74	87.26	+ 4.26
14 "	7	6.2026	0.0221	12.97	87.03	+ 4.03
15 "	8	6.2047	0.0200	13.36	86.64	+ 3.64
16 "	11	6.2055	0.0192	13.50	86.50	+ 3.50
17 "	13	6.2067	0.0180	13.72	86.28	+ 3.28
18 "	28	6.2100	0.0147	14.32	85.68	+ 2.68
19 "	47	6.2110	0.0137	14.51	85.49	+ 2.49
20 "	182	6.2135	0.0112	14.96	85.04	+ 2.04
21 "	526	6.2193	0.0054	16.03	83.97	+ 0.97
22 "	1173	6.2053	0.0194	13.47	86.53	+ 3.53

The conclusions already drawn are borne out in this test- i.e., that it is extremely difficult to dry Golden Syrup completely at room temperature. After 16 months of desiccation, 16.03 per cent water is shown compared with the estimated 17.00 per cent.

EXPERIMENT D18 :- DRYING BY DESICCATION OF GOLDEN SYRUP UNDER STATIC CONDITIONS USING SULPHURIC ACID AND PHOSPHORUS PENTOXIDE.

ARRANGEMENT :- Glass desiccator containing 1000 ccs. fresh sulphuric acid of 1.84 sp.gr.and with 188.7 sq.cms. of surface exposed. The dish used was a glass Petri dish 82 mm. diameter by 13 mm. deep, and the absorbing medium was 20 gms. of ignited sand. Ratio of water to sulphuric acid was 1 : 162, and the ratio of absorbent to sugar solids was 30.4 : 1. The sample surface exposed was 52.8 sq. cms.giving a ratio to desiccant of 1 : 3.6.

SECOND DESICCATOR :- This contained 500 gms. of phosphorus pentoxide mixed with an equal volume of ignited Celite.

Golden Syrup :- 0.7945 gm. taken containing 0.1351 gm. water and 0.6594 gm. solids : 6.0215 gms. water added giving 6.1566 gms. total water.

				RESULTS		
No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from Estimated Total Solids
1	1	0.1272	6.0294	-	-	-
2	2	0.2205	5.9361	-	-	-
3	3	0.3505	5.8061	-	-	-
4	4	0.4773	5.6793	-	-	-
5	5	0.5875	5.5691	-	-	-
6	6	0.7078	5.4488	-	-	-
7	7	0.8428	5.3138	-	-	-
8	8	0.9445	5.2121	-	-	-
9	24	2.4235	3.7331	-	-	-
10	46	4.5080	1.5486	-	-	-
11	94	6.1128	0.0438	11.49	88.51	+ 5.51
12	166	6.1220	0.0346	12.65	87.35	+ 4.35
13	Transferred to P_2O_5 desiccator					
	218	6.1257	0.0309	13.11	86.89	+ 3.89
14	576	6.1325	0.0241	13.97	86.03	+ 3.03
15	Days 46	6.1341	0.0255	14.17	85.83	+ 2.83
16	" 181	6.1400	0.0166	14.91	85.09	+ 2.09
17	" 525	6.1455	0.0111	15.61	84.39	+ 1.39
18	" 1172	6.1285	0.0281	13.47	86.53	+ 3.53

The best result was obtained at Weighing No. 17 after 17 months, but there is a wide divergence from the estimated solids in the syrup. (= 83.00 per cent.).

It is evident that static desiccation is far too slow a method, and that there is no means of judging when a particular drying may reasonably be assumed to be complete.

EXPERIMENT D19 :- DRYING BY DESICCATION OF GOLDEN SYRUP USING VACUUM

ARRANGEMENT :- Glass desiccator with sample above desiccant : vacuum pump kept running throughout : 67-70 cms. vacuum :

DESICCANT :- Fresh sulphuric acid : 1000 ccs. : 1.84 sp.gr. :

DISH :- Glass Petri dish : 92. mm. diameter by 12 mm. deep :

ABSORBING MEDIUM :- Ignited sand : 20 gms. :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 66.48 sq. cm. to 188.7 sq. cm., i.e., approx. 1 to 3 :

RATIO SAND TO SUGAR TOTAL SOLIDS :- 22.9 ; 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 : 162 : sample 25 mm. from desiccant :

RATIO OF SYRUP TO DESICCANT :- approx 19 : 1 .

Golden Syrup :- 1.0497 gm. taken, containing 0.17485 gm. water, and 0.87485 gm. solids (allowing 17.00 per cent water in the syrup). Water added 6.0248 gms., giving a total of 6.2032 gms. water present.

RESULTS

No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from estimated Total Solids
1	2	5.4350	0.7682	-	-	-
2	3	6.0940	0.1092	6.59	93.61	+10.61
3	4	6.1180	0.0852	8.88	91.12	+ 8.12
4	5	6.1250	0.0782	9.54	90.46	+ 7.46
5	6	6.1280	0.0752	9.83	90.17	+ 7.17
6	7	6.1338	0.0684	10.38	89.62	+ 6.62
7	8	6.1365	0.0667	10.64	89.36	+ 6.36
8	Days 22	6.1630	0.0402	13.16	86.84	+ 3.84
9	" 42	6.1647	0.0385	13.32	86.68	+ 3.32
10	" 176	6.1755	0.0277	14.35	85.65	+ 4.35
11	" 520	6.2060	0.0028	17.26	82.74	- 0.26

In this experiment there appeared to be complete absorption of all the water in the syrup, but 520 days were required to achieve this

EXPERIMENT D20 :- DRYING BY DESICCATION OF GOLDEN SYRUP USING VACUUM AND INCREASED RATIO OF SAND TO SYRUP.

ARRANGEMENT:- As in Experiment D18, with increased amount of sand :

DESICCANT :- Fresh sulphuric acid : 1000 ccs. : 1.84 sp. gr. :

DISH :- Glass Petri dish : 90 mm. diameter by 12 mm. deep :

ABSORBING MEDIUM :- Ignited sand, 20 gms. :

RATIO SAMPLE SURFACE TO SULPHURIC SURFACE :- 63.6 sq. cms. to 188.7 sq. cms., i.e., approx 1 to 3 :

RATIO SAND TO SUGAR TOTAL SOLIDS :- 44.2 to 1 :

RATIO WATER TO SULPHURIC ACID :- approx. 1 : 160 : sample 25 mm. from desiccant :

RATIO OF SYRUP TO DESICCANT :- approx 1 to 37 :

VACUUM PUMP :- 65.70 cms. vacuum : pump kept running throughout test.

Golden Syrup :- 0.5450 gm. taken, containing 0.09265 gm. water, and 0.45235 gm. solids (allowing 17.00 per cent water in the syrup). Water added, 6.1585 gms., giving a total of 6.2512 gms. water present.

			RESULTS			
No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from estimated Total Solids
1	1	1.5080	4.7432	-	-	-
2	2	5.2947	0.9565	-	-	-
3	3	6.2100	0.0412	9.45	90.55	+7.55
4	4	6.2173	0.0339	10.79	89.21	+6.21
5	5	6.2210	0.0302	11.47	88.53	+5.53
6	21	6.2548	0.0036	17.67	82.33	-0.67
7	Static drying without vacuum 21 Days	6.2555	0.0043	17.80	82.20	-0.80

This result is surprisingly good, and in view of the difficulty in the previous tests in getting down to the known composition of the sample it must be regarded with reserve - the constant suck of the vacuum pump may have removed some solid matter.

EXPERIMENT D21 :- VACUUM OVEN DRYING OF GOLDEN SYRUP AT LOW TEMPERATURES.

ARRANGEMENT :- Using vacuum-oven shown in Figure 36 : one sample dried at 36°C., and the other at 50°C.

ABSORBING MEDIUM :- Ignited sand - 40 gms. :

DISHES :- Glass Petri dishes :-	No. (1)	No. (2)
Diameter, mm.	92	82
Depth, mm.	12	13
SAMPLE SURFACE EXPOSED, SQ. CM. :-	66.48	52.8
RATIO ABSORBENT TO SUGAR SOLIDS :-	107 : 1	100 : 1

VACUUM :- 70.72 cms. **ROOM TEMPERATURE :-** 16°C.

BAROMETRIC PRESSURE :- 757.5 mm.

Golden Syrup :-		
Gms. Taken	0.4515	0.4800
Water present, gms.	0.0768	0.0816
Total Solids, gms.	0.3747	0.3984
Water added, gms.	12.2903	12.1138
Gms. Total water present,	12.3671	12.1954

No.	Drying Time Hours	36°C. Water lost gms.	RESULTS Water left gms.	Per cent Water	80°C. Per cent Total Solids	Difference from Total Solids known present
1	5	12.3638	0.0033	16.28	83.72	+0.72
2	7	12.3653	0.0018	16.62	83.38	+0.38
3	10	12.3664	0.0007	16.86	83.14	+0.14
		50°C.				
1	1	11.8835	0.3119	-	-	-
2	2	12.1950	0.0004	16.92	83.08	+0.08
3	3	12.1945	0.0009	16.82	83.18	+0.18
4	4	12.1990	- 0.0036	17.75	82.25	- 0.75
5	5	12.1983	- 0.0029	17.61	82.39	-0.61

The rate of loss of water is slow at 36°C. It appears to be satisfactory at 50°C., but the per cent loss is decidedly high for this sample of syrup. The use of the vacuum-oven at 50°C. gives much quicker results.

EXPERIMENT D22 :- VACUUM OVEN DRYING OF GOLDEN SYRUP AT 50°C.

ARRANGEMENT :- Using vacuum-oven shown in Figure 36 : duplicate samples dried on sand :

ABSORBING MEDIUM :- Ignited sand : 20 gms. :

DISHES :- Glass Petri dishes :-	No. (1)	No.(2)
Diameter, mm.	82	82
Depth, mm.	13	12
SAMPLE SURFACE EXPOSED, SQ. CM. :-	52.8	52.8
RATIO ABSORBENT TO SUGAR SOLIDS :-	49.7 : 1	54.1 : 1
VACUUM :- 72 cms. **ROOM TEMPERATURE :-** 15.5°C.		
BAROMETRIC PRESSURE :-	759.5 mm.	756 mm.
Golden Syrup :- Gms. taken	0.4839	0.4457
Water present, gms.	0.0823	0.0758
Total solids, gms.	0.4016	0.3699
Water added, gms.	6.1240	12.0895
Gms. Total water present,	6.2063	12.1653

RESULTS

No.	Drying Time Hours	Water lost gms.	Water left gms.	Per cent Water	Per cent Total Solids	Difference from known Total Solids
			(1)			
1	1	6.1954	0.0109	14.76	85.24	+2.24
2	2	6.2052	0.0011	16.78	83.22	+0.22
3	3	6.2015	0.0048	16.02	83.98	+0.98
4	4	6.2037	0.0026	16.47	83.53	+0.53
5	5	6.2065	-0.0002	17.05	82.95	-0.05
6	6	6.2088	-0.0025	17.53	82.47	-0.53
7	7	6.2070	-0.0007	17.16	82.84	-0.16
			(2)			
1	1	12.1544	0.0109	14.55	85.45	+2.45
2	2	12.1675	-0.0022	17.50	82.50	-0.50
3	3	12.1657	-0.0004	17.10	82.90	-0.10
4	4	12.1692	-0.0039	17.88	82.12	-0.88

The results approach the theoretical in from 2 - 5 hours, and fluctuate rather considerably from hour to hour : it seems probable that oxidation is also taking place.

Drying of Levulose Solutions by Desiccation at room temperature (17°C).

(a) Samples in separate desiccators - % solids found.

Hours contact	50.69 on Celite over H_2SO_4	17.005 on Celite over KOH	Hours contact	50.69 on Celite over KOH	17.005 on Celite over H_2SO_4
24	52.15	60.49	168	84.70	1
90	51.20	17.31	285	51.41	17.44
120	51.16	17.28	333	51.28	17.07
144	-	17.26	453	51.23	17.04
263	-	17.22	978	51.15	17.07
311	-	17.21	1844	50.79	16.97
431	-	17.21	2823	50.76	16.98
956	-	17.14			
1822	-	17.08			
2801	-	17.04			

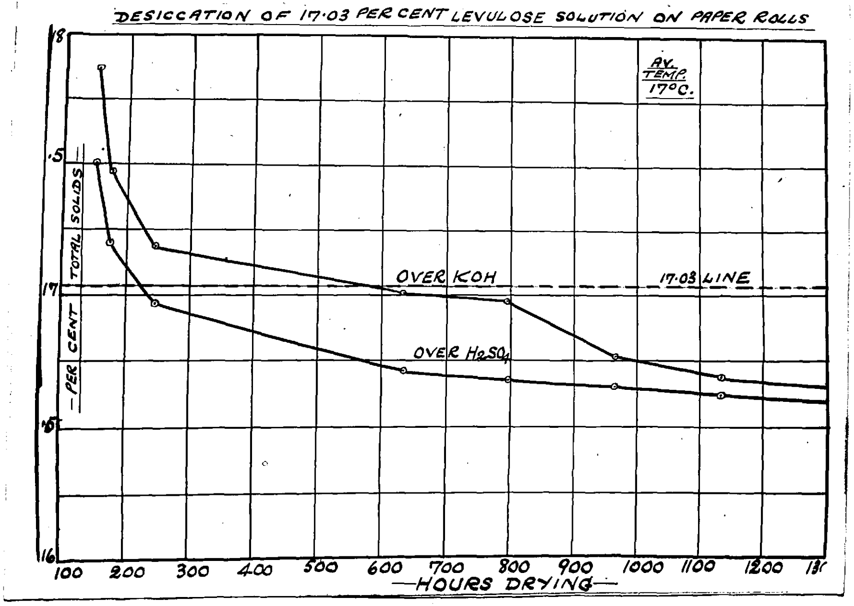


Figure 63.

Drying of Levulose Solutions by Desiccation at room temperature (17°C)

(b) Samples paired in same desiccators (all on celite) - % Solids Found

Hours Contact	Over H_2SO_4		Hours Contact	Over KOH	
	50.69%	17.005%		50.69%	17.005%
18	60.85	51.59	22	74.44	60.79
41	56.75	20.17	46	58.02	21.35
109	51.27	17.21	112	52.32	17.32
139	51.15	17.14	142	51.23	17.25
164	51.12	17.15	166	51.24	17.33
281	50.91	17.10	285	51.09	17.21
329	50.87	17.09	333	51.06	17.20
449	50.87	17.08	453	51.00	17.20
974	50.80	17.10	978	50.74	17.14
1840	50.69	17.06	1844	50.55	17.08
2819	50.76	17.08	2823	50.58	17.07

Drying of Levulose Solutions by Desiccation at room temperature (17°C)

(c) Four samples in one desiccator over 500 ccs. H_2SO_4, all 50.69% Levulose solution. No water added. - % Solids Found.

Hours Contact	On Sand	On Pumice	Hours Contact	On Celite I	On Celite II
29	67.50	71.15	64	72.60	66.88
53	57.16	56.34	94	61.00	62.11
171	54.52	54.14	118	53.85	54.29
195	54.22	53.90	236	51.32	51.11
315	53.90	53.65	284	51.26	51.09
840	53.63	53.12	404	51.13	50.94
1705	52.91	52.79	929	51.13	50.78
2684	52.59	52.66	1794	51.18	50.65
			2773	51.09	50.58

These results show the importance of a suitable adsorbing agent: here celite has proved better than sand or pumice in the same desiccator. The explanation possibly lies in occlusion by the sand or pumice and better porosity with the celite. The final figure 50.58% is below the 50.69% of the original solution; probably water of crystallisation was then coming off. The whole process is too slow for ordinary routine work.

Desiccation of 17.03% Levulose Solution on Paper Rolls at room temperature.

Two samples of 3.6-3.8 gms. levulose solution without addition of water was dropped on to paper rolls in 65 x 35 mms. glass weighing bottles. These were placed in desiccators - one containing 500 ccs. of concentrated sulphuric acid - the other with 500 gms. of KOH pellets.

Hours Contact	Per cent Solids Found.	
	Over H_2SO_4	Over KOH
150	17.51	17.87
173	17.20	17.37
245	16.97	17.18
631	16.72	17.01
797	16.70	16.88
966	16.65	16.76
1133	16.62	16.68
1301	16.60	16.67
1472	16.60	16.63
1637	16.60	16.51
1808	(discarded)	16.50
1873	-	16.47
2518	-	16.43
3382	-	16.33
4374	-	16.32

THE DRYING OF SUGAR SOLUTIONS BY DESICCATION AT LOW TEMPERATURES

No.	Mode of Desiccation	Sugar Dried	% Water present	% Water found	After hrs. Drying	Ratio Absorbent; Sugar Solids	Ratio Water to Desiccant	Surfaces Ratio S : D	Gms. Water added	Gms. Absorbent	Desiccant cc. H_2SO_4	Dish diam. mms.	Gms. Solids weighed	Gms. Water present
1	Static over H_2SO_4 : 2 in 1 desiccator	Levulose soln.	39.92	(1) 40.39 (2) 39.88	788 285	Approx. 4 : 1 (celite)	1 : 76	1 :5.1	9 9	2.5 2.5	1500	82	0.6024 0.6259	0.9061 0.9421
2	as above	"	39.92	(1) 39.97 (2) 39.90	287 500	Approx. 3 : 1 (celite)	1 : 316	1 : 5	4 4	1.5 1.5	1500	82	0.4963 0.5058	0.7464 0.7609
3	as above	Sucrose Soln.	40.16	(1) 40.05 (2) 40.47	451 710	Approx. 2.8 : 1 (celite)	1 : 155	1 :4.6	4 4	1.5 1.5	750	72 (Al)	0.5250 0.5580	0.7830 0.8568
4	Static in separate desiccators	Glucose Soln.	40.16	(1) 40.54 (2) 40.68	644 644	2.8 : 1 (celite)	1 : 156	1:2.8 1:3.6	4 4	1.5 1.5	750	92 82	0.5424 0.5456	0.8081 0.8029
5	Vacuum Desiccation	Levulose Soln.	39.92	(1) 39.97	167	2.8 : 1 (celite)	1 : 175	1 : 3	3.5	1.5	750	92	0.5310	0.7993
6	With Stirring	"	39.92	(1) 39.90	332	2.8 : 1 (celite)	1 : 175	1 : 3	3.5	1.5	750	92	0.5334	0.8029
7	"	"	39.92	(1) 37.83	(Discarded after 3 hrs.- Loss by air current).		---	---	3.5	1.5	750	82	0.5940	0.8943
8	" (using sand)	"	39.92	(1) 40.54	2423	16.9 : 1	1 : 268	1 :3.6	2.0	9.0	750	82	0.5342	0.8041
9	" (celite)	"	39.92	(1) 40.11	22	2.8 : 1	1 : 178	1 : 3	3.5	1.5	750	92	0.5378	0.8089
10	"	Sucrose Soln.	40.16	(1) 37.10	(Discarded after 5 hours)		---	---	3.5	1.5	750	82	0.5027	0.7491

No.	Mode of Desiccation	Sugar Dried	% Water present	% Water Found	After hrs. Drying	Ratio Absorbent : Sugar Solids	Ratio of Water to desiccant	Surfaces Ratio S : D	Gms. Water added	Gms. Absor-bent	Desi-ccant cc. H_2SO_4	Dish diam, mms.	Gms. Solids Weighed	Gms. Water present
11	With Stirring	Glucose Soln.	40.16	40.70	387	2.8 : 1 (celite)	1 : 175	1 : 3.6	3.5	1.5	750	82	0.5337	0.7948
12	"	"	40.16	40.67	2187	2.9 : 1 (celite)	1 : 175	1 : 3	3.5	1.5	750	92	0.5208	0.7760
13	"	Raw Sugar	--	(1)0.57 (2)0.55	2167 2142	---	1: 1316 1; 1363	1 : 3 1 : 3.6	Nil	Nil	750	92 82	--	--
14	"	Golden Syrup	17.00 (Av.)	16.38	2070	2.5 : 1 (celite)	1 : 182	1 : 3.6	4.0	1.5	750	82	0.6121	0.1254
15	"	Sucrose Soln.	40.16	(1)40.59 (2)40.81	196 196	2.9 : 1 2.7 : 1 (celite)	1 : 175 1 : 173	1 : 2.8 1 : 3.6	3.5 3.5	1.5 1.5	750	92 82	0.5235 0.5542	0.7805 0.8256
16	With Stirring and Vacuum	Golden Syrup	17.00 (Av.)	11.16	7	3.3 : 1 (celite)	1 : 191	1 : 2.8	5.25	1.5	1000	92	0.4580	0 0938
17	Circulating pump & Vac.Stir'ng	"	17.00 (Av.)	16.03	526	44 : 1 (Sand).	1 : 161	1 : 3.6	6.13	20	1000	82	0.4548	0.0932
18	Static Drying	"	17.00 (Av.)	15.61	525	30 : 1 (Sand).	1 : 162	1 : 3.6	6.02	20	1000	82	0.6594	0.1351
19	Vacuum Desiccation	"	17.00 (Av.)	17.26	520	23 : 1 (Sand).	1 : 162	1 : 2.8	6.02	20	1000	92	0.8749	0.1749
20	"	"	17.00 (Av.)	17.80	504	44 : 1 (Sand).	1 : 160	1 : 3	6.25	20	1000	90	0.4524	0.0927
21	Vacuum Oven at low Temperature	"	17.00 (Av.)	(1)16.28 (2)17.61	5 5	107 : 1 36° 100 : 1 50° C. (Sand)	-- --	-- --	12.29 12.11	40 20	-- --	92 82	0.3747 0.3984	0.0768 0.0816
22	"	"	17.00 (Av.)	(1)17.05 (2)17.10	5 3	50 : 1) 50 °C 54 : 1) (Sand)	-- --	-- --	6.12 12.09	20 20	-- --	82 82	0.4016 0.3699	0.0823 0.0758

THE DETERMINATION OF WATER BY DESICCATION AT ROOM TEMPERATURE

CONCLUSIONS

TIME OF DRYING :- The time required for drying has been found to be greatly in excess of that reported in the literature.

In most of the tests the moisture content finally reached was below the known percentage present, although constant weight and a satisfactory agreement was obtained in a few experiments.

STIRRING :- There was a marked shortening of the time of drying when the air in the desiccator was stirred. There seems little doubt that stirring is advantageous if precautions are taken against loss of sample in the air stream. The effect of stirring was much less pronounced when the sample was nearly dry - within about 1 per cent of its known water content - that is, in the region where water of crystallization or "bound" water has to be removed.

VACUUM :- The drying time was considerably lessened by using vacuum, particularly when the vacuum pump was kept running constantly so that, in fact, there was slight motion of the remaining air. The vacuum oven at 50°C. was found to give satisfactory results in much less time.

RECOMMENDATIONS :- (a) If desiccation at room temperature is found desirable, the use of vacuum and stirring is recommended. There must be adequate ratios of absorbing medium to sample, and of desiccant to sample.

(b) The use of a vacuum oven at low temperature is generally more satisfactory than desiccation at room temperature. The necessary precautions must be taken (see section on oven-drying).

SECTION 5.

METHODS OF ANALYSIS.

Part 12 :- Determination of Water by Distillation Methods.

THE DETERMINATION OF WATER BY DISTILLATION METHODS.

ABSTRACT.

A survey has been made of the literature of the distillation method of determining water.

The distillation liquids normally used in these methods have been tested for stability and pH value.

Ten types of distillation apparatus have been used experimentally on golden syrup, and on solutions of sucrose, glucose, and, in particular, levulose.

Trials have been made of distillation with pH buffer solutions, and of distillation using a vacuum technique.

The results show that the distillation method is not suitable for the accurate determination of water in thermally sensitive sugars, but may be used for routine comparison purposes when the materials under test are not unduly sensitive to heat.

A method of prodedure is recommended : close attention to experimental details has been found necessary.

Three special types of apparatus have been devised and are described.

The most important factors in the method have been found to be - the use of glass joints and stoppers throughout ; the use of a dispersing medium such as Celite in the flask ; the use of electric hot plate heating, and the thorough washing down of water from the condenser.

DETERMINATION OF WATER BY THE DISTILLATION METHOD.

This procedure consists of heating the sample with some volatile and immiscible liquid, the water from the sample being carried over with the distillate and measured directly in a suitable tube.

Many methods based on this principle have been proposed, varying greatly in experimental detail and in the liquids employed. The ideal aimed at is to distil over all the water quickly without decomposing the sample and liberating chemically formed water.

In general the methods can be divided into two classes, those using liqids heavier than water, and those using liquids lighter than water. The light liquids used include, benzene, toluene, xylene, and various petroleum fractions, while the heavy liquids are usually chloro-substituted hydrocarbons such as trichlorethylene, carbon tetrachloride, and perchlorethylene.

SURVEY OF THE LITERATURE.

The distillation method of determining water appeared with the grant of a German patent in 1901 which covered two methods :-
1. distillation of the test sample with an immiscible liquid of higher boiling point, and 2. heating of the sample as in 1., folloowed by distillation with a liquid of lower boiling point. The distillation liquids recommended were toluene and petroleum fractions, and the method was first applied to cereal products.

Many variations followed, using a wide range of liquids, and applying the method to foods, coal, hops, and cellulose products among others.

A review of distillation methods up to 1908 is given by Hoffmann, (Z. angew. Chemie, 21,2095,1908), who described ten variations of the method, and compared results by distillation with those obtained by drying in vacuo with P_2O_5 or by drying at 80°C. Schwalbe used distillation in 1908 for plant materials, and commented on the necessity of having a distillation liquid of boiling point high enough to drive the bubbles of water through the mass of material. This view is common in the earlier literature, and little success attended the use of lower boiling point liquids until a method of sample dispersion appeared together with improved apparatus and technique.

Testoni (Staz. sper. agrar.Ital.,27,366,1904) first applied the method to sugar-containing materials using turpentine of boiling point 160°C. on molasses.

Van der Linden described a method for water in molasses and other sugar products in 1917. He used xylene in a copper distillation flask connected to a vertical condenser which discharged into a 250 ccs. measuring cylinder graduated to 0.05 cc.

A great improvement of the method resulted from the introduction in 1920 of the Dean and Stark tube enabling continuous reflux to take place, and facilitating the removal of the last traces of water. The Bidwell and Sterling type of trap (1925) represented a further advance in design which has become standard equipment.

Other modifications and improvements of the apparatus have included the incorporation of a built-in condenser, the use of standard glass joints, the standardisation of dimensions, and the adaptation of the trap for distillation liquids heavier than water. Thus Norman (Z. angew. Chem.,38,380,1925) claimed accurate results with a built-in reflux condenser using benzene with such materials as fats, oils, and soaps.

Yamada and Koshitaka modified Norman's apparatus in 1927 by the insertion of an inverted section at the end of the condenser, and claimed that this prevented adhesion of water on the walls of the still-head. (J.Soc.Chem.Ind.(Japan),30,356,1927).

Vacuum distillation using xylene for meat extracts was used by Dedlow and Smith in 1926, in an effort to prevent decomposition of the material by heat. They used a condenser specially cooled by brine. (Ind.Eng.Chem.,18,858,1926).

The use of a dispersion medium :- The application of the distillation method to sugar products was greatly helped by the proposal to use a dispersion medium by Rice in 1929. He used "Filter-cel" a proprietory acid-washed kieselguhr which was placed in the flask and the sample run in on top. (Ind. Eng. Chem.,21,31,1929).

This technique was further studied by Fetzer, Evans, and Longenecker and applied to very viscous corn-syrups. (Ind.Eng.Chem.13,855,1941, Anal.Ed.)

The introduction of liquids heavier than water :-

There are two main objections to the use of liquids lighter than water in the distillation method, firstly the risk of fire, and secondly the fact that most products tested sink in these liquids and are in direct contact with the bottom of the flask

where superheating and decomposition more readily occur.
To eliminate these objections, Thielepape and Fulde (Z. ver.Deut. Zucker Ind. 81,567,1931) introduced the use of alkyl and alkylene chlorides. At first a mixture of trichlorethylene (1 vol.) and trichlorethane (2 vols.) was used, but this was later abandoned on account of its toxicity, and tetrachlorethylene, sp. gr 1.62 and B.Pt. 119°C., with only slight toxic action, was adopted. The apparatus employed was that due to Lundin (Chem. Ztg.,55,762,1931); this is shown in Fig.67.In this apparatus the sample and distilling liquid are placed in a flask of 250-500 ccs. capacity. On distillation the vapour of the tetrachlorethylene and the water rise in the vertical tube and are condensed by the worm condenser. The condensed liquids flow into the graduated tube where separation occurs, the water being trapped in the tube, while the tetrachlorethylene runs back through the side tube (with stopcock). Several measuring tubes may be provided,e.g. 2, 5, and 10 ccs. capacity, to cover a wide range of water content: they are usually graduated in 1/20 ths. cc. This method using heavy distillation liquids has been used by Burke and Tucker (Analyst,60,663,1935) who successfully determined moisture in cereals using tetrachlorethane. They found,however that progressive decomposition occurred when the method was applied to cane sugar syrups and molasses,and concluded that the method was unsatisfactory when appreciable amounts of invert sugar were present Alexander (Ind. Eng. Chem.,Anal.Ed.,8, 314,1936) used carbon tetrachloride with a special tube for routine moisture determinations on

dynamite. Cleland and Fetzer (ibid.,14,124,1942) used Alexander's tube for corn syrups. They found a high "blank" figure for carbon-tetrachloride, and also used a smaller amount than usual of filter-cel as dispersion medium. The water was recovered more rapidly than when using benzene.

H. David (Centr. Zuckerind.,41,44,1936), used perchlorethylene for beet sugar products including raw syrups, cossettes, beet pulp, and filter press cake.

Adherence of water to the apparatus :- There are many references in the literature to the trouble caused by the adherence of fine drops of water to the upper part of the walls of the trap and to the walls of the condenser.

de Loureiro (J.A.O.A.C., 21,645-8,1938) has pointed out two reasons for the adherence :- "The first is mechanical. In an ordinary reflux condenser in which the vapour travels upwards, toluene, the less volatile liquid, condenses below the water, and there is none left to sweep down the condensed droplets of water. The other reason is physico-chemical. At neutral or acid reaction water has more affinity for glass than has toluene hence it tends to deposit along the walls of the apparatus as stubbornly adherent droplets. The condition is reversed when the action is strongly alkaline." "Thenthe glass is easily moistened by toluene, and gravity will cause even the smallest drops of water to slide along the walls."

Two methods are suggested by de Loureiro to surmount these difficulties. One is the use of an apparatus which changes the direction of the vapour flow so that the toluene will wash down the water, and the other is the use of 5 per cent potassium hydroxide solution to rinse the apparatus so that the glass surface is kept alkaline. Miss E. Knight (M.Sc. thesis, McGill University) did not find this alkaline rinse helpful, but advocated allowing the condenser to stand in alkaline solution (e.g. alcoholic potash) when not in use, rinsing with distilled water before using.

Main defects in earlier methods :- The application of the method to sugar products necessitates the use of liquids of low boiling point and if the B. Pt. is much below that of water the method may become tediously long. Elimination of the last traces of water from the sample is the main difficulty with any of the variations of the method. The early types of apparatus were provided with corks, and this was without doubt the cause of many discrepant results. Another most important factor is the means of heating the apparatus. Heating over a naked flame or with a gauze is obviously dangerous with the light inflammable liquids, and the use of an oil-bath or other type of immersion bath is messy and the temperature is not easily controlled. The use of electrical heaters appears to be the only really satisfactory method. In short, this distillation method which at first sight appears simple, must be conducted with exact attention to the correct technique, particularly when dealing with thermally-sensitive materials. The solvent used must be pure and of sufficiently low boiling point ; the apparatus must have glass joints ; and the method of heating must give adequate control of the temperature. Oil-baths are not satisfactory.

THE RATE OF EVAPORATION OF LIQUIDS.

The rate of evaporation for any given single solvent is governed by several factors :-

1. The vapour-pressure of the liquid at the given temperature
2. The rate at which heat is supplied to the liquid
3. The conductivity for heat of the liquid
4. The specific heat of the liquid
5. The latent heat of evaporation of the liquid
6. The degree of association of the molecules
7. The surface tension of the liquid
8. The molecular weight of the liquid
9. The humidity of the atmosphere
10. The rate at which the vapour adjacent to the liquid is removed.

With mixtures the rate of evaporation is further governed by:-

1. The molecular attraction of one component for another
2. The depression of the vapour pressure of one component by another.
3. Where dissolved colloids are present, e.g., lacquers, viscosity is very important.

(See T.H.Durrans, Solvents, Chapman & Hall, 3rd. Ed., p.30, 1933)

Very little reliance can be placed on most of the published information on evaporation rates as the phenomenon is profoundly affected by several factors which are difficult to control or standardise. Hofmann (I.E.C., 24, 135, 1932) has determined the rates for several solvents and has confirmed that approximate results can be calculated from the formula :-

$$\text{Rate} = \frac{(\text{Vapour Pressure} \times \text{Molecular Weight})}{11} \text{ at } 20^\circ\text{C:}$$

the rates being referred to butyl acetate = 100. (See De Heen, J. chim. Phys., 11, 205, 1913).

De Heen found that the evaporation rates of organic liquids are not proportional to their B.Pts. and that while the rate determined by weighing was satisfactory for practical purposes the results were not capable of numerical expression. For pure liquids the slope of the evaporation curves could be used to express the rate of evaporation: the rate is taken as the tangent of the angle the Time/Evaporation per cent makes with the horizontal, divided by the tan of the angle of the similar curve for n. butyl acetate x 100. The per cent evaporation line is obtained by evaporating the solvents in aluminium dishes of uniform size and shape. These were allowed to stand for 1 hour protected from draughts and were then weighed, continuing these weighings each hour for five hours.

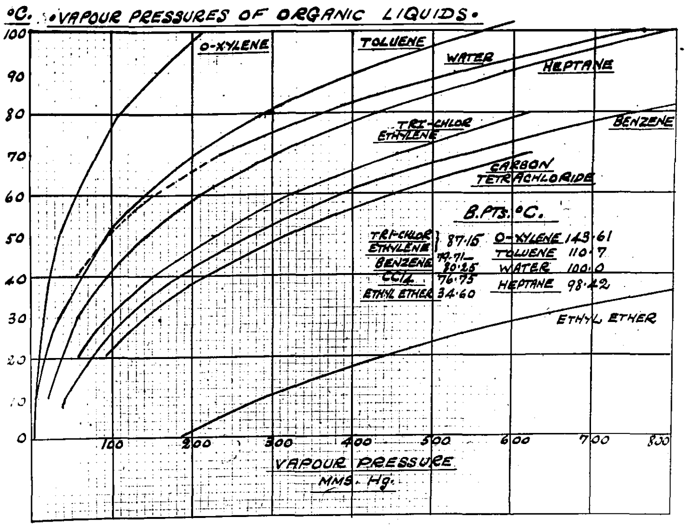


Figure 64.

LIQUIDS USED FOR THE DISTILLATION METHOD FOR WATER.

LIQUID	B.Pt. °C.	Sp.Gr.	PHYSIO-LOGICAL PROPERTIES	REMARKS
Methylene Dichloride or Dichloromethane CH_2Cl_2	40-42	1.346	Narcotic	Highly volatile = 1.8 where ether = 1
Chloroform $CHCl_3$	61.2	1.49-1.50	Acutely toxic	Solubility in water 0.5 % : turns acid i presence of light
Carbon Tetrachloride CCl_4	75-77	1.600-1.608	May form phosgene	Should be free from chlorine & neutral Max.Residue 0.01%
Trichlorethylene C_2HCl_3	86-88	1.469-1.475	Narcotic	Forms HCl slowly in light or catalytically :Insol.in water
Tetrachlorethane $CHCl_2.CHCl_2$	140-150	1.600-1.602	The most toxic of these liquids	Slowly liberates HCl in presence of water
Tetrachlorethylene (Perchlorethylene) $CCl_2.CCl_2$	119-121	1.624-1.632	Less toxic than chloro-form or CCl_4	Stable to moisture : Slightly narcotic & toxic : Sub-cutaneo)usly more toxic than CCl_4.
Benzene C_6H_6	80 (m.Pt. 5°C.)	0.884	Very toxic	Solubility in water 0.2% : volatile.
Toluene $C_6H_5.CH_3$	109-111	0.860-0.871	Toxic,probably less so than benzene	Solubility in water 0.047 % at 20°C.
Xylene $CH_3.C_6H_5.CH_3$	135-145	0.862-0.865	Toxic :approx. equal to benzene & toluene.	---
n.-Heptane C_7H_{16}	99.5-100.2	0.712	Toxic	Very inflammable : the data relates to "Technical" heptane.

Dichloroethane (B.Pt. 80-85°C.) $CH_2Cl.CH_2Cl$, and Dichloroethylene $CHCl.CHCl$, (B.Pt.)=58-60oC.) are both slowly hydrolysed by water, while Pentachlorethane, $CHCl_2.CCl_3$ has B.Pt.162°C., which is too high.

Reference :- "Toxicity of Industrial Solvents",H.M.S.O.,1937 (Report No.80).

MIXTURES OF LIQUIDS USED FOR THE DETERMINATION OF WATER BY THE DISTILLATION METHOD.

No.	By Volume Toluene	Carbon Tetra Chloride	Sp. Gr. Calculated	Sp.Gr. Actual	B.Pt. Calculated	B.Pt. Actual	Remarks
1	10	90	1.510	1.523	79.7	77.5	
2	20	80	1.439	1.440	83.1	79.2	
3	30	70	1.367	1.367	86.6	81.0	
4	40	60	1.296	1.294	90.0	88.0	
5	50	50	1.224	1.210	93.5	86.5	Satisfactory
6	60	40	1.152	1.147	96.9	87.8	
7	70	30	1.081	1.047	100.4	93.5	
8	80	20	1.009	1.005	103.8	95.0	Sp.Gr. too near to 1.000
9	90	10	0.938	0.929	107.3	100.0	

No. 9 Mixture burned with difficulty : No. 8 burned when a taper was held to it but the flame went out when the taper was removed.

Other Mixtures :- By Volume

No.	Composition		B.Pt. °C.
1	Carbon tetrachloride Toluene	50 50	89.5
2	Carbon Tetrachloride Toluene	30 70	93.5
3	Carbon Tetrachloride Xylol	60 40	93.2

These mixtures did not ignite with a taper, but burned when a burner flame was played on them : the flame went out when the burner was removed.

ACIDITY EFFECTS WITH THE IMMISCIBLE LIQUIDS USED IN THE ESTIMATION OF WATER BY DISTILLATION.

The liquids were steam-distilled where practicable, and then fractionally distilled, the fraction distilling within 1° of the listed boiling point being collected.

Thirty ccs. of each liquid were refluxed with 10 ccs. of twice-distilled water for one hour. The water was separated and cooled and its pH value determined by the Glass Electrode. A sample of each liquid was allowed to stand over NaOH for a week : the results shown refer to the pH values of water extracts made from (a) the solvent decanted from the NaOH, and (b) the solvent distilled from the NaOH.

Liquid	B.Pt. °C.	pH Value		
		Untreated	After NaOH Undistilled	After NaOH Distilled
Carbon Tetrachloride	76	4.7	9.6	8.4
Benzene	80	6.2	8.5	7.2
n-Heptane	100	6.8	8.4	4.6
Tetrachlorethylene	120	7.7	8.4	6.8
Toluene	110	6.4	9.0	6.8
Xylene	135-145	4.6	9.2	7.4
Tetrachlorethane	145	5.0	8.6	7.2
Trichlorethylene	86-88	6.0	8.3	6.7
Chloroform	61	6.8	8.7	7.3
Original Water	---	6.25	---	---

THE DISTILLATION METHOD FOR ESTIMATION OF WATER.

GENERAL NOTES ON THE VARIOUS TYPES OF APPARATUS :-

THE DISTILLATION METHOD FOR ESTIMATION OF WATER.

GENERAL NOTES ON THE VARIOUS TYPES OF APPARATUS :-

1. The Fuel Research Station type ("F.R.S." type) :- Figure 81

Using benzene this apparatus gave rapid distillation at 115°C. temperature in the oil-bath. The speed was mainly due to the enclosure of the graduated trap and the shortness of the vapour pipes. The enclosed tube was found to clog frequently with bubbles of benzene, and would be more efficient if a channel were provided so that a wire could be inserted to clear the bubbles.

At certain conditions of temperature and humidity in the atmosphere it was found that moisture tended to condense on the outside of the apparatus at the top : this water ultimately ran down into the moisture tube and vitiated the result.

A defect of this type is the condenser : the immiscible liquid channels on the large condenser surface and does not wash down the condensed water. This also applies to the sides of the upper portion of the apparatus. Elaborate washing down is thus necessary at the end, and with a large surface to wash, loss of water may result. With certain materials such as coal the apparatus "bumps" badly and the condenser may lift up and allow vapour to escape. Another difficulty with coal is that the very fine particles often entrain in the vapour and blur the meniscus reading.

Other points noted were the difficulty of reading the tube graduations through the rest of the apparatus, and the relative difficulty of cleaning the apparatus as compared with other types. The short vapour travel is a good point in this design : the water tube can, of course be removed for reading.

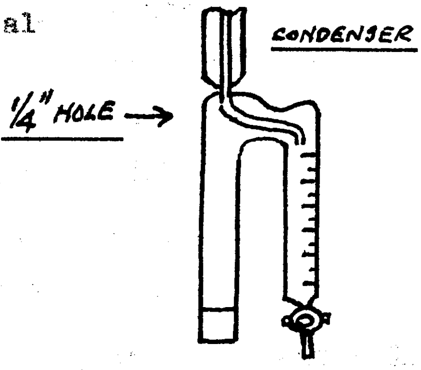
2. The Tate and Warren Tube (Figure 73) :-

The calibrated tube in this apparatus is too narrow to permit of easy cleaning, and for the same reason the water does not drop to the bottom of the tube unless the liquid is stirred by a wire ; this is particularly troublesome at the start of the estimation. These calibrated tubes are better when provided with a flat or rounded bottom and not a point as in this design. The Tate and Warren apparatus used in this work took much longer to start distilling, and distilled much more slowly than the Dean and Stark type (Figure 70).

Heating the trap in an electric oven to 110°C. before use did not materially help the settling of the water in the trap ; there was much emulsification and the water clung even more closely to the sides than in the previous tests. With all types of apparatus it was found desirable to clean the glass with chromic acid mixture before each estimation.

3. The Dean and Stark apparatus :- This apparatus is very similar to the Tate and Warren type. A modification of the trap is described in British Standard Methods for Testing Coal and Coke 1016-1942, and is shown here.

The Fuel Research Station type of apparatus is also described in this publication. The standard procedure recommends that the receiver and condenser be cleaned with a mixed dichromate/H_2SO_4 before each test.



Modified trap.

ESTIMATION OF WATER BY THE DISTILLATION METHOD USING 48.16 PER CENT LEVULOSE SOLUTION WITH DIFFERENT IMMISCIBLE LIQUIDS.

Levulose solution dispersed by addition of 10 gms. celite.

(a) Dean and Stark Apparatus:-

Distillation Liquid	Time in minutes and per cent $\left(\begin{smallmatrix}\text{solids}\\ \text{water}\end{smallmatrix}\right)$ found.							
1. BENZENE B.Pt. 80°C.	15	35	70	150	195	240	360	540
Solids	71.6	60.7	53.3	49.8	48.4	48.4	47.9	47.9

10 gms. celite added to 10.6 gms. levulose solution and 100 ccs. solvent used :no charring apparent : Oil Bath Temperature = 125-130°C.

---

2. n.-HEPTANE

	Time in minutes							
B.Pt. 100°C.	15	30	60	90	120	180	240	300
Water	36.6	48.3	50.7	51.7	52.2	53.0	53.3	53.7
Solids	63.4	51.7	49.3	48.3	47.8	47.0	46.7	46.3

10 gms. celite used as dispersion agent : 100 ccs. solvent : charring almost negligible.

Oil Bath Temperature = 130-135°C.

---

3. TOLUENE

	Time in minutes				
B.Pt. 110°C.	35	60	90	270	450
Water	50.4	51.5	52.1	52.9	54.4
Solids	49.6	48.5	47.9	47.1	45.6

10 gms. celite used as dispersion agent : 100 ccs. solvent (toluene NaOH-treated) : charring very slight, merely a brown ring round flask at the surface of the liquid. Oil Bath Temperature= 138°C.

Distillation Liquid

4. XYLENE

B.Pt. 135-140°C.

Time in minutes and % Solids and Water

	60	90	120	300	480	840
Water	39.6	52.3	53.9	54.5	57.7	59.3
Solids	60.4	47.7	46.1	45.5	42.3	40.7

10 gms. celite used as dispersion medium : 100 ccs. solvent : xylene residues were very much discoloured and the celite formed hard brown lumps with the levulose.

(b)"F.R.S." Apparatus (Fuel Research Station type) :-

1. BENZENE

B.Pt. 80°C.

TIME IN MINUTES.

	60	300	480	840 *
Water	43.8	50.3	50.7	66.9
Solids	56.2	49.7	49.3	33.1

10 gms. celite : 100 ccs. Solvent : residue white, no apparent charring. Oil Bath Temperature=124-130,and at 140°C. between 480 and 840 minutes.

* Water leaking in .

---

2. n.-HEPTANE

B.Pt. 100°C.

TIME IN MINUTES.

	3o	60	90	120	180	300
Water	45.3	48.8	51.9	52.6	52.9	54.6
Solids	54.7	51.2	48.1	47.4	47.1	45.4

Conditions as for Benzene : very slight charring Oil Bath Temperature= 130-135°C.

3. TOLUENE

TIME IN MINUTES

B. Pt. 110°C.	35	60	90	270	450
% Water	40.2	47.6	50.3	53.3	53.6
% Solids	59.8	52.4	49.7	46.7	46.4

Oil Bath Temperature= 141°C. 10 gms. celite : 100 ccs. solvent : slight charring.

---

4. XYLENE

TIME IN MINUTES

B.Pt. 135-140°C.	30	60	90	120	180	300
% Water	51.3	53.3	54.5	55.1	55.7	56.9
% Soilds	48.7	46.7	45.5	44.9	44.3	43.1

Oil Bath Temperature= 150°C. 10 gms. celite used 100 ccs. solvent : Considerable charring.

(c) Thielepape and Fulde Apparatus :-

1. CARBON TETRACHLORIDE

TIME IN MINUTES

B.Pt. 76°C.	60	120	180	300	600
% Water	43.2	44.7	46.1	48.9	50.2
% Solids	56.8	55.3	53.9	51.1	49.8

Oil Bath Temperature= 115°C. 10 gms. celite : 100 ccs. solvent : no charring : distillation extremely slow.

---

2. TETRACHLORETHYLENE

TIME IN MINUTES

B.Pt. 120°C.	60	120	180	300	600
% Water	36.5	45.9	48.2	52.0	54.4
% Solids	63.5	54.1	51.8	48.0	45.6

Oil Bath Temperature= 140°C. Conditions as for CCl_4.

(d) Tate and Warren Apparatus :-

1. BENZENE

TIME IN MINUTES

B.Pt. 80°C.	30	60	300	480
%Water	25.2	30.1	31.7	32.2
% Solids	74.8	69.9	68.3	67.8

Oil Bath Temperature= 124°C.

10 gms. celite and 100 ccs. Solvent : no charring : Distillation very slow.

---

2. n.-HEPTANE

TIME IN MINUTES

B.Pt. 100°C.	60	120	360	480	720	1200	1700
% Water	51.6	51.9	53.2	53.6	53.9	53.2	54.4
% Solids	48.4	48.1	46.8	46.4	46.1	46.8	45.6

Oil Bath Temperature= 125-130°C.

Conditions as for benzene :very slight charring.

---

3. TOLUENE

TIME IN MINUTES

B.Pt. 110°C.	35	60	270	450
% Water	51.2	52.0	53.8	54.1
% Solids	48.8	48.0	46.2	45.9

Oil Bath Temperature= 138°C.

Conditions as for benzene : moderate charring.

---

4. XYLENE

TIME IN MINUTES

B.Pt. 135-140°C.

	15	35	70	150	195	240	360
% Water	39.4	56.6	56.9	58.2	58.5	59.3	64.1
% Solids	60.6	43.4	43.1	41.8	41.5	40.7	35.9

Oil Bath Temperature= 145°C.

Conditions as for benzene : considerable charring.

SUMMARY OF RESULTS FOR THE DETERMINATION OF WATER IN A 48.16 % LEVULOSE SOLUTION BY THE DISTILLATION METHOD.

APPARATUS	DISTILLING LIQUID	B.Pt. °C.	% WATER	% SOLIDS	TIME HOURS
Dean & Stark	Benzene	80	51.6	48.4	4
	n-Heptane	100	53.3	46.7	4
	Toluene	110	52.9	47.1	4½
	Xylene	135-140	54.5	45.5	5
Fuel Research Station Type "F.R.S."	Benzene	80	50.3	49.7	5
	n-Heptane	100	54.6	45.4	5
	Toluene	110	53.3	46.7	4½
	Xylene	135-140	56.9	43.1	5
Thielepape & Fulde Type	Carbon Tetrachloride	76	48.9	51.1	5
	Tetrachlorethylene	120	52.0	48.0	5
Tate & Warren	Benzene	80	31.7	68.3	5
	n-Heptane	100	53.2	46.8	6
	Toluene	110	53.8	46.2	4½
	Xylene	135-140	59.3	40.7	4

It is evident that the distillation method with the types of apparatus used is not suitable for the determination of water in sugar solutions so thermally sensitive as those of levulose. There is progressive decomposition of the sugar as the distillation proceeds.

The results shown by Golden Syrup by distillation methods bear out the conclusions reached above : the Syrup contained about 46 per cent of reducing sugars, of which slightly less than half consists of levulose.

Distillation Method for Estimation of Water.

Summary of Results using the Vacuum Distillation Method.

No.	Material Tested	Water Present	Water Found	Apparatus	Remarks Solvent, additions.
1	Water	5.09	4.90	Hercules	CCl_4 -tetrachlorethane
2	"	5.09	5.00	Dean & Stark	n.-Heptane
3	"	5.09	5.00	" "	Xylol
4	Levulose Solution	4.44	4.10	" "	Benzol
5	"	3.09	2.80	" "	" + 5g.Celite
6	"	0.568	0.305	Micro-tube	Toluene+ " "
7	"	4.80	4.65	Dean & Stark	Benzol+10g.Celite
8	"	4.83	4.40	App.with corks	" " "
9	"	7.99	7.80	"	" " "
10	"	7.56	6.40	"	" & Glass wool
11	$CuSO_4$	2.16	2.15	Dean & Stark	" alone
12	Levulose	5.56	5.20	App.with corks	" & Glass wool
13	"	5.58	5.20	Tate & Warren	" " "
14	"	5.58	5.40	" "	Benzene + 10g.Cel.
15	"	5.55	4.70	App.with corks	" " "
16	$CuSO_4$	2.71	2.10	Dean & Stark	Toluene alone
17	"	2.71	2.20	App.with corks	Benzene alone
18	"	1.80	1.20	Tate & Warren	Xylol alone
19	Levulose	5.68	5.08	" "	Toluene + 10g.Na oxalate
20	"	5.56	5.50	Dean & Stark	Benzene + Celite 10 gms.
21	"	4.75	4.15	Tate & Warren	" + Sand 20 gms.
22	"	4.75	4.22	Dean & Stark	" + 5g.Na Ox. & 5g.Celite
23	Water	5.00	-	Tate & Warren	" + 20g.Pumice (Bumped violently : spoiled).

Distillation Method for Moisture in Levulose Solution.

Tests using mixed Distillation liquids and Special apparatus

Levulose Solutions :- No. 7 = 61.73 : No. 8 61.546 per cent Water.

No.	Gms. Levulose Solution	Distilling Liquid	B.Pt. °C.	Gms. Water present	Gms. Water found	Time Mins.	Apparatus
1.	6.2941	n.-Heptane	100	3.90	3.90	50-140	D. & S.
2	6.3610	Benzol	86	3.92	3.90	40-115	T. & W.
3	6.2489	Toluene	110	3.86	3.89 4.00	76 185	D. & S.
4	6.3670	Xylol	144	3.93	3.95 4.22	16 191	T. & W.
5	6.3794	CCl_4	76	3.94	3.90	36	L. & P.
6	6.4050	C_2Cl_4	120	3.95	3.90	9	Hercules
7	1.8692	Benzol	86	1.154	1.22	36	Micro tube with corks
8	6.2087	Benzol	86	3.83	3.80	60	Special 1
9	6.4049	CCl_4/Toluene 30/70	93.5	3.95	3.95	20	" 1
10	5.3708	CCl_4	76	3.11	3.10	135	" 2
11	6.4177	CCl_4/Xylol 60/40	84.3	3.95	3.50	140	" 2
12	6.4525	n.-Heptane	100	3.97	3.95	105	" 1
13	6.5303	CCl_4/Toluene 10/90	100	4.02	3.97	190	" 2
14	6.5140	CCl_4/Toluene 20/80	95	4.01	3.50	205	" 2
15	6.4312	CCl_4/Toluene 40/60	87.8	3.96	3.70	205	" 1
16	6.5155	CCl_4/Toluene 60/40	88.0	4.01	3.80	176	" 1
17	6.5145	CCl_4/Toluene 70/30	81.0	4.01	3.90	176	" 2
18	6.5086	CCl_4/Toluene 80/20	79.2	4.01	3.80	90	" 1
19	6.5097	" " 90/10	77.5	4.01	3.55	170	" 2
20	6.4775	" " 50/50	86.5	3.99	4.00	95	L. & P.
21	6.5145	Benzol/C_2Cl_4	81.3	4.01	4.00	95	D. & S.
22	6.0370	" both 90/10	81.3	3.02	3.02	150	"
23	6.5690	CCl_4	76	2.30	2.07	150	L. & P.
24	6.6830	Benzol	86	2.34	2.28	100	D. & S.
25	6.3852	" /CCl_4 : 90/10	81	2.24	2.24	100	L. & P.

Distillation with Buffer Solutions of known pH Values.

No.	Apparatus	Liquid Used	Buffer Soln. 5 ccs. pH	Time Mins.	Water Recovered ccs.	Final pH	Remarks
1.	D.& S.	Benzol	4.0	90	5.00	3.82	Some emulsification; Straight meniscus.
2.	"	"	8.0	120	5.0	8.35	No emulsification; Perfect meniscus.
3.	"	"	Sat.Na oxalate	120	5.0	6.71	Water part hazy; Straight meniscus.
4.	"	"	10.0	90	5.0	8.11	Much emulsification; Indistinct meniscus.
5.	T.& W.	"	Sat Li Carb.	90	5.0	7.05	Distn. very rapid; Clean meniscus.
6.	D.& S.	"	12.0	160	4.75	6.80	Ppt. in water layer; Meniscus "fuzzy"
7.	T.& W.	"	6.0	160	5.00	8.36	Good clear separa'n. Best meniscus obtd.
8.	Hercules	"	2.0	160	4.95	3.94	Much water on condenser walls.
9.	L.& P.	"	11.0	160	4.95	5.48	Permanent emulsion at meniscus.
10.	D.& S.	Toluene	Dist. Water	40	5.00	3.29	Much water on condenser; clear meniscus.
11.	T.& W.	"	2.0	40	5.00	5.87	Clear meniscus.
12.	D.& S.	"	4.0	100	4.95	6.94	Water globules in Condenser.
13.	T.& W.	"	8.0	100	5.00	6.80	Clear meniscus.
14.	D. & S.	"	10.0	60	4.95	8.80	Meniscus rather hazy. no emulsification.
15.	T.& W.	"	6.0	60	4.95	7.10	Clean meniscus : no emulsification.
16.	D. & S.	Xylol	8.0	60	4.90	5.44	Clear meniscus
17.	T. & W.	"	2.0	60	4.95	2.50	Clear meniscus

T. & W. = Tate and Warren : D. & S. = Dean and Stark :

L. & P. = Langeland and Pratt.

In general toluene gives less emulsification than benzene or xylol. The worst emulsions occur with alkaline buffer solutions, but acid buffers cause more clinging of water to the condenser walls.

COMPARISON OF RESULTS BY VARIOUS METHODS FOR THE DETERMINATION OF WATER IN GOLDEN SYRUP.

DISTILLATION METHODS:-	B.Pt. of LIQUID °C.	PER CENT WATER @ 4 HRS.	6 HRS.
1. Warren & Tate apparatus - n.-Heptane	100	17.36	18.21
2. Dean & Stark apparatus			
Benzene	80	17.27	18.36
Toluene	110	18.00	18.20
Xylene	135-140	18.42	19.18
3. Fuel Research Station apparatus "F.R.S." type			
Benzene	80	17.06	17.47
Toluene	110	17.80	17.88
Xylene	135-140	18.39	18.96
4. Apparatus using corks Dean & Stark pattern			
Benzene	80	16.60	17.29
Toluene	110	17.55	17.86
Xylene	135-140	18.31	19.77
5. "Hercules" apparatus (Alexander) -			
Carbon Tetrachloride	76	16.30	17.05
Tetrachlorethylene	120	18.00	18.93
Heavy Mixture (40/60 Toluene/CCl_4)	88	17.09	17.82
6. Langeland & Pratt apparatus-			
Carbon Tetrachloride	76	16.70	17.90
Tetrachlorethylene	120	17.72	18.30
Heavy Mixture (40/60 Toluene/CCl_4)	88	17.59	17.72
7. Thielepape & Fulde apparatus-			
Carbon Tetrachloride	76	17.63	17.87
Tetrachlorethylene	120	18.01	19.50
Heavy Mixture (40/60 Toluene/CCl_4)	88	17.56	17.73
8. Special Apparatus No.1			
Carbon Tetrachloride	76	17.01	17.70
Tetrachlorethylene	120	18.22	18.96
Benzene	80	17.55	18.21
Toluene	110	17.90	19.36
Xylene	135-140	18.27	20.08
Refractometric Brix°		17.93	

COMPARISON OF RESULTS BY VARIOUS METHODS FOR THE DETERMINATION OF WATER IN GOLDEN SYRUP.

DISTILLATION METHODS :-	B.Pt. of LIQUID °C.	PER CENT WATER 4 HRS.	PER CENT WATER 6 HRS.
9. Special Apparatus No.2-			
Carbon Tetrachloride	76	16.88	17.20
Tetrachlorethylene	120	17.80	18.32
Benzene	80	17.50	18.12
Toluene	110	18.06	19.30
Xylene	135-140	18.52	18.93
10. Special Apparatus No.3			
Carbon Tetrachloride	76	16.71	16.80
Tetrachlorethylene	120	18.00	18.60
Benzene	80	17.72	17.99
Toluene	110	17.22	17.54
Xylene	135-140	18.68	18.73

COMPARISON OF RESULTS BY VARIOUS METHODS FOR THE DETERMINATION OF WATER IN KNOWN SOLUTIONS OF SUGARS.

METHOD	SUGAR SOLUTION		
	SUCROSE	GLUCOSE	LEVULOSE
Known Composition, per cent	40.21	40.43	40.01
1. Vacuum oven : 60°C., 70 cms. vacuum 8 hours heating	40.27	40.68	40.00
2. Steam oven : 98°C., 8 hours heating	40.08	40.41	40.78
3. Refractometric Brix°, 20°C.	40.22	41.15	40.75
4. Distillation-Dean & Stark apparatus-Toluene : 4 hours	37.35	40.15	38.15
-ditto- : 8 hours	39.70	40.50	39.80

DETERMINATION OF WATER BY THE DISTILLATION METHOD.

Advantages of the method :- These may be summarised as follows :-

a. The water is estimated directly.

b. There may be considerable saving of time, depending on the sample under test.

c. There is little opportunity for oxidation to occur.

d. A much larger quantity of the sample can be taken, thus reducing the error due to a large multiplier.

e. In the use of chlorinated hydrocarbons as distilling liquids the fire risk is eliminated, and since the sample usually floats on the surface of these liquids there is less risk of decomposition by local superheating.

f. The water is measured free from other volatile substances unless these are soluble in water.

Disadvantages :-

a. There is often great difficulty in getting all the water to distil over.

b. At the temperature necessarily used there is danger of decomposition of thermally sensitive substances.

c. Inflammable liquids introduce considerable risk of fire.

d. Several of the liquids commonly used are dangerously toxic.

e. Water may cling very tenaciously to the glass surfaces.

f. In some estimations much "bumping" of solutions is met with.

g. The actual temperature used requires very careful regulation.

h. The cleaning and drying of the apparatus is troublesome.

i. The water may disperse through the immiscible liquid ; there is also often a "hanging" drop at the meniscus line.

j. With glass-jointed apparatus (the use of which is essential), there is sometimes trouble due to the joints "freezing" with viscous or sticky samples.

k. In washing down the last traces of water, there is danger of the adhering droplets being washed back into the flask and not into the trap.

Precautions necessary for the distillation method for water :-

1. The use of glass-jointed apparatus is essential.
2. The amounts of sample and liquid used should be kept standard.
3. The apparatus should be scrupulously clean, in particular the lower portion of the condensing surface and the water trap.
4. The water trap should be calibrated, and the apparatus correction factor should be checked periodically (by distilling over known weights of water).
5. The condenser water should be run at room temperature as far as practicable, to avoid condensation of water on the outside of the condenser.
6. The glass surfaces in contact with the water should be made alkaline to give the water less affinity for the glass than toluene has, and thus minimise the adherence of the water to the glass.
7. The use of a spiral of copper wire serves to move bubbles of air either liquid, and also aids in clearing up the meniscus line and bringing it to the correct shape.

8. The final reading should not be taken for at least 15 minutes after the final distillation period.
9. The source of heat should ensure constant conditions to keep the rate of distillation as constant as possible : the degree of superheat should be low enough to minimise "bumping".
10. The immiscible liqid should be saturated with water before use : water is usually slightly soluble in these liquids.
11. The condenser top should be lightly plugged with cotton wool.
12. Washing down of the last traces of water is definitely necessary : a spray tube with several small holes was found to be satisfactory in most cases, but use of a small brush may also be necessary.
13. Lagging of the distillation neck aids distillation considerably.
14. The chlorinated hydrocarbons are prone to decomposition particularly if of technical grade. This can be kept down by standing over borax for some days and re-distilling.
15. Owing to the sugar syrups and solutions e.g. levulose, sticking to the bottom of the flask, serious decomposition may occur by local heating. An attempt to add the solvent first and then weigh on the levulose by difference did not help matters with light liquids as the sugar stuck even more firmly to the flask and the mass was much more difficult to remove or break up than when the solvent was added after the sugar solution.
16. There appears to be much more clinging of sugar solution to the sides of the flask in the tests made with liquids heavier than water. The solids tend to mass on the glass and charring then soon occurs : this seems a disadvantage of this type of apparatus.

Further testing ofnthe Distillation Method for Moisture.

Method of Heating :- The oil-bath method was found to be extremely messy and difficult to control. In seeking a substitute method of heating various baths were tried, but the best method found was suspension of the flasks over an electrical hot plate without actual contact with the plate. With benzene for example it was found adequate to heat with the flask suspended about three quarters of an inch above the hot plate. By adjusting this distance the rate of distillation is easily controlled. A trial was made with a metal container packed with asbestos wool in which the flask was bedded but this was found to be less satisfactory than naked heating since the heating up of the system then took longer, and the rate of heating was then less easy to control. Flat-bottomed flasks were found more convenient for this work than round bottomed flasks, since weighing was easier with the flat base. It was found possible to heat three flasks at once over a round hot plate of 8 inches diameter, although a tendency was present when using carbon tetrachloride for the water floating on top to drift to the cobler parts of the flask at the edge just off the hot plate and this slowed the rate of distillation.

Vacuum Distillation :- tests were made using a vacuum technique with the object of preventing the destruction of the more easily destroyed sugars such as levulose.

Dual purpose apparatus :- Several types of distillation apparatus were devised which could be used with solvents both lighter and heavier than water. This type of apparatus was found useful in enabling a mixture of solvents to be tried with a view to the production of a non-inflammable liquid of suitable density and boiling- point. (See Figure 76).

Technique of the Distillation Method.

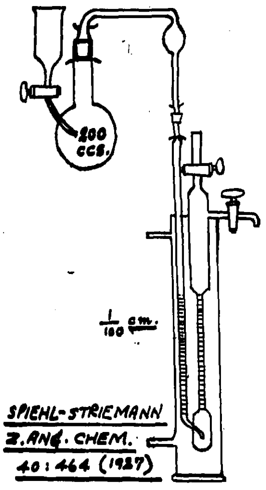
1. Weigh 10 gms. of freshly-ignited celite in a counterpoised nickel 'sugar' basin and transfer to a dry stoppered distilling flask of 250 ccs. capacity,flat-bottomed.
2. Counterpoise flask and celite on the balance.
3. Pipette into the flask 5 ccs. of the sugar solution as quickly as possible, avoiding disturbance of the celite, and distributing the solution evenly over the celite surface.
4. Find weight of sugar solution added.
5. Add 100 ccs. of the chosen solvent from a measuring cylinder and rotate the flask carefully untill all adhesions are freed.
6. Fit up the apparatus with the flask bottom 30 mms. from the hot plate, fill the trap with solvent through the condenser, and start heating.
7. Use a copper wire spiral to send down adhering water.

With liquids lighter than water the reading can be taken approximately while the apparatus is running ; with liquids heavier than water the hot plate can easily be removed for a few minutes while the approximate reading is taken.

It is convenient to have the measuring traps marked in ccs. both back and front, and to have the 0.1 cc. 'rings' etched three quarters round the tube circumference.

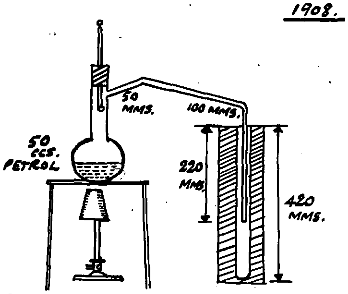
Observation of the clinging of water droplets to the apparatus :-

This was done by distilling over water from buffer solutions of known pH value.



SPIEHL-STRIEMANN
Z. ANG. CHEM.
40 : 464 (1927)

THÖRNER: Z. ANGEW. CHEM., 21, 148,
1908.



ESTIMATION OF WATER
IN BUTTER : C. E. GRAY
Z. ANGEW. CHEM., 890, 1908

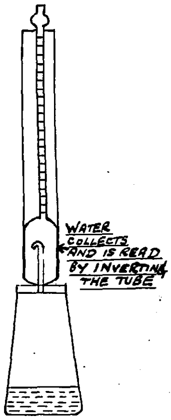
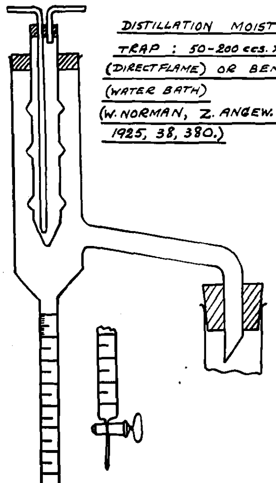


Figure 65.



DISTILLATION MOISTURE
TRAP : 50-200 ccs. XYLOL
(DIRECT FLAME) OR BENZOL
(WATER BATH)
(W. NORMAN, Z. ANGEW. CHEM.
1925, 38, 380.)

Scale ½ size.

DISTILLATION METHOD
FOR WATER USING HEAVY
LIQUIDS : APPARATUS
WITH CORKS

A = CONDENSER VENT
B = RETURN TUBE
C = CONDENSER
M = GRADUATED TUBE
T = DISTILLATION TUBE

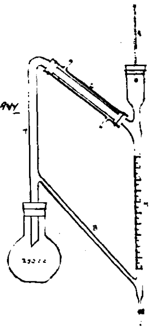
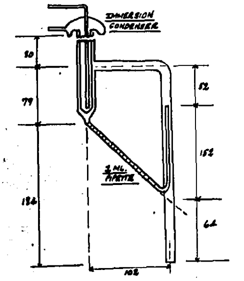


Figure 66.

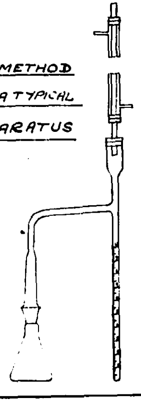


TRAP FOR SMALL AMOUNTS OF WATER
BY PERCHLORETHYLENE DISTILLATION
W. H. LINDSAY, I.E.C., ANAL. ED., 18, 1, JAN. 1946
P. 69.

DIMENSIONS IN MM.

Scale ½ size

DISTILLATION METHOD
FOR WATER : A TYPICAL
TOLUENE APPARATUS



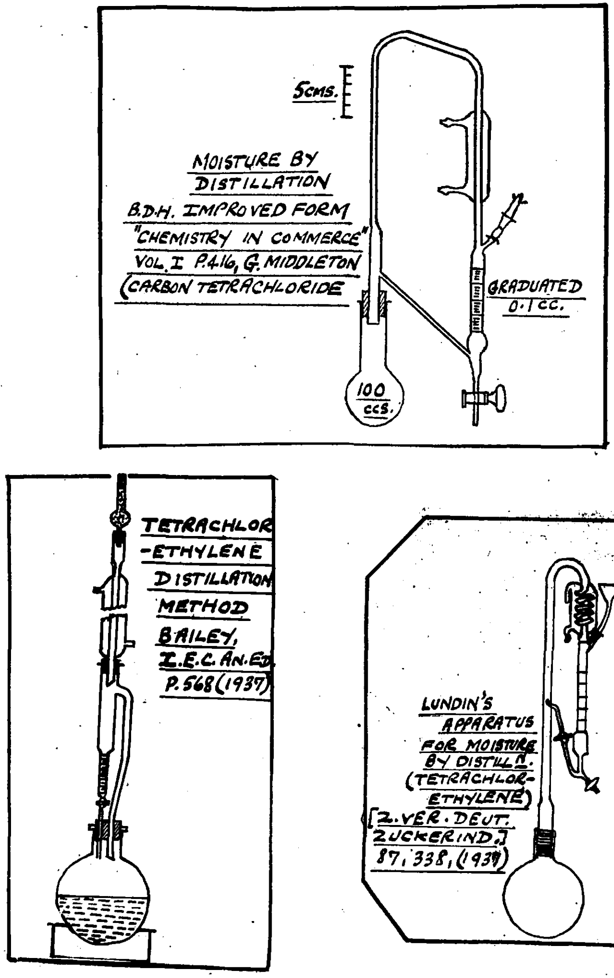


Figure 67.

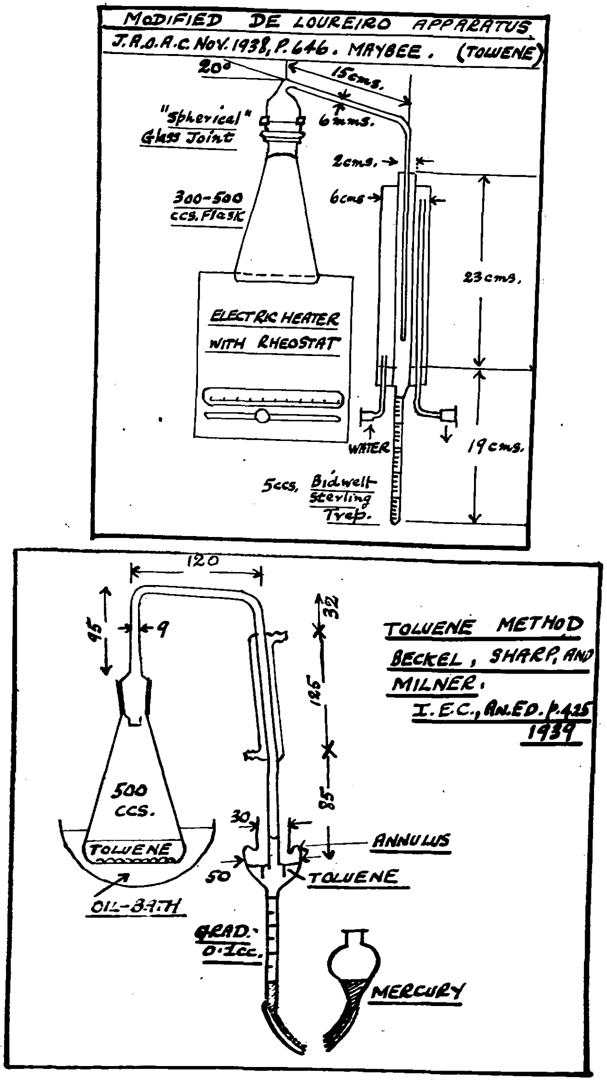


Figure 68.

Various forms of apparatus for the estimation of Water using toluene : Nos. 1 and 2 for very small amounts of water, No. 3 with wide bore for large amounts : all necessitating the use of corks.

Figure 69.

The Dean and Stark Apparatus for Moisture Estimation.

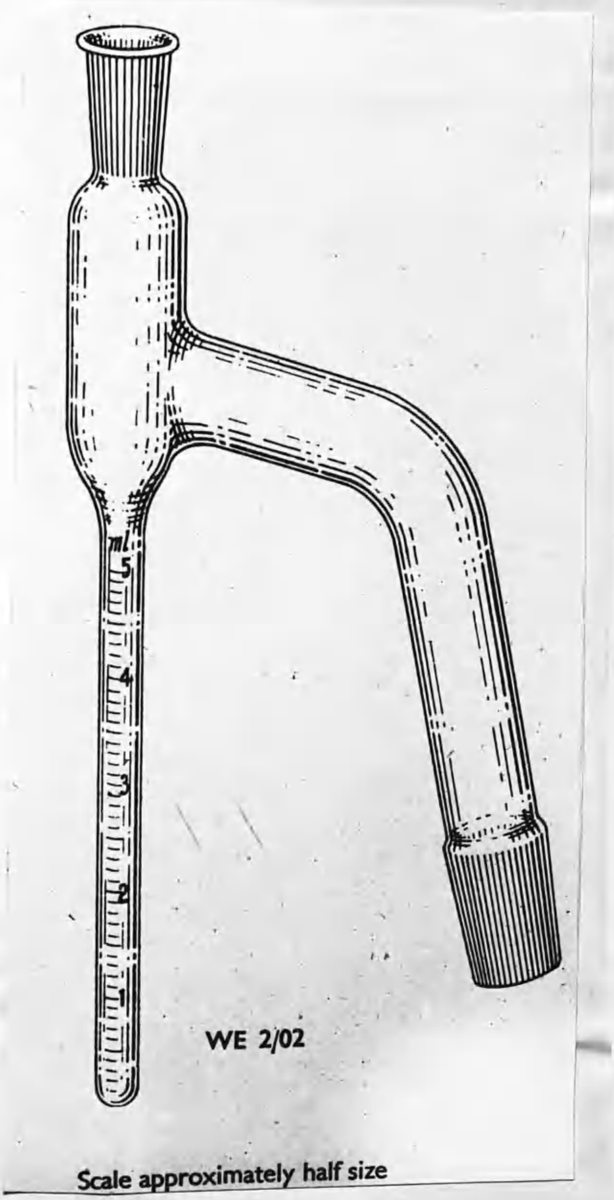


Figure 70.

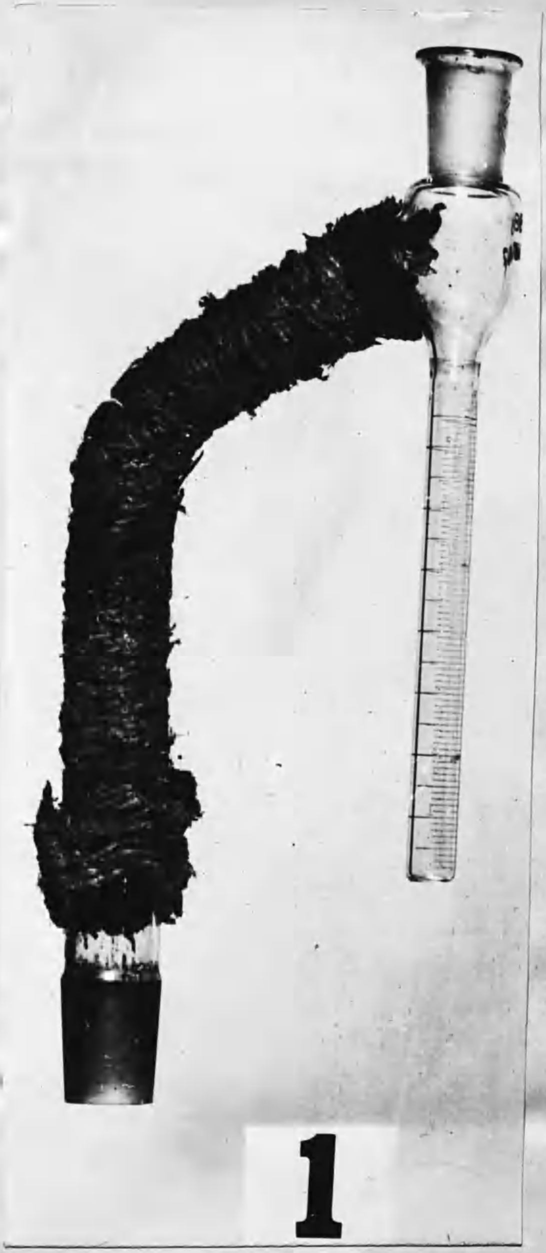


Figure 71.

British Standard Specifications for the Dean and Stark Apparatus for the Estimation of Water.

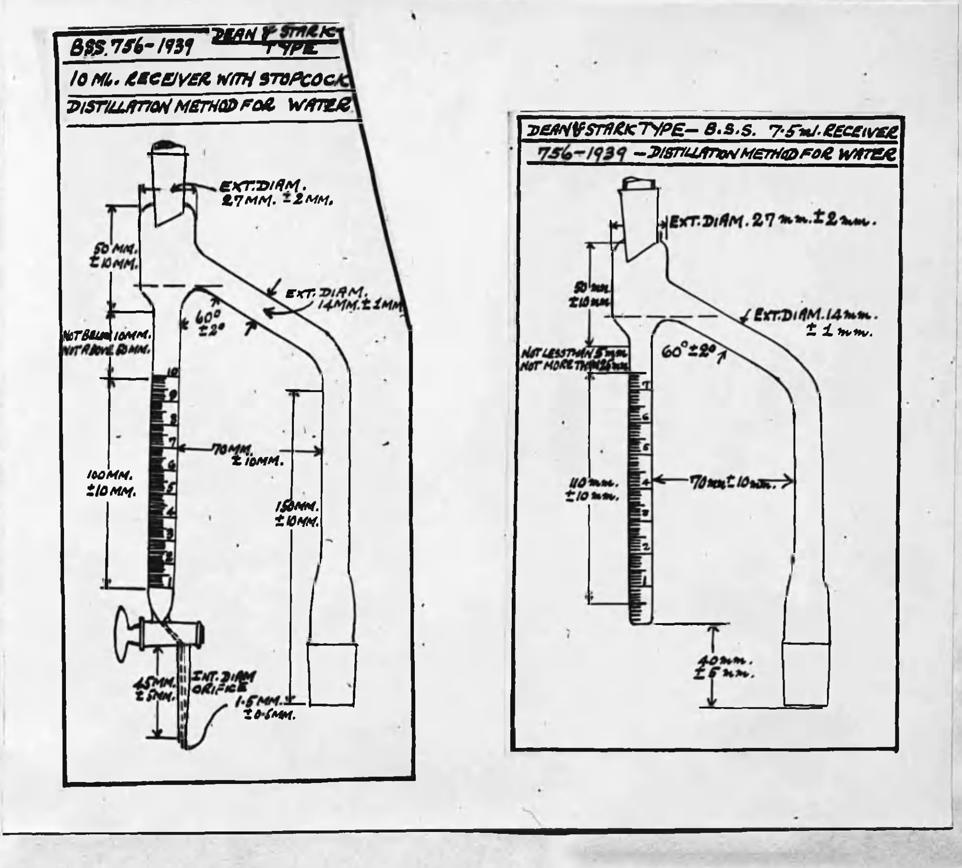


Figure 72.

The Tate and Warren Apparatus for Moisture Estimation.

Figure 73.

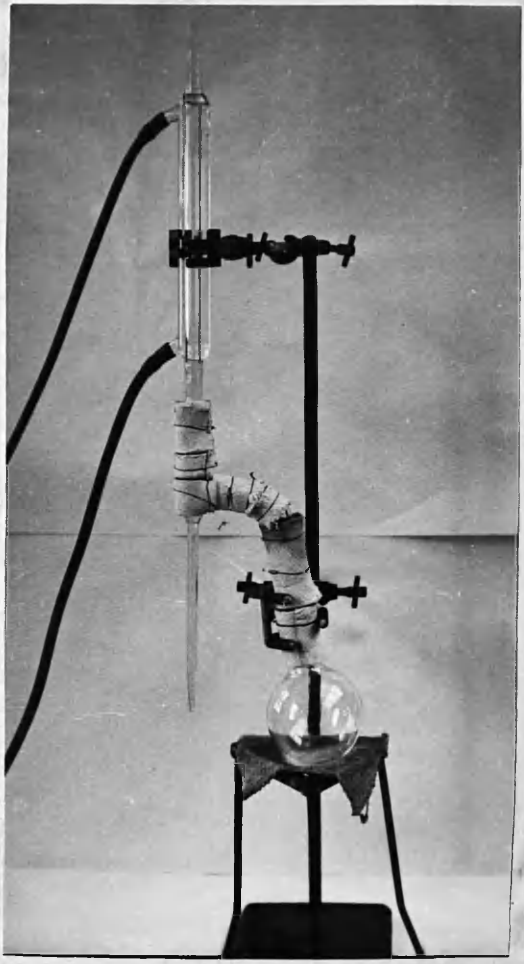


Figure 74.

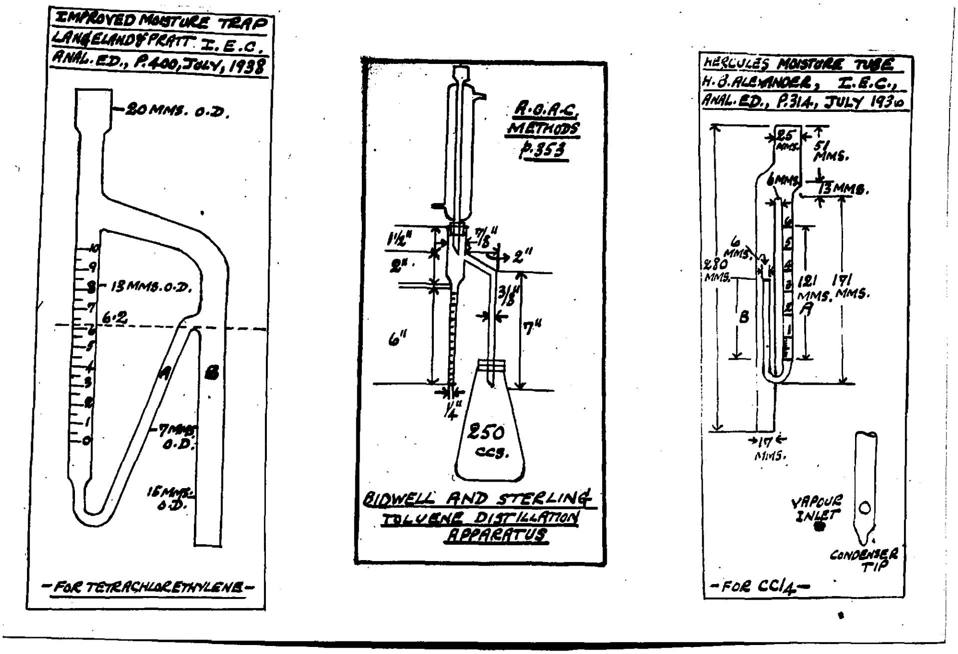


Figure 75.

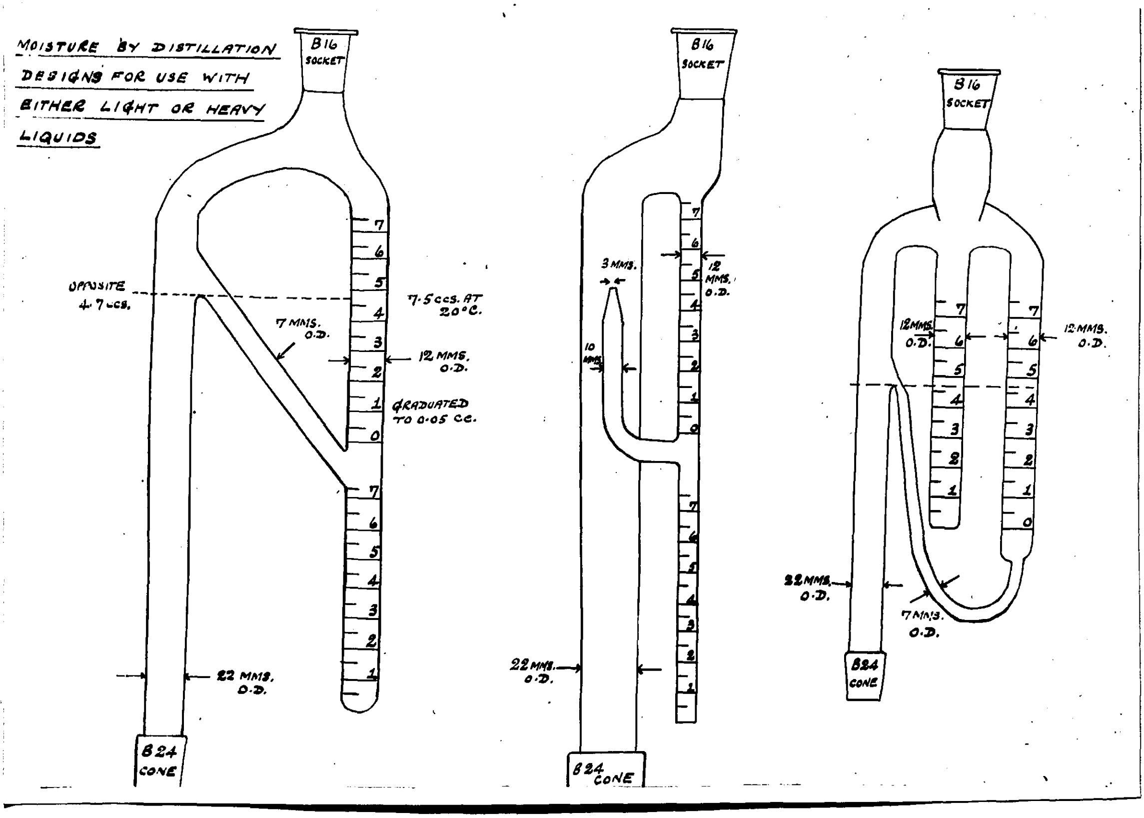


Figure 76.

Thielepape and Fulde type of Apparatus for Estimation of Water by Distillation : for use with liquids of high density, e.g., chlorinated hydrocarbons.

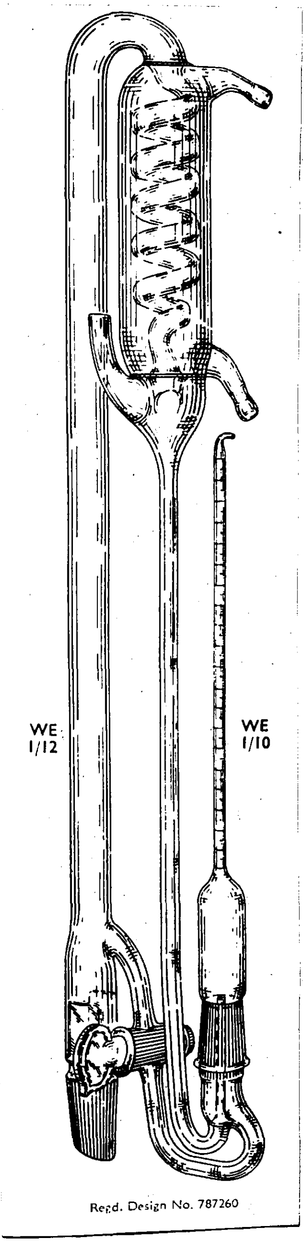


Figure 77.

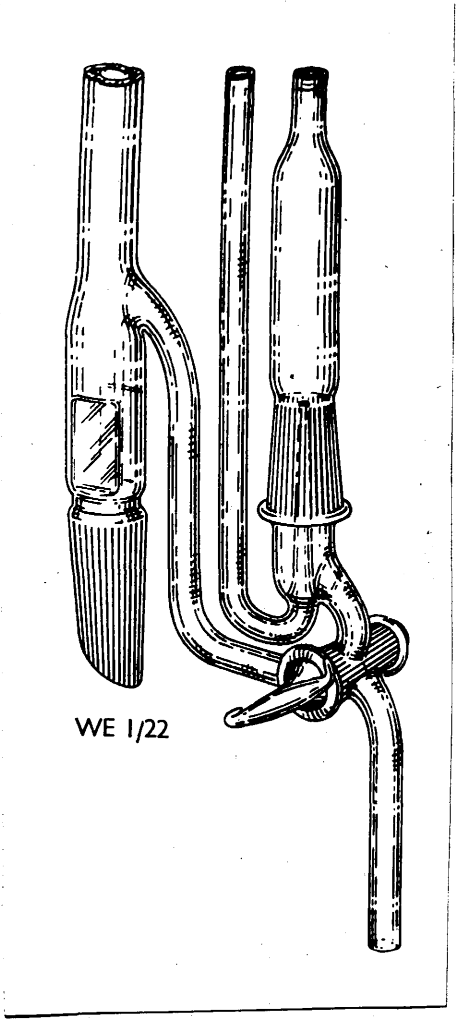


Figure 78 : Special arrangement of Stopcock.

Hercules Moisture Tube (2), and modification (1) for use with liquids both lighter and heavier than water.

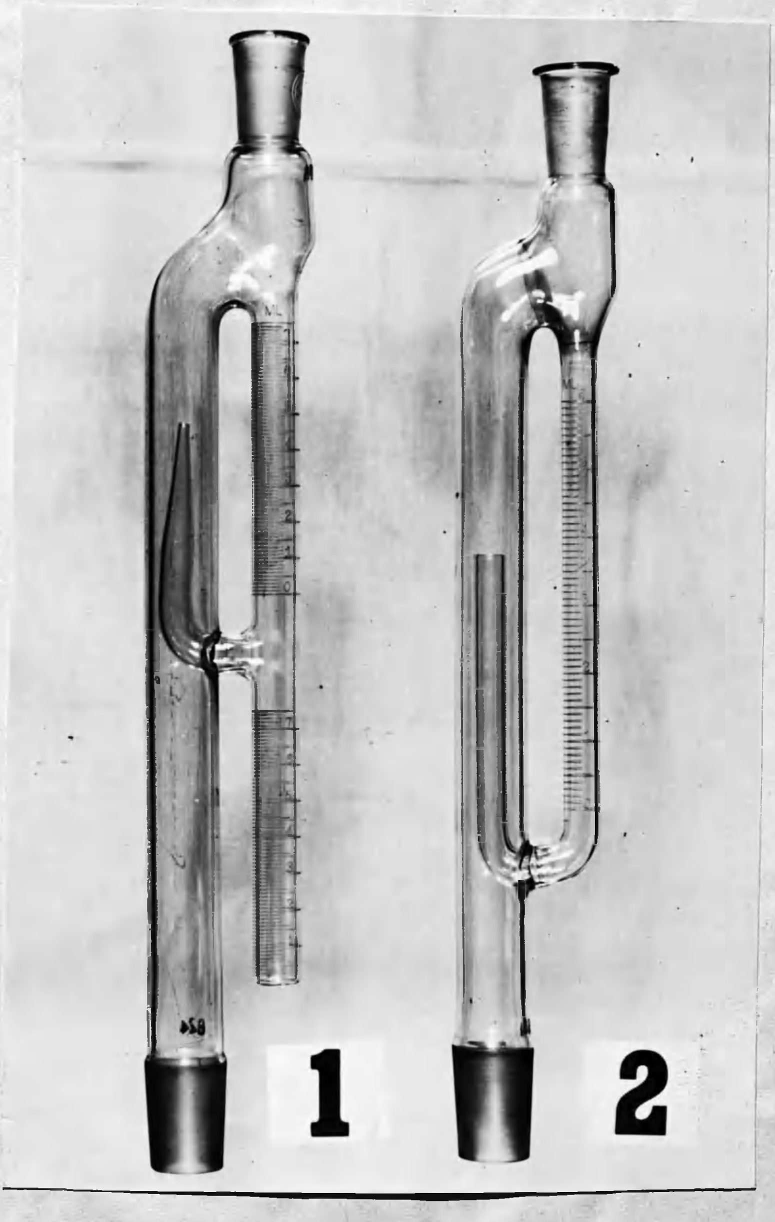


Figure 79.

Apparatus for the Estimation of Water by Distillation.

Type for use with Heavy Liquids.

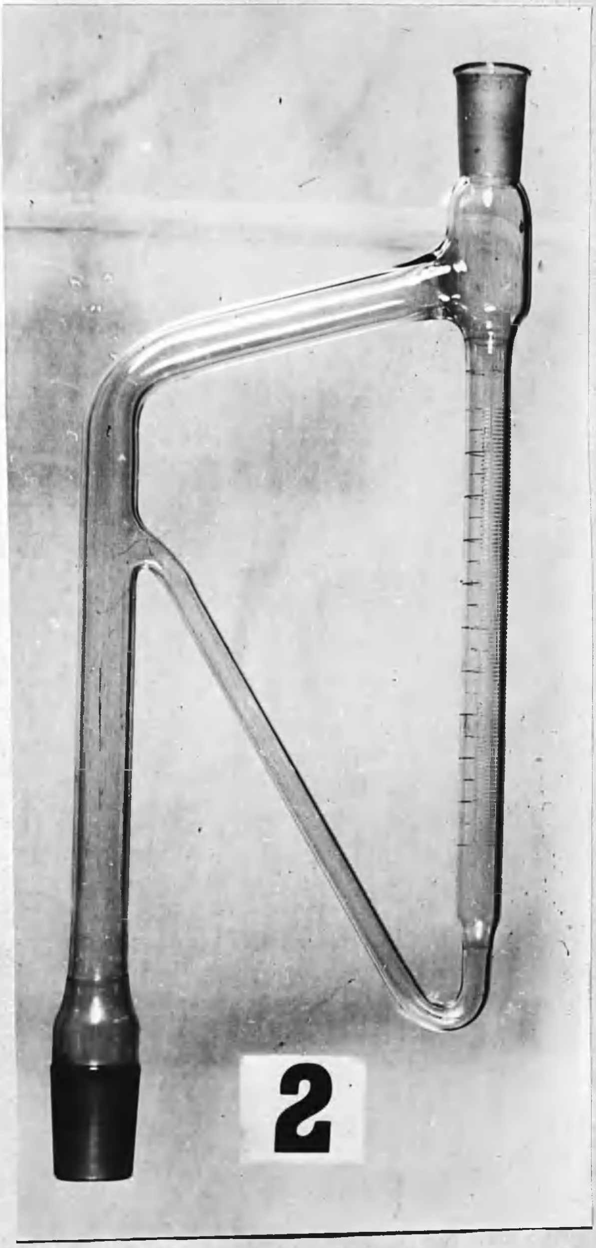


Figure 80.

Fuel Research Station ("F.R.S.") Type.

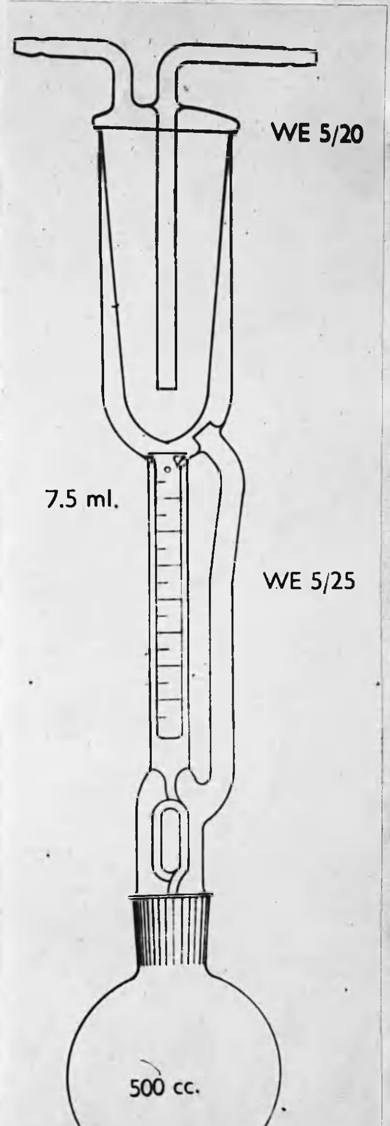


Figure 81.

Special types of apparatus for estimation of moisture by Distillation : applicable with both light and heavy density Liquids.

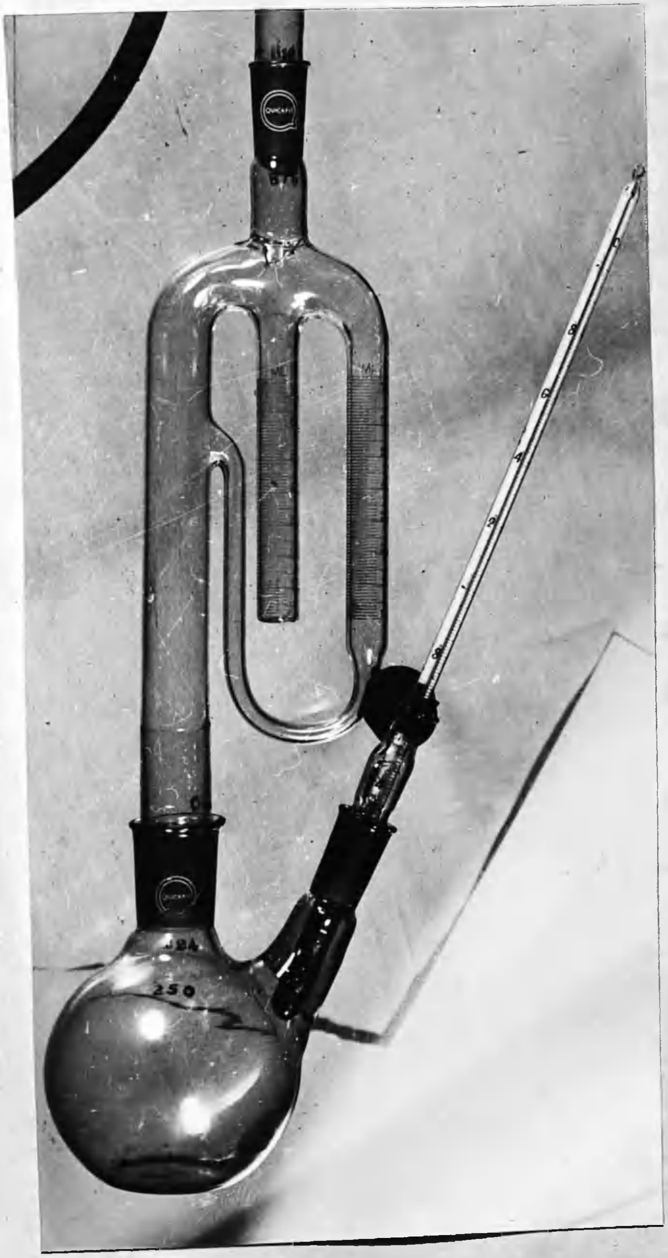


Figure 82.

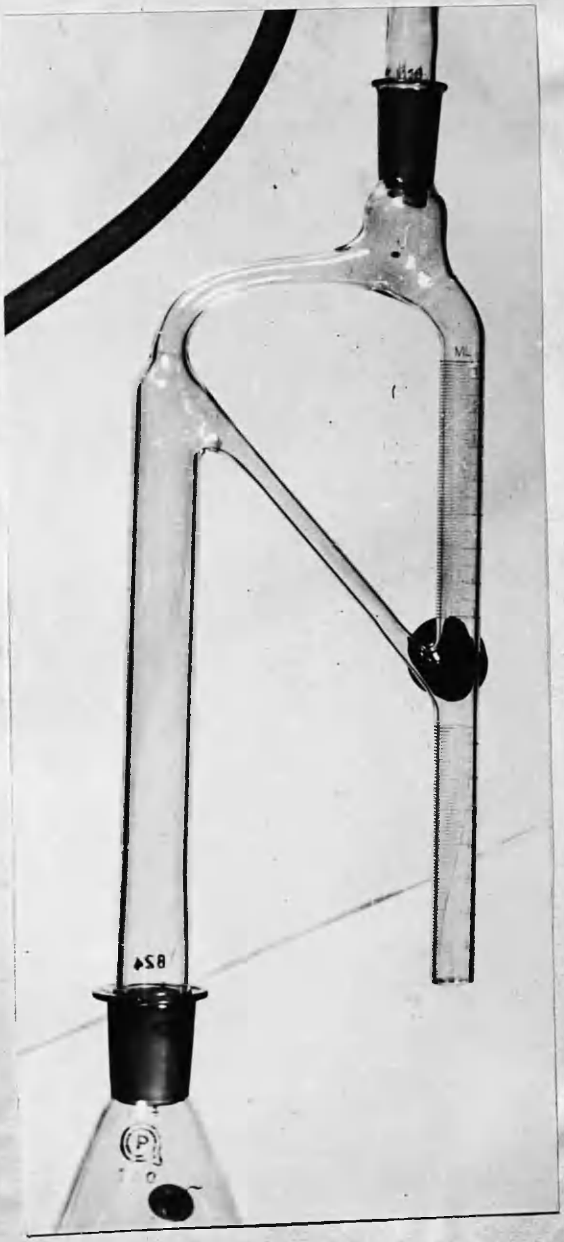


Figure 83.

SECTION 5.

METHODS OF ANALYSIS.

Part 13 : The Determination of Water by Chemical Methods.

Summary of Methods for determining Water :

Chemical Methods :-

The Carbide Method :

The Karl Fischer Method :

Conclusions.

METHODS OF DETERMINING WATER.

1. Oven Drying :-

Methods :- 1. Alone
2. With sand, pumice, kieselguhr, or other adsorbent.
3. In thin films (Rice)
4. With air current (e.g. Spencer oven)

Temperatures :-
1. Below 100°C. (usually vacuum oven type)
2. At or near 100°C. (steam-oven)
3. Above 100°C. (Electric ovens : Simon-Carter oven).

Usual dishes:-
Glass, porcelain, silica : aluminium, nickel, silver, and platinum.

2. Physical methods :-

1. Specific Gravity bottle :- 1. Direct, 2. Oil mixture, 3. 50 per cent solution.
2. Refractometers :- Ordinary and Dipping types.
3. Hydrometers :- of various scales and types.
4. Viscosimetric methods.
5. Critical Solution Temperature:- Phase separation of alcohol/petroleum mixtures.
6. Freezing point method (as for milk)

3. Electrical Methods :-

1. Electro-magnetic density.
2. Dielectric constant.
3. Electrical Resistance.
4. Infra-red heating.
5. High Frequency heating.
6. Dielectric heating.

4. Distillation Methods :-

1. Using liquids lighter than water. (Normal boiling-point
2. Using liquids heavier than water. (range-77-120°C. or higher.

5. Chemical methods :-

1. Selected chemical reactions :-
   1. Fischer s Iodine/SO_2 method.
   2. Acetyl chloride method
   3. Acetic anhydride method
   4. Benzoic anhydride method
   5. Naphthyl phosphorus oxychloride method
   6. Cinnamyl chloride method
   7. Sodium formate method
   8. Methylene dichloride method.

METHODS OF DETERMINING WATER (Continued).

5. Chemical Methods (Continued) :-
    2. Methods involving Evolution of Gas :-

        1. Acetylene methods - from Calcim carbide
        2. Hydrogen methods - Sodium amalgam, hydrides, etc.
        3. Ammonia - from Mg_3N_2.

---

6. Desiccation Methods :-
    1. Not Evacuated :-
        1. No stirring
        2. Air in desiccator stirred
        3. Heated above room temperature
        4. Desiccator rotated
        5. Desiccant stirred or circulated
        6. Sample dish rotated
        7. Air circulated round closed system by a circulating pump.
        8. Sample stirred.
        9. Both air in desiccator and desiccant stirred

    2. Evacuated :-
        1. No stirring
        2. Residual air stirred
        3. Heated above room temperature
        4. Desiccator rotated
        5. Desiccant stirred or circulated
        6. Sample dish rotated
        7. Sample stirred
        8. Both residual air and desiccant stirred.

    3. Methods of Stirring :-
        1. Fan Magnet system
        2. Mercury seal
        3. Gland
        4. Circulating pump

---

7. Absorption Methods :- For Water Vapour :-

    1. Absorption tubes, e.g., Calcium chloride.
    2. Volumetric method, using sulphuric acid.

Note :- References for most of these methods will be found in the Bibliography.

CHEMICAL METHODS FOR THE DETERMINATION OF WATER.

The Carbide Method :- This method depends on the liberation of acetylene from finely divided calcium carbide by reaction with water. Several ways of recording the end-point of this reaction have been devised :-

1. The pressure developed by the evolved acetylene is measured,
2. The volume of acetylene evolved is measured,
3. The loss of weight of the system due to loss of the evolved acetylene is measured,
4. The acetylene evolved is caused to combine chemically, and is then estimated in the compound formed.
5. The rise of temperature caused by the reaction is measured.

The values obtained with this method are influenced by the state of division of the material and by the physical condition of the carbide, for example its state of division and its freshness, this last factor depending largely on the conditions of its storage. Fisher and Tomlinson (1932) state that :-"The reaction is rapid at first, but after a few minutes becomes very slow, and does not actually cease for many hours."

In estimating water in flours by this method it was found that a proportion of the water in flour did not react with the carbide ; this proportion appears to be almost a constant percentage of the flour. A similar correction must be determined for each material tested by the carbide method. The above authors claim that the method takes only 20 minutes, and that it is subject to smaller errors than the usual oven methods. Their special container has been patented (Br. Pat. 365,247).

THE KARL FISCHER METHOD FOR MOISTURE DETERMINATION.

The simple method of weighing, heating, and weighing again is by no means invariably applicable for determining water since many substances are damaged by heat, since volatile materials other than water are expelled by heat, and since water is obstinately retained even at temperatures well above its boiling point.

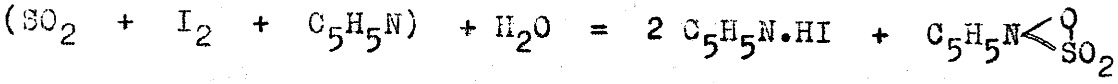
In 1935, Dr. Karl Fischer of the Edeleanu Company, Berlin, published a description of a very useful volumetric method which overcomes these difficulties (Angewandte Chemie, 48, 394, 1935). This procedure, although originally developed for finding the water content of liquid sulphur dioxide, has proved applicable in a much wider field and is now employed not only to determine water but many other substances.

The fundamental principle involved is the oxidation of sulphur dioxide by iodine in the presence of water, thus:-

$$SO_2 + I_2 + 2H_2O \rightleftharpoons H_2SO_4 + 2HI$$

As this is a reversible reaction it is obviously necessary to convert it to an irreversible one by fixing the two acids formed. Fischer achieved this by adding pyridine together with anhydrous methyl alcohol. His reagent thus consists of a solution of iodine and sulphur dioxide in anhydrous pyridine mixed with anhydrous methyl alcohol.

So long as it is kept entirely free from water, Fischer's reagent has a distinct brown colour due to the free iodine it contains. When it comes in contact with water free iodine is used up and the brown colour is replaced by a distinct chrome yellow colour due to the formation of the stabilised acid products, pyridine hydriodide and anhydro-N-pyridinium sulphonic acid :-



$$(SO_2 + I_2 + C_5H_5N) + H_2O = 2\ C_5H_5N.HI + C_5H_5N{<}\begin{smallmatrix}O\\SO_2\end{smallmatrix}$$

Brown reagent + Water = Yellow Derivatives

The reagent is run from a burette into a flask containing the sample, when the colour immediately changes from brown to yellow. As soon as all the water to be estimated has been used up, the brown colour of free iodine again appears in the flask. No indicator is therefore required. It is necessary to prevent interference from atmospheric or other adventitious moisture during the titration. Small dry narrow-mouthed flasks are therefore used, and the burette is provided with a P_2O_5 tube. The reagent is so sensitive that the brown iodine colour formed in the flask when titration is complete can be destroyed by breathing gently into the mouth of the flask when the yellow colour of the spent reagent appears.

One-litre quantities of Fischer's reagent are prepared thus :- Dissolve 84.7 gms. of resublimed iodine in a mixture of 269 ccs. of pyridine and 667 ccs. of synthetic anhydrous methyl alcohol ; cool in ice and cautiously add 64 gms. of liquid sulphur dioxide.

The water content of the methyl alcohol and the pyridine should not exceed 0.1 per cent since the presence of as much as 6 gms. of water per litre will completely exhaust the reagent.

The reagent must be standardised daily to obtain its equivalent in terms of water : this is done against methyl alcohol containing a known amount of water.

Extensive studies of the Fischer method have been made by D.M.Smith, W.M.D.Bryant, and J.Mitchell (Ammonia Department, E.I. du Pont de Nemours & C.o.),(J.A.C.S., 61,2407-2412,1939 : 62,1-3,4-6,608-609, 3504-3505,1940 : 63, 573-574,1700-1701,2924-2927,2927-2930,1941 : and I.E.C., Anal.Ed.,12,390-391,1940). This group of workers think that while the reaction between the reagent and water cannot be definitely expressed stoichiometrically, it can be represented in two steps. In the first step the iodine, sulphur dioxide and pyridine combine with the water to give the 1:1 complex of pyridine and sulphur trioxide, and this then reacts with the mathanol to give the pyridine salt of methyl sulphuric acid. The second stage is thus :-

$$C_5H_5N < \begin{matrix} O \\ SO_2 \end{matrix} \quad + \quad CH_3OH \quad = C_5H_5N < \begin{matrix} H \\ SO_4.CH_3 \end{matrix} .$$

They have applied the method to determine alcoholic hydroxyl, acid anhydrides, organic acids, carbonyl compounds, water in the presence of carbonyl compounds, water of hydration of salts, and the moisture content of native and processed cellulose.

The method requires modifications of treatment for various materials : the degree of fineness of grinding and the time of contact required vary widely, and must be determined for any specific case.

One of the greatest advantages of the Fischer method is the saving of time possible ; thus oven methods require 2-6 hours on the average, whereas the Fischer process is completed in 10-60 minutes,depending upon the time the material must remain in contact with the reagent to obtain complete extraction of the water.

The estimations are unaffected by fluctuations in barometric pressure, and only one weighing is required as compared with three for the oven method.

Since there is a definite change of potential at the end-point, the Fischer reaction can be observed very satisfactorily by electrometric measurement. Two methods have been proposed : the first, by Almy, Griffin, and Wilcox, (I.E.C., Anal.Ed., 12 392, 1940), uses one electrode of platinum and one of tungsten, and measures the change of potential with a sensitive galvanometer : the second method, by Foulk and Bawden (J.A.C.S., 48, 2045-51, 1926), applied to the Fischer method by Wernimont and Hopkinson (I.E.C., Anal.Ed., 15, 272-4, 1943), is the 'dead-stop' end-point method, involving the use of two platinum electrodes with an impressed voltage across them, the end-point being indicated by a sudden decrease of the current to zero. The current flow may be measured with a galvanometer or with a cathode ray "Magic Eye" electronic tube. This adaptation has been described by McKinney and Hall, (ibid., 15, 460-62, 1943), and has been applied to cereal products by R.H.Fosnot and R.W.Haman, (Cereal Chemistry, 22, 41, 1945).

REAGENTS AND STANDARDISATION.

FISCHER REAGENT :- The original reagent has been modified by the American workers : it is now prepared as below:-

A 1 litre conical flask is placed on a large balance and 700 ccs. of purified pyridine placed in it. The flask is tared and gaseous Sulphur dioxide is added through a rubber tube until 380 gms. have been added. After cooling the solution is transferred to a 3-litre container and 1 litre of pyridine and 200 ccs. of methanol are added. The solution is cooled in an ice bath and 500 gms.

of resublimed iodine added slowly with shaking.

Anhydrous methanol :- Commercial methanol is allowed to stand over 'Drierite' for several days. It is then distilled from 'Drierite' and collected in a receiver protected from atmospheric moisture by means od 'Drierite'.

Standard Water solution:- Five ccs. of distilled water are added to 1 litre of anhydrous methanol. This solution is dispensed from an au automatic burette, protected from atmospheric moisture by 'Drierite'

Standardisation :- The following factors are needed:-

1. The relationship between the Fischer solution and the standard water solution is called factor R. This factor when multiplied by the ccs. of Fischer reagent gives equivalent volume of standard water solution. R is determined by titrating 15 or 20 ccs. of the Fischer reagent to a dead-stop end-point with the water solution,

$$\underline{R} = \frac{\text{Ccs. standard water solution}}{\text{Ccs. Fischer reagent.}}$$

2. Constant b gives the correction necessary for the amount of water in the 25 ccs. of methanol used to dissolve the test sample. It is determined by titrating 25 ccs. of the 'anhydrous' methanol with Fischer reagent until the brown iodine colour appears, and then back-titrating with the standard water solution to a dead-stop end-point. Then b = (ccs. Fischer reagent x R)- ccs. std.water soln

3. The water factor W may be defined as the gms. of water per cc. of standard water solution. This factor, multiplied by the net weight of standard water solution gives the weight of water in the sample.

The Karl Fischer Method for the Determination of Water.

Storage of the Reagent.

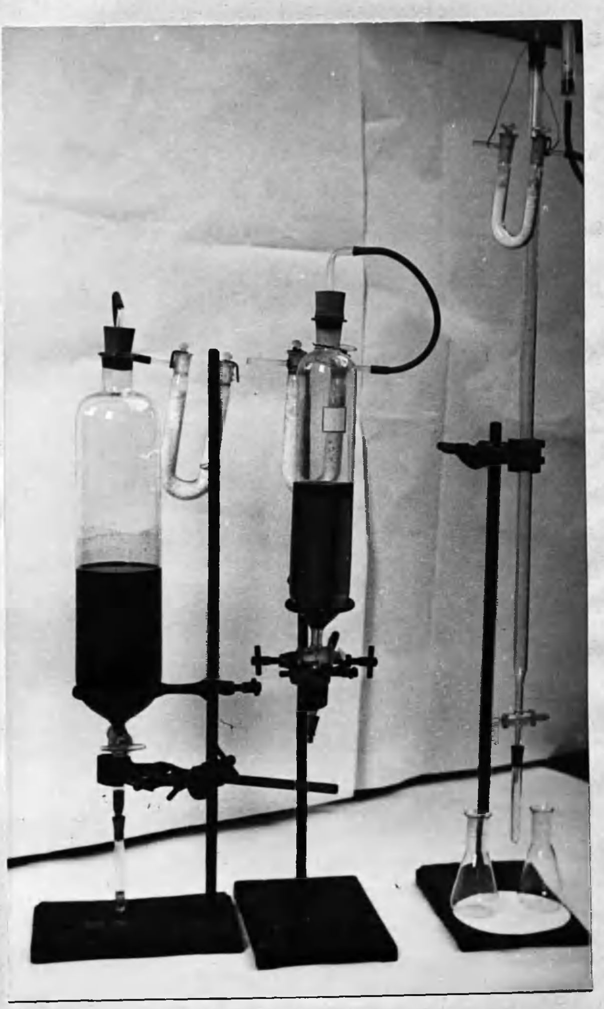


Figure 84.

THE FISCHER METHOD FOR WATER DETERMINATION

EXPERIMENTAL

The reagent was prepared and standardised according to the details of Smith and co-workers (loc.cit.). The fresh reagent was found to have a water equivalent equal to about 75 per cent theoretical strength (By Fischer's original equation 1 litre of solution is equal to 7.2 gms. water).

Various solid sugars were tested by the method covering the two vital factors of grain size and time of contact :-

No.	Sugar		Type	Grain Size	% Moisture in Vacuum Oven- 10 hours at 70°C.
1	Sucrose	A	Caster	All through 80 mesh sieve	0.09
2	"	B	Std. Gran. (Cane)	0·01" – 0·02"	0.11
3	"	C	"	0·02" – 0·03"	0.16
4	"	D	"	0·01" – 0·02"	0.13
5	"	E	Std. Gran (Beet)	0·02" – 0·03"	0.21
6	Dextrose		Anhydrous	0·003" – 0·005"	0.37
7	Levulose		"Dextrose-free"	0·006" – 0·009"	2.39
8	Lactose		"Biological"	0·001" – 0·003"	0.46
9	Maltose		---	0·009" – 0·010"	0.96

The sucrose samples B to E were standard granulated 'cane-sugar' from separate sources. The determinations in the vacuum oven were made on 10 gms. samples for the sucrose, 5 gms. for the lactose, and 2 gms.for the remaining sugars. The grain sizes were determined by standard sieves.

titration of very alkaline liquids will suffer similar interference. Acids which react with methanol liberating water also interfere e.g. boric acid, but acetic acid does not interfere.

In general it would appear that Fischer's method can be used for foodstuffs since in absence of a catalyst the reaction of iodine with the organic compound is slow in comparison with the reaction with water and sulphur dioxide. Richter (Angew. Chem., 48, 776,1935) says " Even with foodstuffs containing a high percentage of sugar such as marmalade the method gives results agreeing with xylol distillation : with substances in coarse division, such as cheese, where occlusion occurs, low results are obtained."

SUMMARY OF FISCHER REAGENT PREPARATION DETAILS.

Methanol,pyridine, iodine, and sulphur dioxide used:-

Constituent	Original Fischer Reagent	Smith and Bryant Reagent	Almy,Griffin,& Wilcox's * Reagent
Methyl Alcohol	1000 ccs.	667 ccs.	496.3 gms.
Pyridine	158 gms.	269 ccs.	313.9 "
Iodine	50.8 "	84.7 gms.	126.2 "
Sulphur Dioxide	38.4 "	64 "	63.6 "
Standard Water Solution	5 ccs. in 500 ccs. Methanol	18 ccs. wgd. to 1 litre Methanol	10 gms. water wgd. to 2 litres Methanol.

* Calculated on gms. basis.

The heating of the sample with methanol before the period of contact was given was found to facilitate the dispersion of the material and to help in the complete extraction of the water. The small loss of methanol had no effect on the results.

The Fischer method has been applied to the determination of water in fats, butter, and margarine by Kaufmann and Funke,(Fette u. Seifen, 44, 386-390,1937),to potato starch moistures by Porter and Willits, (J.A.O.A.C.,27,179-194,1944), to soya beans by Krober and Collins (Oil and Soap, 21, 1-5,1944),to pine oils and terpene solvents by Grotlisch and Burstein (I.E.C., Anal.Ed.,382,1945),and to Penicillin sodium salt (micro-determinations),by Levy, Murtaugh, and Rosenblatt (ibid., 17,193,1945). The authors last named compare the Fischer method with P_2O_5 vacuum desiccation for 6-9 days with at least 4 micro-balance weighings,which they characterise as long and tedious, open to error by the hygroscopicity of the sample, and giving a large scatter of results in replicate determinations. C.M.Johnson (ibid., 17, 312,1945) used the method for water in dried food materials such as carrots, peas, and beets, and found reults to be higher than those by the vacuum oven method (38 hours at 70°C.). The main difficulty with the method lay in the time of contact necessary which he found to vary from 30 minutes to 24 hrs.

Substances which react with free iodine cannot be dealt with by the Fischer method, although if the reaction is slow with iodine a good approximation to the water content can be made by carrying out a rapid determination. Inorganic oxides interfere by forming salts with the acids formed in the titration, and it is likely the

To determine W, 0.03-0.15 gm. portions of water are weighed into dry flasks containing 25 ccs. of anhydrous methanol. Fischer reagent is then slowly added to these until excess is present : this excess is at once back-titrated with standard water solution to a dead-stop end-point. Then,

$$\underline{W} = \frac{\text{Gms. water weighed}}{(\text{Ccs. Fischer reagent} \times R)-(\text{Ccs. Std.Water Soln.})-\underline{b}.}$$

The final formula for per cent water in a test sample is then :-

$$\%\ \text{Water} = \frac{(\text{Ccs.Fischer reagent} \times R)-\text{Ccs. Std. Water Soln.})-b\ W\text{x}100}{\text{Weight of Sample}}$$

Frequency of Checking Factors :- The reagent gradually weakens in storage, so that factor R must be determined each working day. It is desirable to check factor b for the methanol each day also. The standard water solution remains constant within the limit of experimental error and need only be determined for each batch of standard water solution.

PROCEDURE :- A sample containing 50-150 mgms. water is weighed into a dry titration flask, 25 ccs. of methanol added and the mixture brought to the boil in a water-bath. The solution is cooled and Fischer reagent added to about 1-2 ccs. excess, shown by the colour change from yellow to brown. Contact time is now allowed to ensure complete extraction of water, and on its expiry the flask is placed below the std. water burette, the 'magic eye' adjusted to the completely open position and the std. water added till the eye closes. To overcome reaction lag the final additions should be slow.

Estimation of Water by the Karl Fischer Method.

Results with samples of sucrose of various grades and with pure Lactose, Maltose, Dextrose, and Levulose.

No.	Gms. Sugar Taken	Description	Vacuum Oven at 70°C. 10 Hrs.	Time of Contact at 18°C. Minutes 5	30	60	240
1	10	Sucrose A (Caster)	0.09	0.007	0.06	0.06	0.07
2	10	Sucrose B (Standard Granulated)	0.11	0.012	0.08	0.10	0.10
3	10	Sucrose C (Std. Gran.)	0.16	0.013	0.11	0.11	0.14
4	10	Sucrose D (Std.Gran.)	0.13	0.007	0.09	0.10	0.12
5	10	Sucrose E (Beet White)	0.21	0.012	0.15	0.19	0.22
6	5	Dextrose	0.37	0.100	0.27	0.31	0.38
7	2	Maltose	0.96	All dissolved with 34 ccs. reagent added.			
8	5	Lactose	0.46	Voluminous white precipitate.			
9	0.5	Levulose	2.39	2.64	2.70	2.75	2.80

			Steam Oven 5 Hrs. at 99°C.	Time of contact at 60°C. Minutes 5	30	60
1	10	Sucrose A	0.10	0.03	0.08	0.09
2	10	" B	0.13	0.05	0.10	0.12
3	10	" C	0.16	0.09	0.13	0.14
4	10	" D	0.15	0.09	0.12	0.13
5	10	" E	0.21	0.09	0.21	0.21
6	5	Dextrose	0.42	0.22	0.29	0.33
7	2	Maltose	1.01	-	-	-
8	5	Lactose	0.52	-	-	-
9	0.5	Levulose	2.96	2.72	2.79	2.80

Sucrose samples A to D were of cane origin.

THE FISCHER METHOD FOR WATER DETERMINATION

Estimation of water in solid sugars:-

No.	Sugar	Per Cent Moisture Time of Contact at 18°C.				at 60°C.		
		5 mins.	30 mins.	1 hr.	4 hrs.	5 mins.	30 m.	1 hr.
1	Sucrose A	0.007	0.06	0.06	0.07	0.03	0.08	0.09
2	" B	0.012	0.06	0.08	0.10	0.05	0.10	0.12
3	" C	0.013	0.11	0.11	0.14	0.09	0.13	0.14
4	" D	0.007	0.09	0.10	0.12	0.09	0.13	0.14
5	" E	0.012	0.15	0.19	0.22	0.09	0.21	0.21
6	Dextrose	0.100	0.27	0.31	0.38	0.22	0.29	0.33
7	Levulose	2.64	2.70	2.75	2.80	2.72	2.79	2.80
8	Lactose	Voluminous white precipitate.						
9	Maltose	All dissolved at 34 ccs. reagent added - no visible end-point.						

In the titration of lactose a voluminous white precipitate appeared which increased in bulk as the reagent was added : this was with 5 gms. lactose. Using 0.5 gm. lactose, the lactose first seemed to dissolve and then was reprecipitated leaving a bulky precipitate at the addition of 18.25 ccs. when an end-point appeared. This gave an apparent water percentage of 5.04 which would indicate that the reagent and the sugar are interacting in this case.

With levulose the sample dissolved completely in the 10 ccs. of methanol used, but the end-point was satisfactory. Maltose also dissolved completely but the end-point was not easily discerned.

THE FISCHER METHOD FOR WATER DETERMINATION.

Estimation of water in Golden Syrup :-

Test No.	Gms. Syrup Taken	Time of Contact	Temp. of Contact °C.	Per Cent Water	Remarks.
1	0.3065	10 mins.	60	16.90	It was found particularly necessary with golden syrup to give ample time for the reaction to go to completion. The optimum time lay between 15 and 17 minutes. There was a general tendency with this method towards low results : the large difference between maximum and minimum results is striking.
2	0.2595	10 "	60	16.80	
3	0.4410	10 "	60	16.68	
4	0.4790	10 "	60	16.49	
5	0.9275	10 "	60	17.10	
6	0.1750	10 "	60	16.70	
7	0.3180	10 "	60	16.78	
8	0.1975	10 "	60	16.89	
9	0.2260	10 "	60	16.29	
10	0.3040	10 "	60	16.58	
11	0.2117	10 "	60	17.26	
12	0.6630	10 "	60	16.66	
13	0.2018	10 "	60	16.23	
14	0.3510	10 "	60	16.89	
15	0.2190	10 "	60	17.19	
16	0.3310	10 "	60	17.00	
17	0.3665	10 "	60	16.84	
18	0.3428	10 "	60	16.93	
19	0.7880	10 "	60	16.73	
20	0.3962	10 "	60	16.91	

Mean result	16.79
Minimum	16.29
Maximum	17.26

The persistence of the brown shade of the end-point was timed, and the final end-point was taken when the shade persisted for 30 seconds by stop-watch.

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THE DETERMINATION OF WATER AND SOLIDS.

Classification :-

1. Chemical Methods.
2. The Karl Fischer Method.
3. Distillation Methods.
4. Oven and Desiccation Methods : Comparisons.
5. Miscellaneous Methods.
6. Electrical Methods.

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