PHYSICOCHEMICAL STUDIES ON DUSTS.

A - ANALYSIS OF SILICIOUS DUSTS

B - SOME SORPTION PROPERTIES OF SILICIOUS DUSTS

by

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SECTION B - SOME SORPTION PROPERTIES OF SILICIOUS DUSTS.

Part 1 :- The Adsorption of Amino-acids and Dipeptides on Finely divided Silica.

Part II :- The Inhibition of the Adsorption of Amino-acids on Finely divided Silica.

Appendix.

SUMMARY.

Various important theories on the mechanism of the pathogenic reaction involved in the production of silicosis are critically surveyed. The favoured "solubility theory" suggested three topics for further physicochemical investigation.

(1) (a) The effect of various inorganic anions and cations on the determination of dissolved silica by the Molybdenum Blue method is studied.

The following ions do not interfere:-

Anions : Carbonate, chloride, nitrate, sulphate.

Cations: Aluminium, calcium, magnesium, manganese.

The extent and nature of the interference caused by the following ions is discussed:-

Anions : Dichromate, phosphate.

Cations: Copper, ferrous iron, ferric iron.

The effect of copper is noteworthy, in that compound formation is indicated, the apparent ratio of copper to silica in the complex being 12 : 1.

(b) Methods for the removal of copper and iron interference and for the determination of dissolved silica in the presence of dichromate ion are described.

Various methods for the removal of phosphate interference have been investigated but they have been found to be unsuccessful.

(2) /

(2) The use of infra-red spectroscopy for the determination of the free silica content of mineral dusts has been investigated. It is concluded that it is possible to determine the free silica content of a dust by this method.

A comparison of this method with two established methods has been carried out.

(3) (a) Adsorption isotherms for a number of amino-acids and dipeptides on a finely divided silica powder have been obtained. All the substances examined, with the exception of dl-leucylglycine, exhibit normal adsorption characteristics, the extent of adsorption decreasing with increasing temperature. The extent of adsorption of dl-leucylglycine on finely divided silica increases with increasing temperature between 25°C and 40°C, and, thereafter, decreases in the normal manner, the extent of adsorption being less at 45°C than at 25°C. No definite explanation of this result has been obtained, but it may be a result of a change in the type of adsorption, this change taking place above 40°C.

(b) A study on the use of galactose as an inhibiting agent for the adsorption of amino-acids on a finely divided silica powder at various pH values has been carried out. It is concluded that galactose is only partially successful in suppressing the adsorption of amino-acids on finely divided silica.

INTRODUCTION.

The work reported in this thesis is a section of the programme of research on surface studies on silica carried out in this department. This work is related to the silicosis problem and it is necessary, therefore, at this stage, to discuss the action of the disease and the various theories put forward as an explanation of the mechanism involved.

Silicosis is the most important form of pneumokoniosis - the pulmonary manifestation of dust inhalation - and was defined by the International Silicosis Conference in 1930 as a "pathological condition of the lungs due to the inhalation of free silica dust ---".

While the symptoms and the results of the disease have been familiar since the time of the Romans, Agricola (1) observing the high mortality rate among the hard rock miners in the Carpathian district, it was not until the beginning of this century that the unique significance of silica in the production of silicosis was appreciated. Unfortunately, there are many processes in the industrial world to-day in which silicosis and the various other forms of pneumokoniosis are common, e.g.

Anthracosis - "a dust disease of the lung found in coal miners, it is ill defined and is presumed to depend on inorganic dust in coal" (2)

and Asbestosis - "a fibrosis of the lungs with characteristic microscopical stigmata due to breathing asbestos dust, a silicate of magnesium" (2)

Amongst these industrial processes can be listed

(a) All processes involving rock drilling and grinding, e.g. quarrying, mining, refractory and pottery manufacture.

(b) Processes such as the polishing, grinding and buffing of castings

by /

by means of sand-blasting, grindstones and hones, etc. (i.e. foundry work).

Silicosis and the other pneumokoniosis diseases are brought about by continual exposure to air containing high concentrations of dust. While the air in country districts contains 0.1 - 0.2 mg. of dust/cu. metre, - a large portion of it being organic matter - the dust concentration in manufacturing towns may reach a level of 2.0 mg./cu. metre or more. In industrial establishments, the dust concentration varies enormously, it may be less than 1 mg./cu. metre in a well controlled plant and over 500 mg./cu. metre at the working face of a mine in which no dust control is practised.

The air inhaled by man travels to the lungs which are non-symmetrical structures encased in the chest. They communicate with the nose and mouth through the trachea or windpipe. The trachea is normally 1 - 2 cm. in diameter and 10 cm. long. It branches into bronchi, and they, in turn, subdivide into bronchioles which lead to the terminal air sacs or alveoli in which the gas exchange between the air and the blood takes place.

As dust laden air is inhaled, the dust particles 15 - 25 μ in size are likely to be caught in the nasal passages or at the back of the throat. They may pass, however into the trachea, but, it is unlikely that they will enter the alveoli. The collection of such particles depends on their contact with the moist walls of the respiratory tubes.

Lining /

Lining the trachea, the bronchi and the bronchioles are large numbers of whip-like appendages called cilia, which carry upwards by their own wave-like motions, and by a stream of mucus moving towards the nose and the mouth, the particles trapped on them. These particles are then either swallowed or expectorated.

When particles or foreign bodies of any kind reach the alveoli, scavenger cells called phagocytes are brought out in large numbers to engulf them. These cells, having the power of independent movement, may travel through the lung walls into a special drainage system known as the lymphatics which drain into the lymph nodes. The lymph nodes are situated along the bronchi and the bronchioles where the dust-laden cells are removed by means of the cilia to the nose and mouth.

Under normal circumstances, these protective mechanisms, which are fully described by Gardner (3), are adequate to prevent significant accumulation of foreign particles in the lungs.

However, continuous working in a very dusty atmosphere for a prolonged period may lead to a break-down of the protective mechanism. It is the break-down of the protective mechanism which starts the series of events - culminating in fibrosis of the lungs - known as silicosis.

As stated previously, particles above 15 μ in size do not normally reach the alveoli but are trapped on the walls of the trachea or bronchi and removed. McCrae (4) found that 70% of the particles in silicotic lungs were less than 1 μ in size, while the largest did not exceed 10.5 μ /

10.5 µ in size. Mavrogordato (5), confirming this fact, defines the troublesome particles as being between 0.5 µ and 10.0 µ in size. More recent work by Schulz and Tebbens (6) supports this conclusion. In a series of animal experiments using graded dust samples, they found that the degree of fibrosis produced, increased with decreasing particle size. It is concluded therefore, that those particles between 0.5 µ and 10 µ in size are dangerous, though some workers give wider limits.

Pneumokoniosis occurs, as stated above, as a result of the breakdown of the protective mechanisms of the respiratory system. However, the exact mechanism of the disease is not known although many theories have been brought forward. It is necessary, at this point, to discuss the more important of these theories.

Mechanical Theory.

The oldest theory of silicosis, which dates from 1860 (7) is the mechanical theory.

Haldane (8) while investigating the pathogenicity of materials used for stone dusting, found that soft materials, such as chalk and clay, were harmless, while hard material, such as granite and flint, produced inflammation of the lung tissue. He concluded, therefore, that hard sharp quartz particles would wound and tear the soft tissues of the lungs. However, there were many doubts about the truth of this theory, and it was attacked by Gardner (9) in 1923 and by Kettle (10) in /

in 1932. Gardner, working with sharp-edged silicon carbide (carborundum) powder found that this material did not produce silicosis although it is harder than quartz. Kettle found that, using a fine quartz dust of proved toxicity which had been coated with a layer of ferric oxide, no silicotic nodules were produced.

As a result of their work and that of other workers, this theory has now been abandoned.

Chemical Theory.

This theory was first postulated in 1918 by Lanza (11) who found that the pathogenicity of a dust increased with increasing silica content.

Gye, in association with Purdy (12, 13) and Kettle (14), substantiated this theory. These workers produced, in mice treated with amorphous silica and with colloidal silicic acid, a lesion characterised by acute inflammation and necrosis.

The fact that mineral dusts containing a high percentage of silica were the most active was also observed by Sayer (15).

However, Hefferman (16) obtained results, in a study of silicosis in Derbyshire industries, which apparently contradict this theory. He found that ganister-brick makers, exposed to a dust containing 83% of finely divided silica (with 9% of clay), did not contract silicosis. He concluded, however, that the clay mixed with the silica exerted some influence on the pathogenic nature of the free silica.

Policard /

Policard (17) showed that cells which had been poisoned by silicic acid did not disintegrate but tended to preserve their structures as if they were "mummified".

Kettle (18) suggested that silica was leached from the dust particles by the lung fluids and dissolved therein as "colloidal" silicic acid which acts as a cell poison. Further work by Kettle (9) showed that silicious dusts were toxic, while non-silicious dusts were innocuous. In the same paper, he showed that the dissolution of a soluble substance from a dust was necessary in the production of silicosis. He demonstrated this in the following manner. A thin layer of ferric oxide on the surface of quartz particles which had been shown by animal tests to be toxic rendered the dust innocuous. This coating of ferric oxide did not alter the sharpness of the particles but prevented any silicious material dissolving from their surface.

The work of Kettle and other workers has led to the gradual evolution of the modern solubility theory which states that dusts which liberate silica into solution at the greatest rate are the most active in the production of silicosis.

Much work in this field has been carried out by King (19,20) and his results, on the whole, support the solubility theory. For example, he has shown that quartz and flint, which have high solubilities in blood plasma, are amongst the most toxic mineral dusts, while shale dusts /

dusts, which have a low silica solubility, are of low pathogenicity. Moreover, shale dusts depress the solubility of silica dust to a marked extent and render the dust almost completely non-toxic.

Gardner, Dworski, and Delahant (21) giving the Donald E. Cummings Memorial Lecture at St. Louis, Missouri, on the 11th May, 1944, outlined the use of aluminium therapy in the treatment of silicosis. This treatment is based on the work of Denny, Robson, and Irwin (22) who have shown that the presence of finely divided metallic aluminium in a silica-laden atmosphere prevented the development of silicotic lesions in the lungs of animals exposed to such an atmosphere. The fact that the presence of aluminium depresses the solubility of the silicious dust further strengthens the solubility theory.

However, the relationship between the solubility of a dust and its pathogenicity does not always hold, as a study of Table 1(based on the work of King) shows. Various discrepancies between solubility and pathogenicity are indicated. For example, Gardner (23), in a study of 20 Angstrom silica dust produced as a condensate from furnaces, found that this dust, although extremely soluble, did not affect the lungs of experimental animals. He suggested that this was due to the fact that the material was so soluble that it was eliminated from the body before it could become toxic. King (19, Table 1) found that if large amounts of this material were injected into animals, the result was /

TABLE 1.

(After King)

Material	Solubility	Particle Size	Pathogenicity
Quartz (Racemic Mixture)	Great	All sizes	Strong
Quartz (Dextro-rotatory)	Great	2 & 2.5 µ	Strong
Quartz (Laevo-rotatory)	Great	2 & 2.5 µ	Strong
Quartz & Kaolin. 1% $Al(OH)_3$ freshly precipitated	Low solubility to insoluble	All sizes but 5 µ	Strong, after protective alumina disappeared
Clay-shale (8% quartz, kaolin, mica & carbonate)	Low	5 µ	Low
Sandstone, 70% quartz	Low, less than clay-shale	5 µ	Strong
20°A Silica	Completely soluble	-	10 mg. - none 16-20 mg. - strong 50 mg. - toxic
Olivine	Low to medium - Greater than sandstone	5 µ	Low

was fatal, while, small doses produced no fibrogenesis.

The fact that the solubility theory does not always hold has led to the hypothesis (24) that the process involved in the production of silicosis is a combination of the mechanical and solubility theories. Carborundum, although it has sharp edges, does not cause silicosis as there is no dissolution of silicic acid at the surface of the carborundum particle. Conversely, one would expect that quartz particles with no sharp edges should not produce silicosis.

Policard (25) has shown that desert sand, which is rounded, does not produce silicosis, although it has a high silica content. These facts give some backing to the above hypothesis, but further research is required before this hypothesis will be as universally favoured as the solubility theory.

While there are some anomalies in the solubility theory, one must agree with King (19) who states that "the solubility theory has been too useful to abandon because of the discovery of some discrepancies and anomalies although it is difficult to reconcile these differences."

Sericite Theory.

In 1933, Jones (26, 27), during a study of the anthracite mines of the South Wales coalfield, concluded that sericite was the chief agent in the production of silicosis. He observed, on examining mineral /

mineral residues obtained from silicotic lungs that it was not quartz, or any other form of free silica, that formed the bulk of these residues but that it was silicate minerals in the form of minute fibres. He suggested that this explained why the South African quartz-bearing rock was extremely toxic, while Indian quartz-bearing rock, which contains a higher percentage of quartz, had not caused a single case of silicosis. He observed that, in the South African rock, there are, between the quartz grains, many fibres of sericite, while in the Indian rock such fibres of sericite between the quartz grains are either absent or very rare. He claimed therefore, that this explains why rocks which have a low free silica content produce dusts which cause silicosis, the causative agent being sericite.

The theory was widely publicised throughout the world and criticisms came quickly.

Haldane (28), in 1934, stated that he had found nothing to indicate that sericite had anything to do with the production of silicosis, while the evidence pointing to dusts containing a high percentage of free silica was overwhelming. He also stated that the high percentage of sericite present, compared to free silica, in the mineral residue from silicotic lungs was the result of the greater solubility, in alkaline solutions, of free silica compared to the natural silicates.

Kettle /

Kettle (29), while admitting that sericite might cause silicosis, did not agree with Jones' statement that silicosis was not produced in its absence.

Lemon and Higgins (30) conducted animal tests using sericite and silica. They found that they could produce experimental silicosis by injecting silica, but, they could not produce silicosis by injecting sericite. Fallon and Banting (31) have reported similar results.

The sericite theory is no longer accepted.

Freshly Fractured Surface Theory.

The freshly fractured surface theory, first postulated by Heffernan (32) in 1935, is second in importance only to the solubility theory.

Heffernan suggested that silica was biologically active by virtue of the presence of unsatisfied valencies at the particle surfaces. Satisfaction of these valencies could take place by hydration in the atmosphere. To support this theory, he had to postulate that only freshly fractured material was active. However, it is most probable that the fresh surfaces would reach equilibrium with the surrounding atmosphere quickly, and therefore it would be unlikely that any dust would reach the alveoli in an active state.

Denny, Robson, and Irwin (22), in the work described previously, explained /

explained the fact that they produced silicosis in rabbits, in such a short period as six months, as the result of using freshly fractured dust.

Kitto and Paterson (33) and, more recently, Clelland (34) have shown that the solution potential of a dust decreases on ageing. This would connect the freshly fractured surface theory and the solubility theory, but work on ageing effects is still very incomplete and no definite conclusion can be reached.

Gardner (35) has shown that a commercial silica dust, which had been stored for a number of years, did not show any decrease in pathogenicity with time. In later experiments, Gardner (36) studied the parenteral injection of graded quartz, the grading being carried out by water sedimentation and decantation which involved the suspension of the quartz in water for several days before injection; consequently, there was ample time for the complete hydration of the surface of the quartz. However, he was still able to produce experimental silicosis.

Although the theory has been shown to have many defects, many workers have accepted it and used it to explain certain experimental phenomena. For example, Heffernan (37) has used it to explain the mechanism involved in aluminium therapy.

In /

In 1947, the freshly fractured surface theory was given fresh impetus by Policard (25) who cited the following.

(1) He observed that sheep in the North African desert are continuously exposed to the inhalation of sand but do not develop silicosis. He explained this as due to the fact that the sand was weathered, and therefore has no unsatisfied valency forces.

(2) He also observed that there was a high incidence rate amongst sand-blasters who work with weathered sand. He stated that this weathered sand is broken up into small particles by heat and impact and fresh surfaces produced.

The work of Bagnold (38), cited by Heywood (39), disproved the "desert sand" theory. He has shown that the majority of the sand particles are greater than 200 mesh in size and that the airborne dust breathed by the sheep comes from adjacent lands and is almost entirely non-silicious. These facts account for the failure of desert sheep to develop silicosis, and, also, for the high incidence rate amongst sand-blasters, since they are exposed to very fine particles produced by fracture of the large particles. It is unlikely, therefore, that freshly fractured surfaces show any special activity.

In 1949, Weyl (40) suggested a new approach to the freshly fractured /

fractured surface theory. He brought forward evidence that nasent oxygen is present at the surface of ground silica, and suggested that the presence of this oxygen explains the peculiar effect of silica on animal tissue. As nasent oxygen at the surface of the particle would dissipate rapidly, he had to assume that freshly fractured silica is the only active form. This phenomenon is more clearly shown by clays and Weyl concludes, therefore, that clays can cause silicosis. This is contrary to the result obtained by Smith and Collis (41) who have shown that clays may inhibit the production of silicosis.

A detailed discussion of the freshly fractured surface theory has been published by Wright (42) who has also summarised the unique biological properties of silica in the following manner:-

"(1) Silicon dioxide (SiO_2), whether crystalline or amorphous (10,23) when injected into any tissue (not only the lungs) of a large variety of animals in a suitable form, will produce a series of pathological changes culminating in fibrosis, which are unlike those produced by any other mineral that has been investigated.

(2) In order to produce these effects, the particles of silica must be less than about 3 µ in average diameter (36) but more than about 100°A. The upper limit is well established but the exact /

exact position of the lower limit has not yet been fully investigated. It is known that even if the particles are of colloidal size, they are very toxic (10) but they produce an acute inflammatory reaction not readily distinguishable from that cause by many other substances.

(3) This property of silica is a function of its surface as evidenced by the fact that:

  (a) It is only shown by particles less than a certain size.
  (b) Within limits, the effect of a given weight of silica is proportional to the fineness of the particles of which it is composed.
  (c) It is apparently exerted without obvious loss of material.
  (d) It is inhibited by the presence of a substance such as aluminium or iron oxide which may be adsorbed on to the surface of the silica.

(4) Apart from its own effects, silica has the property of facilitating the proliferation of tubercle bacilli in animal tissue (10), a property which is not shown by other necrotizing substances.

(5) It appears that the effect of silica is that of a tissue poison rather than a cell poison."

In /

In conclusion, in spite of its many defects, the freshly fractured surface theory, like the solubility theory, is still popular and is the basis of much research.

Overloading Theory.

The Medical Research Council, as a result of an extensive research programme, has concluded that airborne dust with a quartz content seldom greater than 4% may be an important factor in the production of pneumokoniosis due to overloading of the lungs.

Gough (43) has stated that coal workers' pneumokoniosis is pathologically distinct from classical silicosis. The fundamental lesion is a nodule, but it is smaller and less firm than that in classical silicosis. This nodule is surrounded by a zone of emphysema and he suggests that this may be caused by dust accumulating in the lung and interfering with the normal working of the lung.

He also states that there are two types of coalworkers' pneumokoniosis -

(a) "Simple pneumokoniosis" caused by accumulation of coal dust, the latter being responsible for only a small amount of reticulin fibrosis.

(b) "Infective pneumokoniosis" caused by the combined action of tubercle and coal dust producing infective nodules consisting of /

of collagen - like fibrous tissue which later combine to form massive fibrosis.

Heppleston (44) has confirmed the work of Gough and he also concludes that dust accumulation, rather than any physical or chemical activity of silica, was the chief agent in the production of simple silicosis.

This theory is still being developed and is not fully accepted, although, it has been noted by Jones (45) that 15 years ago a dust containing less than 50% free silica was considered to be non-toxic and that, now, anthracite dust containing less than 2% free silica is responsible for about 80% of the pneumokoniosis in this country.

The various theories described above have been evolved in an attempt to explain the mechanism of the production of silicosis. However, it would appear that these various theories when taken on their own give an oversimplified explanation and that the mechanism is a combination of these various theories.

In this work an attempt has been made to study various factors which are important in the light of these theories.

The topics which have been studied are:-

(a) <u>Analysis of silicious dusts</u>.

(i) An investigation into the estimation of dissolved silica by the molybdenum /

molybdenum blue method. The determination of dissolved silica is important in research work based on the study of the solubility theory.

(ii) The determination of free silica by infra-red spectroscopy. Present methods of silica determination do not give very satisfactory results when they are applied to airborne dust. It is necessary, therefore, to obtain a method which will give accurate results so that an exact correlation between the free silica content and the pathogenicity of a dust can be obtained.

and (b) Some sorption properties of silicious dusts.

A study of the adsorption of several amino-acids and dipeptides on finely divided silica dust has been carried out as it is possible that adsorption reactions may play an essential part in the mechanism of the production of silicosis and other forms of pneumokoniosis.

SECTION A

ANALYSIS OF SILICIOUS DUSTS

PART I - THE ESTIMATION OF DISSOLVED SILICA BY MOLYBDENUM BLUE METHOD.

Introduction.

Many workers have carried out research based on the so-called solubility theory of silicosis. As a consequence of this, much effort has been directed to the accurate determination of small amounts of dissolved silica. Originally, gravimetric methods (46, 47) were favoured; but more recently, these relatively inaccurate and time-consuming methods have tended to be replaced by colorimetric methods.

The original method of Jolles and Neurath (48) developed by Dienert and Wandelbulcke (49) depends on the formation at suitable pH values of yellow silicomolybdic acid, believed to be a complex of the composition $H_8Si(Mo_2O_7)_6H_2O$(50). This original method suffers from several disadvantages. These are -

(1) Lack of sensitivity:- at low silica concentration.

(2) Beer's Law (51) is not obeyed at high concentration.

(3) Instability of colour developed.

Because of these defects, the method has largely been replaced by the method of Isaacs (52) which depends on the reduction of the yellow silicomolybdic acid to Molybdenum Blue "$Mo_3O_88H_2O$". This indirect method is the most sensitive method for the estimation of silica, the colour developed is stable and obeys Beer's Law. Many reducing agents have been used for this reduction, the following being the most important /

important: (a) 1 - amino - 2 naphthol - 4 - sulphonic acid (53); (b) stannous chloride (54); (c) sodium sulphite (55); (d) hydroquinone (56); (e) hydroxylamine (57); (f) 4 - hydroxyphenylglycine (58).

It has recently been stated by Strickland (59), that pH is not the sole factor in the formation of silicomolybdic acid. He concluded that two different forms of silicomolybdic acid exist, dependent upon the number of equivalents of acid present per gram-ion of molybdate. If the molybdate present as the ion MoO_4'', is acidified with up to 1.45 - 1.50 equivalents of acid per gram-ion of molybdate then the main product of the reaction is the silicomolybdic acid of the literature known as α - silicomolybdic acid. The β - silicomolybdic acid is formed when silicic acid reacts with molybdate which has been acidified with more than two equivalents of acid per gram-ion of molybdate. These forms have the same empirical formula but different anion structures, and yield reduction complexes with different extinction coefficients. The extinction from a given concentration of combined silica is twice as great with the β - acid as with the α - acid. Strickland has stated therefore, that, to ensure the formation of the β - complex only, it is desirable to react silicic acid or silicate solution with an ammonium molybdate solution containing between 3 and 5 equivalents of acid per gram-ion of molybdate; if this exceeds 7-10 equivalents of acid per gram-ion of molybdate; the reaction is impracticably slow. Gibb (60) has shown that the method of analysis used in the present work (a modification /

modification by Clelland (34) of the method of Harrison and Storr (61) complies with Strickland's criterion for ensuring the formation of the β- complex only.

The present investigation was planned in order to find the effect of impurities, likely to be present in mine dusts, on the determination of dissolved silica in a borate buffer solution (pH 7.5).

Preparation of Solutions.

(a) Solutions of Interfering Ions.

0.01M solutions containing the following ions were made up from "Analar" materials.

Interfering Anion	Salt Used	Interfering Cation	Salt Used
Carbonate	K_2CO_3	Aluminium	$Al(NO_3)_3$
Chloride	KCl	Calcium	$CaCl_2$
Dichromate	$K_2Cr_2O_7$	Copper	$CuSO_4$
Nitrate	KNO_3	Iron (Ferrous)	$FeSO_4$
Phosphate	KH_2PO_4	Iron (Ferric)	$Fe_2(SO_4)_3$
Sulphate	K_2SO_4	Magnesium	$Mg(NO_3)_2$
		Maganese	$MnSO_4$

For the first group, a common cation (potassium) was used throughout; for the second, anions were selected from those which had already been shown (by work on the first group) to be non-interfering.

(b) /

(b) Standard Silica Solution.

Finely ground quartz (25 mg.) was fused with "Analar" sodium carbonate and the cooled melt dissolved in distilled water. The excess of alkali was neutralised with sulphuric acid and the solution made up to 1 litre with distilled water.

(c) Borate Buffer Solution.

Boric acid (11.16 g.) and sodium borate (1.81 g.) were dissolved in distilled water and the solution made up to 1 litre. This solution has a pH 7.5.

(d) 5% Ammonium Molybdate Solution.

"Analar" ammonium molybdate (6 g.) was dissolved in a little distilled water. The solution was then filtered through a Whatman's No. 542 paper and made up to 100 ml. with distilled water. 6N sulphuric acid (20 ml.) was then slowly added to the solution with constant stirring.

(e) Reducing Solution.

"Analar" sodium sulphite (60 g.) and "Analar" hydroquinone (10 g.) were dissolved in distilled water and the solution made up to 500 ml. with distilled water.

Experimental Procedure.

Solutions containing 25 ml. of borate buffer solution (pH 7.5), 4 ml. of standard silica solution, and 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 /

10, 11, and 14 ml. of 0.01 M solution of the ion under test were placed in a cellulose acetate (Lusteroid) tubes and each solution made up to 43 ml. by addition of distilled water.

5% ammonium molybdate solution (2 ml.) was added to each tube, the solution stirred for 30 seconds and the yellow coloration allowed to develop for 5 minutes. Reducing solution (5 ml.) was then added to each tube and the solution stirred for 30 seconds. The blue colour produced was allowed to develop for 30 minutes and its intensity was then measured by an EEL colorimeter using an Ilford red filter (No. 608).

The recorded silica concentration (mg./25 ml. of borate buffer solution), obtained from calibration curves was plotted against mg.-ion of inorganic ion present.

In studying the effect of copper ion, some of the work was done with a "Spekker" photoelectric absorptiometer, and graphs of optical density vs. mg.-ion of copper present were obtained. An Ilford red filter (No. 608) was again used.

To ensure constant analytical condition and hence increased accuracy, all reagents were measured out in a series of test tubes equally spaced on a rack so that they could be added simultaneously to all the test solutions. The test solutions were similarly placed on another rack. Stirring was carried out, using a number of correspondingly-spaced spatulas on a wooden block.

Calibration of Colorimeter.

Various /

Various volumes of standard silica solution were pipetted into cellulose acetate (Lusteroid) tubes containing 25 ml. of borate buffer solution and the silica determined in the normal manner. A graph of colorimeter reading against silica concentration was plotted, and from this graph, concentrations of silica could be obtained, expressed as mg. silica/25 ml. of solution. The accuracy of the method has been shown by Gibb (60) to be ± 1.75%.

Summary and Discussion of Results.

It was found that the following ions did not interfere.

Anions :- Chloride, nitrate and sulphate.

Cations:- Aluminium, calcium, magnesium and manganese.

The ions which interfered are listed and discussed below.

(a) Anions.

(1) Carbonate (Fig. 1).

Increasing concentration of carbonate ion was found to increase the recorded silica concentration in a linear fashion. This result was unexpected but can be explained in the following manner.

Although "Analar" potassium carbonate was used in the test, it was found to contain 0.04% of silica as an impurity. This silica impurity was found to be responsible for the difference between the recorded and actual silica concentrations. It can be concluded therefore, that carbonate does not interfere.

(2) Dichromate (Fig. 2).

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FIG. 1.

EFFECT

OF

CARBONATE ION

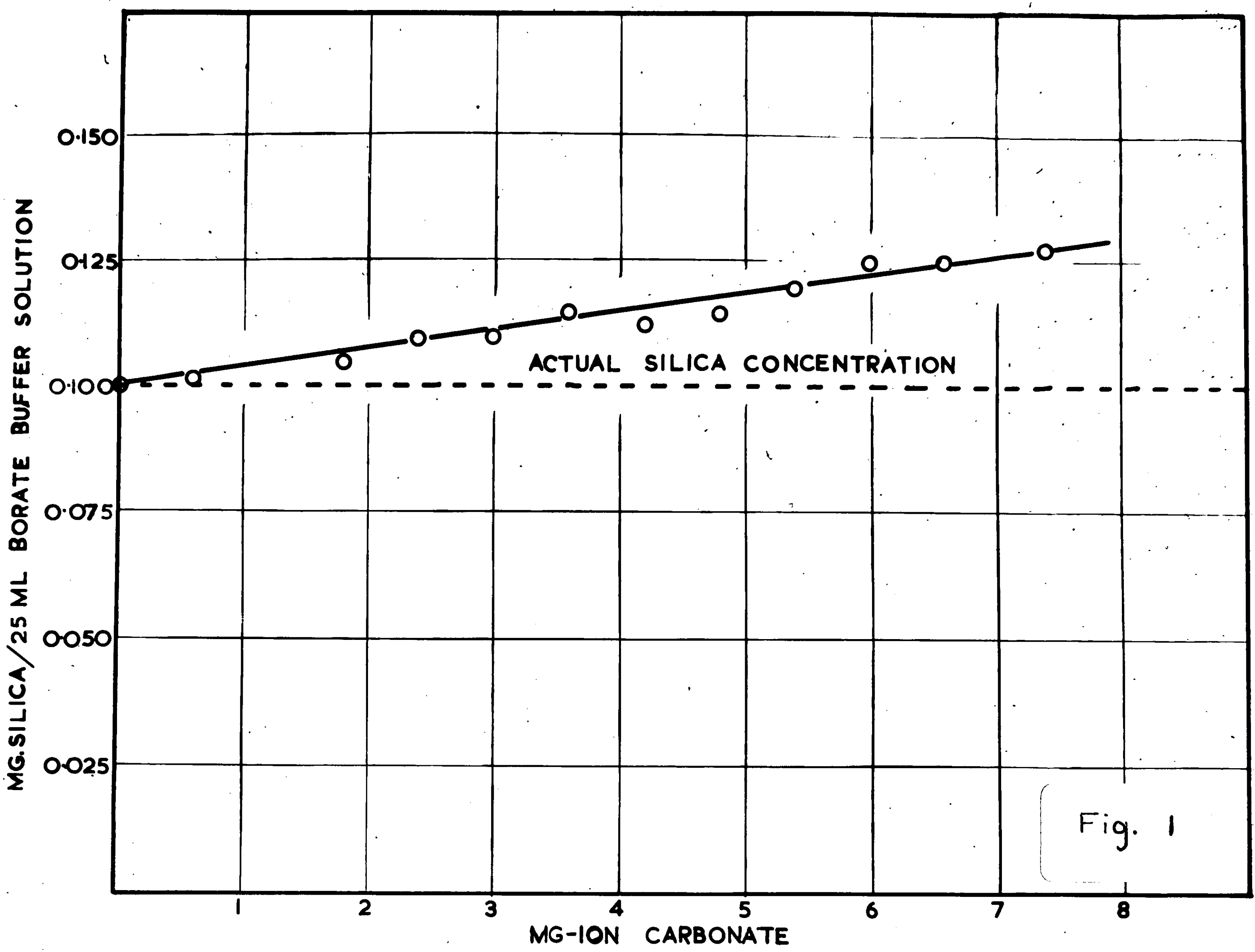

O·150
O·125
O·100
O·075
O·050
O·025
MG.SILICA/25 ML BORATE BUFFER SOLUTION
1
2
3
4
5
6
7
8
MG-ION CARBONATE
ACTUAL SILICA CONCENTRATION

Fig. 1

FIG. 2.

EFFECT

of

DICHROMATE ION

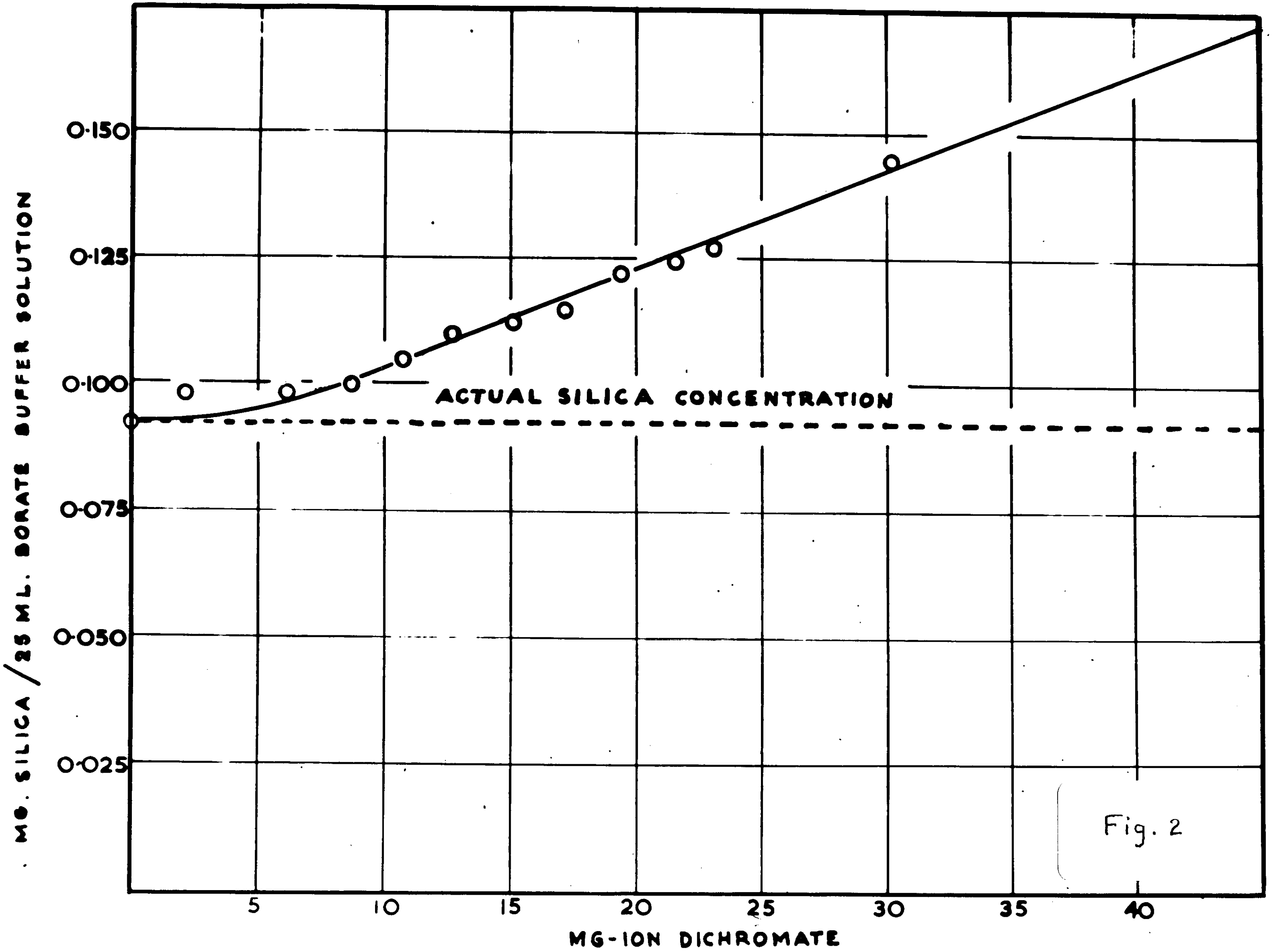

0·150
0·125
0·100
0·075
0·050
0·025
MG. SILICA / 25 ML. BORATE BUFFER SOLUTION
ACTUAL SILICA CONCENTRATION
5
10
15
20
25
30
35
40
MG-ION DICHROMATE

Fig. 2

The presence of dichromate ion led to a recorded silica concentration higher than the actual, the former increasing as a linear function of dichromate ion concentration. This effect is to be expected in view of the strong colour of dichromate solution.

It can be concluded therefore, that the chromic ion would also interfere as the estimation is carried out at pH 2.5, so that any chromium ion present would be in the oxidised state.

(3) Phosphate (Fig. 3).

Phosphate reacts with molybdate to form phosphomolybdates and would be expected therefore to interfere in this method of analysis, giving recorded silica concentrations increasing with increasing concentration of phosphate ion. However, the results obtained (Fig. 3 Curve 1) show that the recorded silica concentration first rises to a maximum and thereafter decreases to a steady value as the concentration of phosphate ion increases.

This is contrary to expectations, and an explanation must be sought. A control test, in which silica was omitted, was therefore conducted in the prescribed manner. The resulting plot of colorimeter reading vs concentration of phosphate ion (Fig. 3 Curve 2.) was found to be very similar in form to the plot of recorded silica vs concentration of phosphate ion. It seems therefore that the unexpected result is entirely due to the presence of the phosphate ion, and not to any combined /

FIG. 3.

EFFECT OF PHOSPHATE ION

1 - Silica + phosphate ion.

2 - Phosphate ion only.

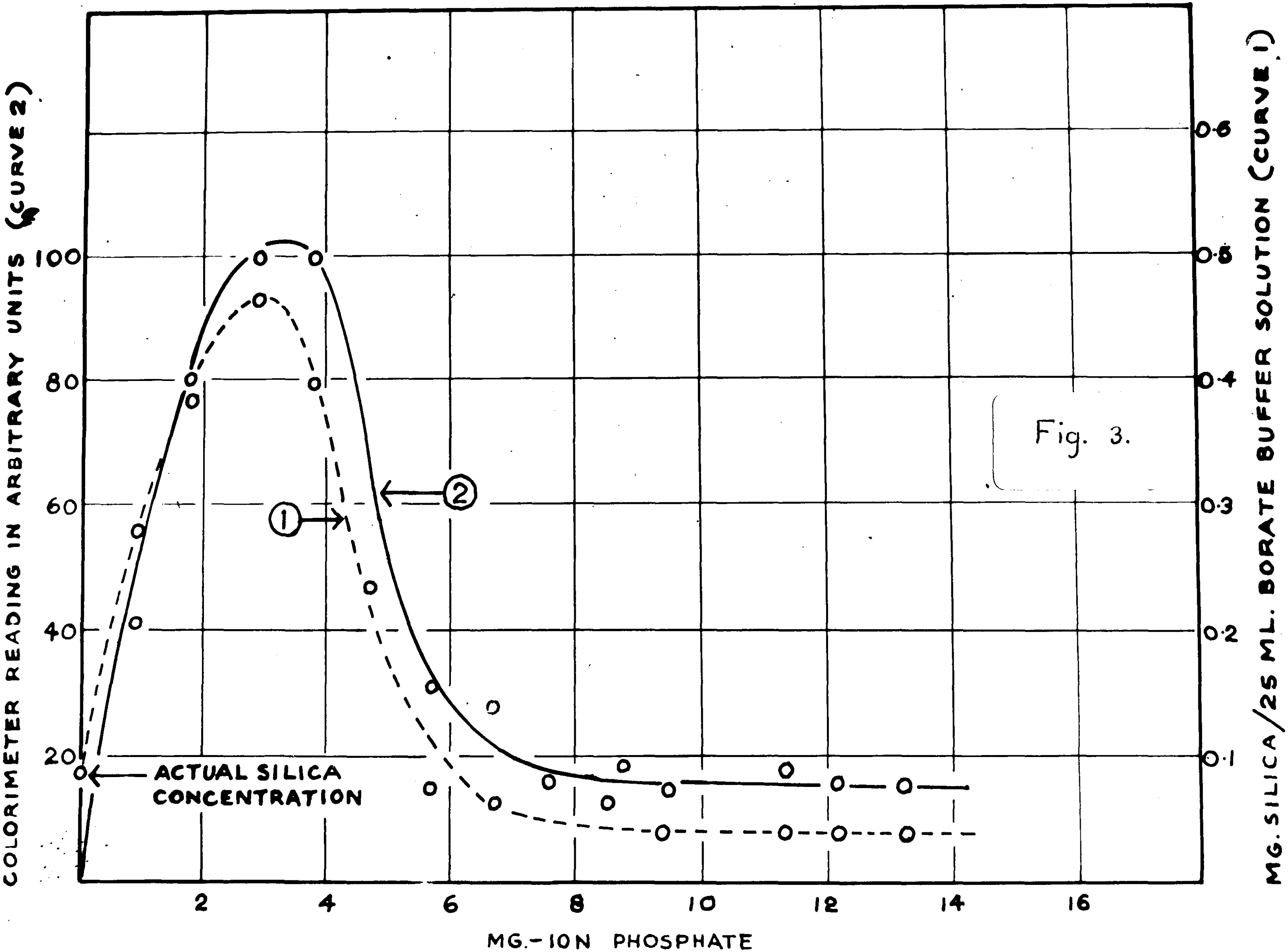


Fig. 3.

COLORIMETER READING IN ARBITRARY UNITS (CURVE 2)
MG. SILICA/25 ML. BORATE BUFFER SOLUTION (CURVE 1)
MG.-ION PHOSPHATE
100
80
60
40
20
0·6
0·5
0·4
0·3
0·2
0·1
2
4
6
8
10
12
14
16
ACTUAL SILICA CONCENTRATION
①
②

combined effect.

The form of the curve may be explained as follows. As the concentration of phosphate ion increases, the phosphomolybdate formed on interaction of phosphate with ammonium molybdate will tend to precipitate in either a solid or colloidal form. (The gravimetric estimation of phosphate by the phosphomolybdate is an established analytical method). The phosphomolybdate in either of these forms will not be reduced to the blue complex. The concentration of phosphate, estimated as reduced complex, will therefore, tend to remain constant, once the equilibrium concentration of phosphomolybdate in solution has been attained. The fact that the curve passes through a maximum before descending to a steady value can be explained by supersaturation of the phosphomolybdate in solution.

King (62) has recently published work on the effect of various inorganic ions on the Molybdenum Blue Method. The results he has obtained on the effect of phosphate are similar to those reported here. He has found that the silicomolybdate complexes show marked visible changes with increasing phosphate ion concentration, changing from intense yellow at 1.2 mg. phosphorus to colourless at 2.0 mg. phosphorus. He suggests that this is due to changes in the nature of the complex at these relatively high values of phosphate which could /

could alter the molecular value of molybdate to phosphate in the complex.

(b) Cations.

(i) Ferrous and Ferric Iron (Figs. 4 & 5).

The curves show that increasing concentration of ferrous and ferric iron decreases the recorded silica concentration in linear fashion. It is to be expected that these ions will affect the estimation, since (a) they give coloured solutions, and (b) ferric iron reacts with molybdic acid to form ferric molybdate.

However ferrous iron (63) has been used for the reduction of silicomolybdic acid to Molybdenum Blue and it is therefore, concluded that ferrous iron should have no effect on the estimation.

The solvent used in this work was a borate buffer solution of pH 7.5; and at this pH both ferrous and ferric iron are precipitated as the corresponding hydroxide. Ferrous hydroxide, however, rapidly absorbs oxygen, forming ferric hydroxide which would react with the acid molybdate solution forming ferric molybdate which would interfere with the estimation.

In the test to determine the effect of ferrous iron, it was observed that precipitate obtained was brown in colour, instead of the white or greenish colour of ferrous hydroxide. Examination of this precipitate showed that the iron present was in the ferric state. This, /

FIG. 4.

EFFECT

OF

FERROUS ION.

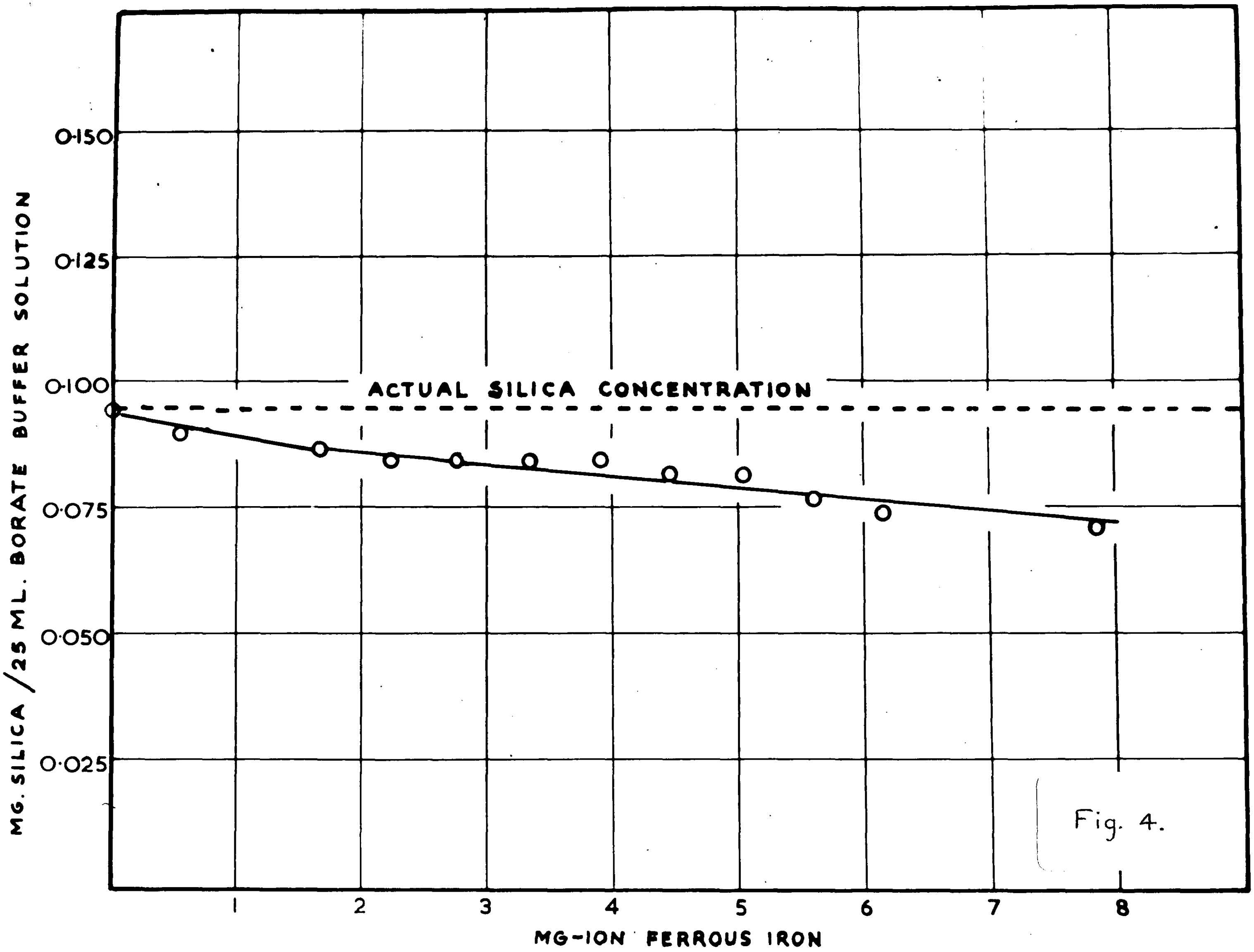

ACTUAL SILICA CONCENTRATION
MG. SILICA /25 ML. BORATE BUFFER SOLUTION
0·150
0·125
0·100
0·075
0·050
0·025
MG-ION FERROUS IRON
1
2
3
4
5
6
7
8

Fig. 4.

FIG. 5.

EFFECT

of

FERRIC ION

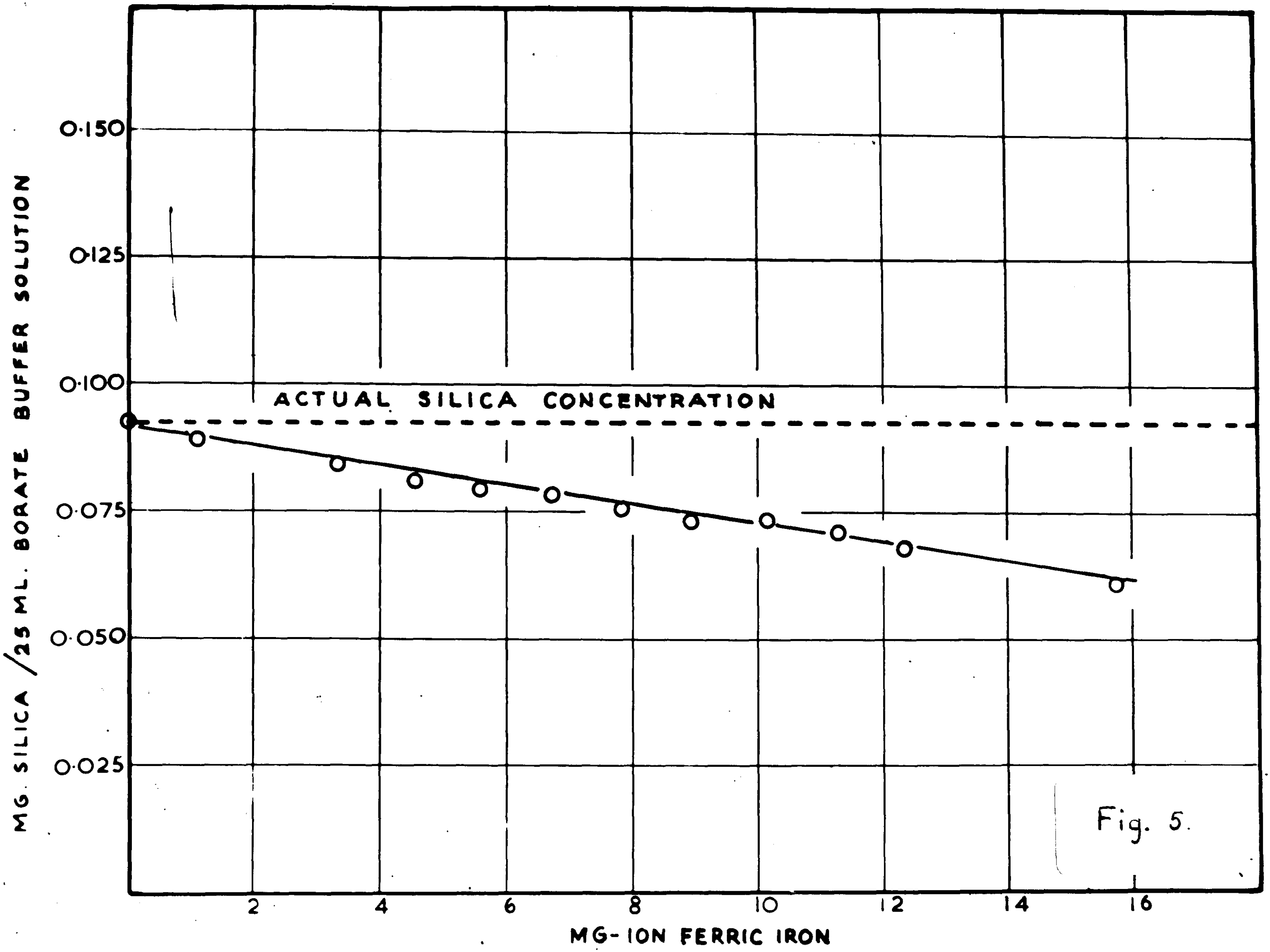

ACTUAL SILICA CONCENTRATION
MG. SILICA /25 ML. BORATE BUFFER SOLUTION
0·150
0·125
0·100
0·075
0·050
0·025
2
4
6
8
10
12
14
16
MG-ION FERRIC IRON

Fig. 5.

This, therefore, leads to the conclusion that the mechanism of interference is the same in both cases and that the presence of iron interferes in the estimation as a result of the formation of ferric molybdate.

(ii) Copper (Figs. 6, 7, 8, 9, 10).

Increasing concentration of copper ion increased the recorded silica concentration until a steady value was obtained (Fig. 6). Interference is to be expected, in view of the colour of copper solutions; but it would be expected that increasing concentration of copper ion would cause a linear increase in the recorded silica concentration. The attainment of a steady value, therefore, requires further study.

The form of Fig. 6 indicates some type of complex formation. It was decided, therefore, to repeat the above test using varying amounts of silica solution. A "Spekker" photoelectric absorptiometer was used in preference to the EEL colorimeter.

The apparent silica concentration was determined for:-

(a) 4 ml. of standard silica solution and varying amounts of copper solution made up as described previously;

(b) 6 ml. of standard silica solution and varying amounts of copper solution made up as described previously; and

(c) a "blank" solution containing varying amounts of copper solution made /

FIG. 6.

EFFECT

OF

COPPER ION

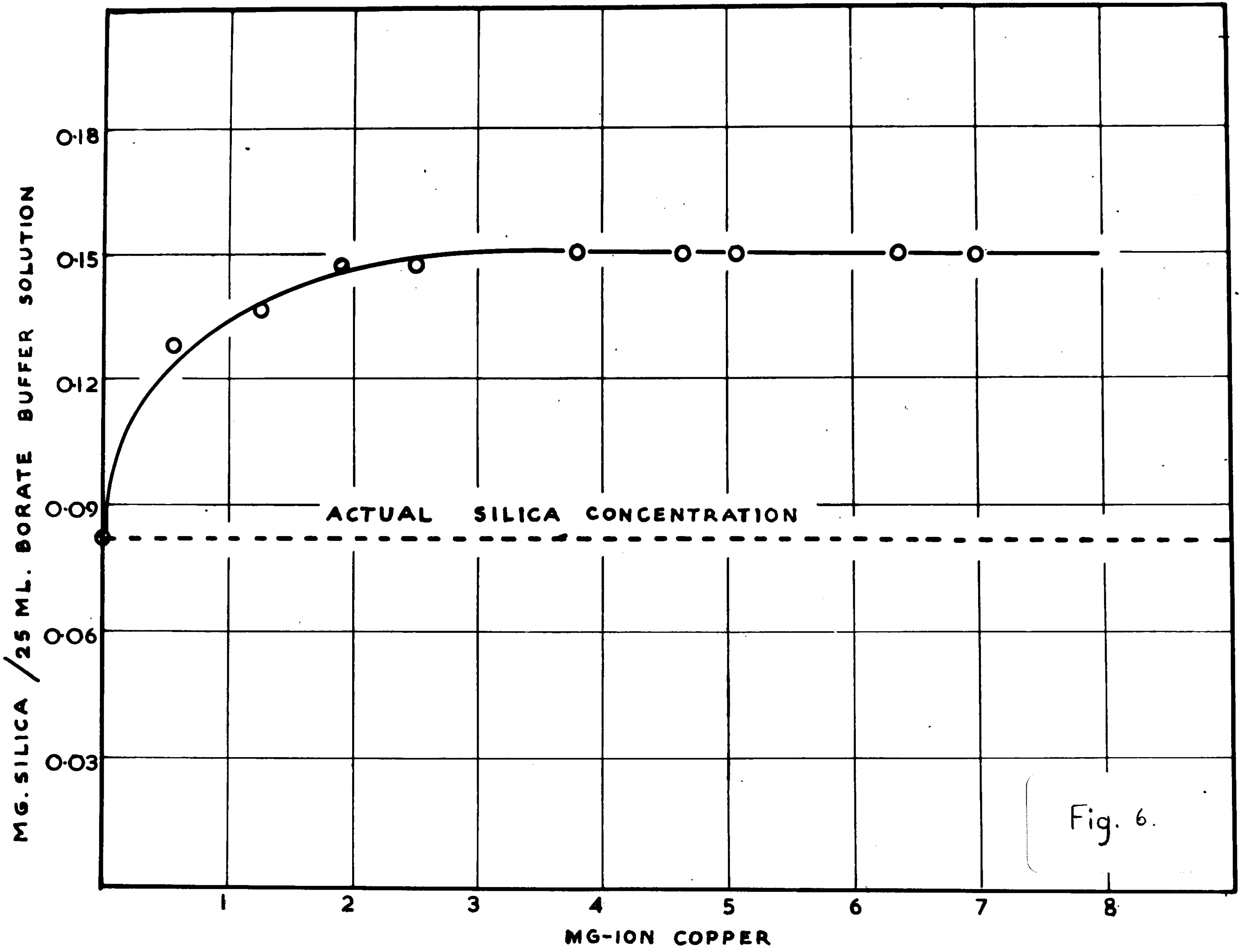

0·18
0·15
0·12
0·09
0·06
0·03
MG. SILICA /25 ML. BORATE BUFFER SOLUTION
1
2
3
4
5
6
7
8
MG-ION COPPER
ACTUAL SILICA CONCENTRATION

Fig. 6.

made up as described previously.

The results (Fig. 7) show that the copper ion alone does not react with molybdic acid, or with the reducing solution, and that the effect shown is a combined one.

It was decided, therefore, to plot the optical density of the solution against the logarithm of the copper ion concentration (Fig. 8) as this gives a method of determining the ratio of copper ion to silica present in the complex. Instead of the normal curve, this type of diagram gives two straight lines; the junction of these lines giving the amount of copper ion involved in the reaction.

	(a)	(b)
Volume of Standard silica solution (ml.)	4.0	6.0
Concentration of silica (mg.)	0.10	0.15
Log. concentration of copper ion (mg. X 10) (From Fig. 8)	1.110	1.275
Concentration of copper ion (mg.)	1.288	1.883

$$\text{Molecular Ratio} \quad \frac{\text{Copper}}{\text{Silica}} = \frac{\frac{1.288}{63.5}}{\frac{0.10}{60}} \qquad \frac{\frac{1.883}{63.5}}{\frac{0.15}{60}}$$

$$\fallingdotseq \frac{12}{1} \qquad \frac{12}{1}$$

The above calculation indicates that the ratio of copper ion to silica present in the complex is 12 : 1.

As a further indication of compound formation, colour development curves (Fig. 9) were obtained in the normal manner for:-

(a) /

FIG. 7.

EFFECT OF COPPER ION

-x- 4 ml. Sio_2soln. + varying amts. of 0.01M. $CuSO_4$ soln.

-o- 6 ml. SiO_2soln. + varying amts. of 0.01M. $CuSO_4$ soln.

-●- "Blank" soln. containing varying amts. of 0.01M. $CuSO_4$ soln.

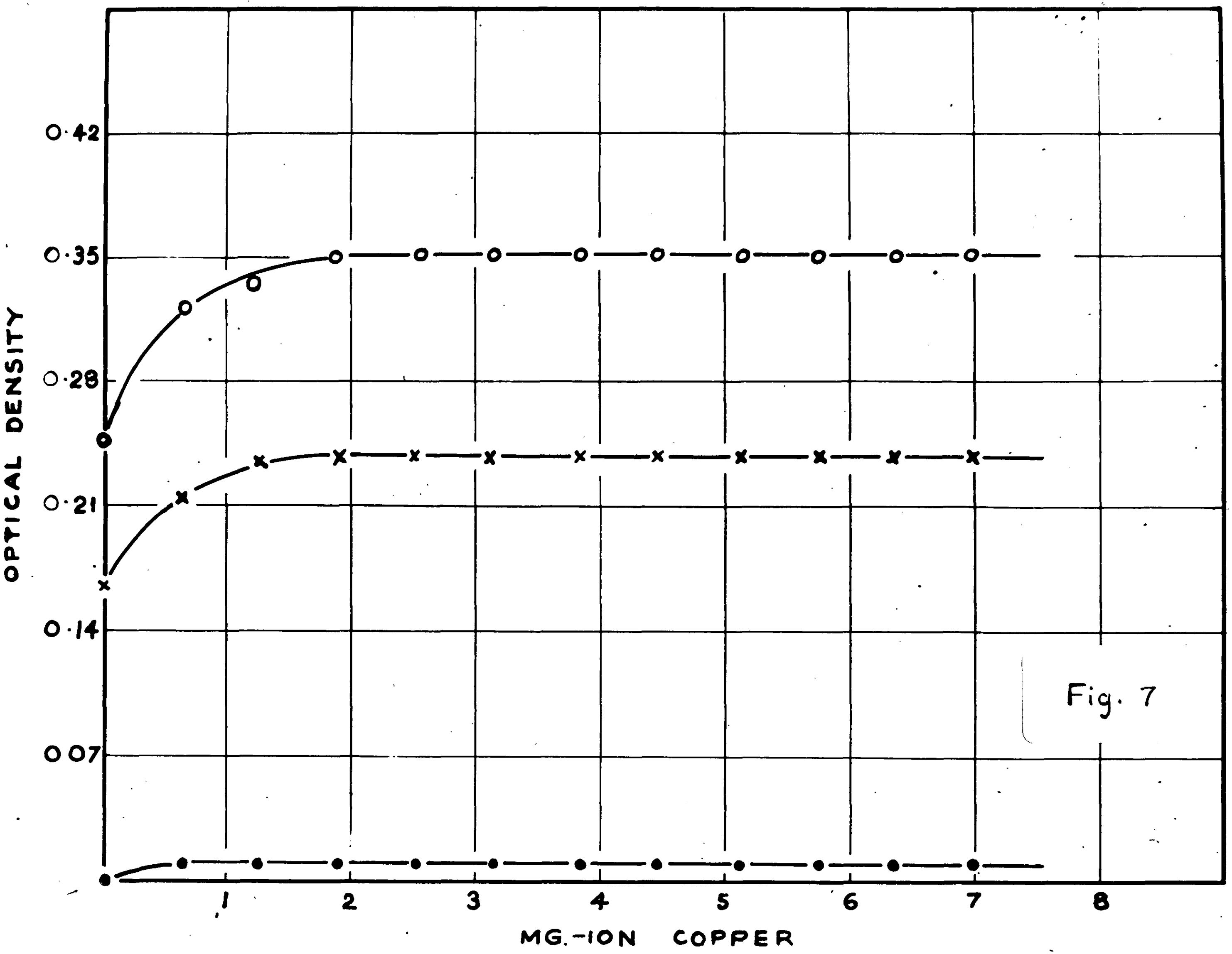

O·42
O·35
O·28
O·21
O·14
O O7
OPTICAL DENSITY
1
2
3
4
5
6
7
8
MG.-ION COPPER

Fig. 7

FIG. 8.

EFFECT OF COPPER ION

-x- 4 ml. SiO_2soln. + varying amts. of
0.01M. $CuSO_4$ soln.
-o- 6 ml. SiO_2soln. + varying amts. of
0.01M. $CuSO_4$ soln.

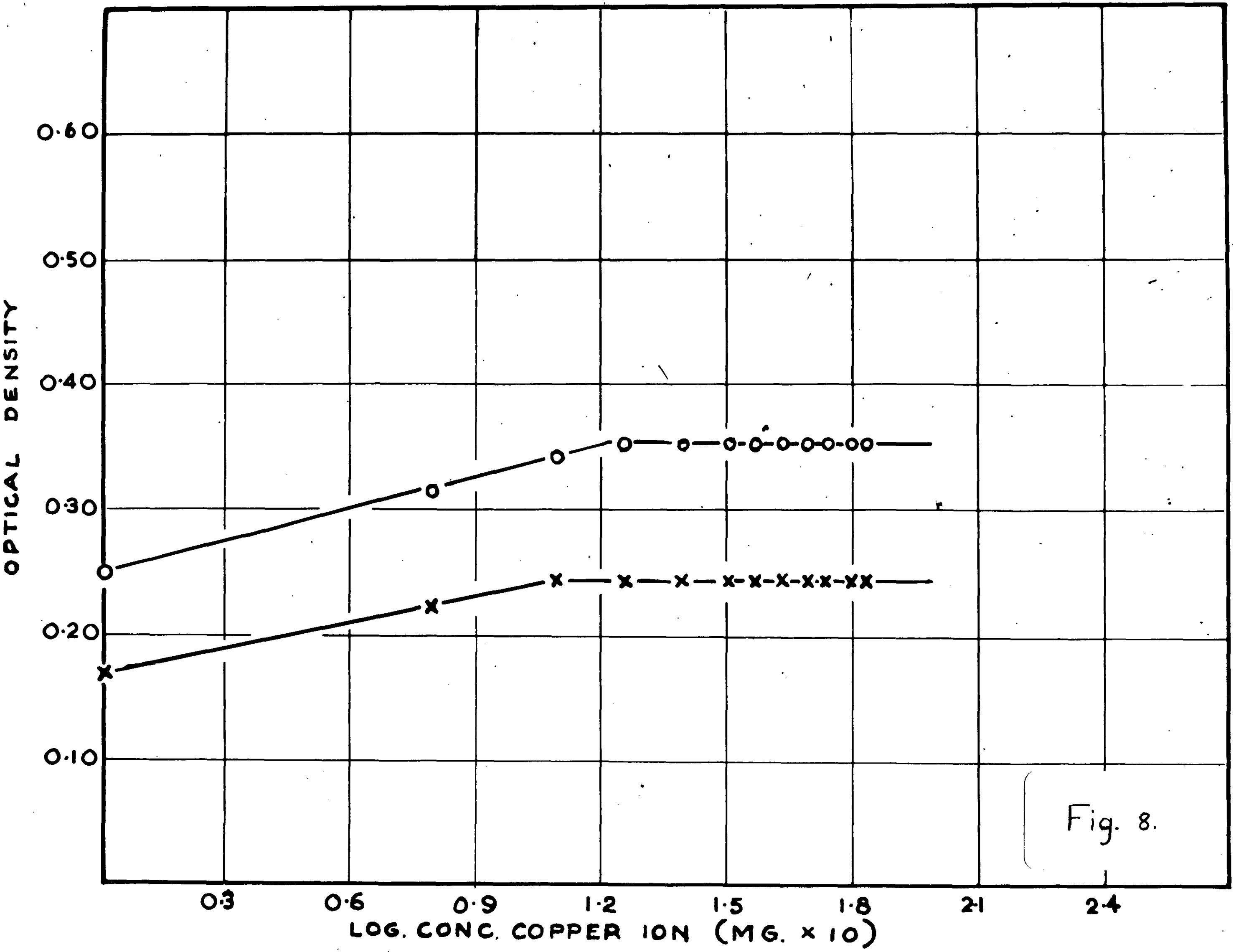

OPTICAL DENSITY
0·60
0·50
0·40
0·30
0·20
0·10
0·3
0·6
0·9
1·2
1·5
1·8
2·1
2·4
LOG. CONC. COPPER ION (MG. × 10)

Fig. 8.

(a) reduced silicomolybdate

(b) reduced silicomolybdate containing copper solution; and

(c) copper solution.

A study of Fig. 9 shows that there is a marked difference in the colour development curves obtained for (a) and (b), again, indicating compound formation.

A study of the ultra-violet and visible light absorption spectra of the three solutions (Fig. 10)

(a) Reduced silicomolybdate

(b) copper solution

(c) Reduced silicomolybdate containing copper solution

shows that absorption maxima occur at 2200Å , 2900 Å and 7750 Å. However, the absorption bands obtained for solution (c) are broader and more intense. This is an indication of compound formation.

It is concluded that copper ion interferes in the estimation because of compound formation, the complex formed having the molecular ratio of copper ion to silica of 12 : 1.

Conclusions.

(1) Of the anions examined, carbonate, chloride, nitrate and sulphate in the concentrations used, do not interfere with the estimation.

(2) Of the cations examined, aluminium, calcium, magnesium and manganese, in the concentrations used, do not interfere with the estimation.

(3) /

FIG. 9.

COLOUR DEVELOPMENT CURVES

-o- Reduced silicomolybdate + copper soln.

-x- Reduced silicomolybdate

-●- Copper soln.

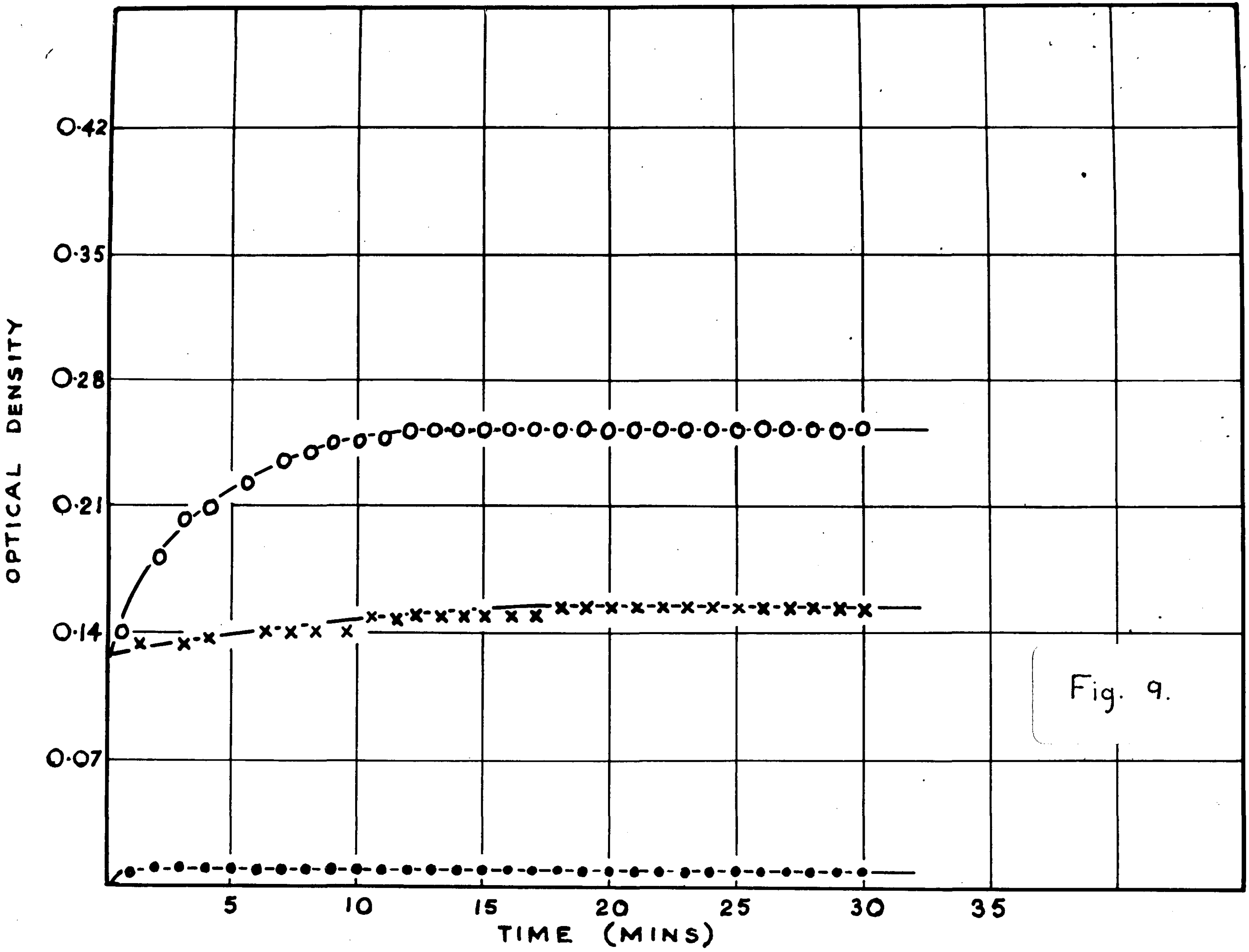


Fig. 9.

OPTICAL DENSITY
0·42
0·35
0·28
0·21
0·14
0·07
5
10
15
20
25
30
35
TIME (MINS)

FIG. 10.

ULTRA-VIOLET AND VISIBLE LIGHT
ABSORPTION SPECTRA

(a) Reduced silicomolybdate.

(b) Copper soln.

(c) Reduced silicomolybdate + copper soln.

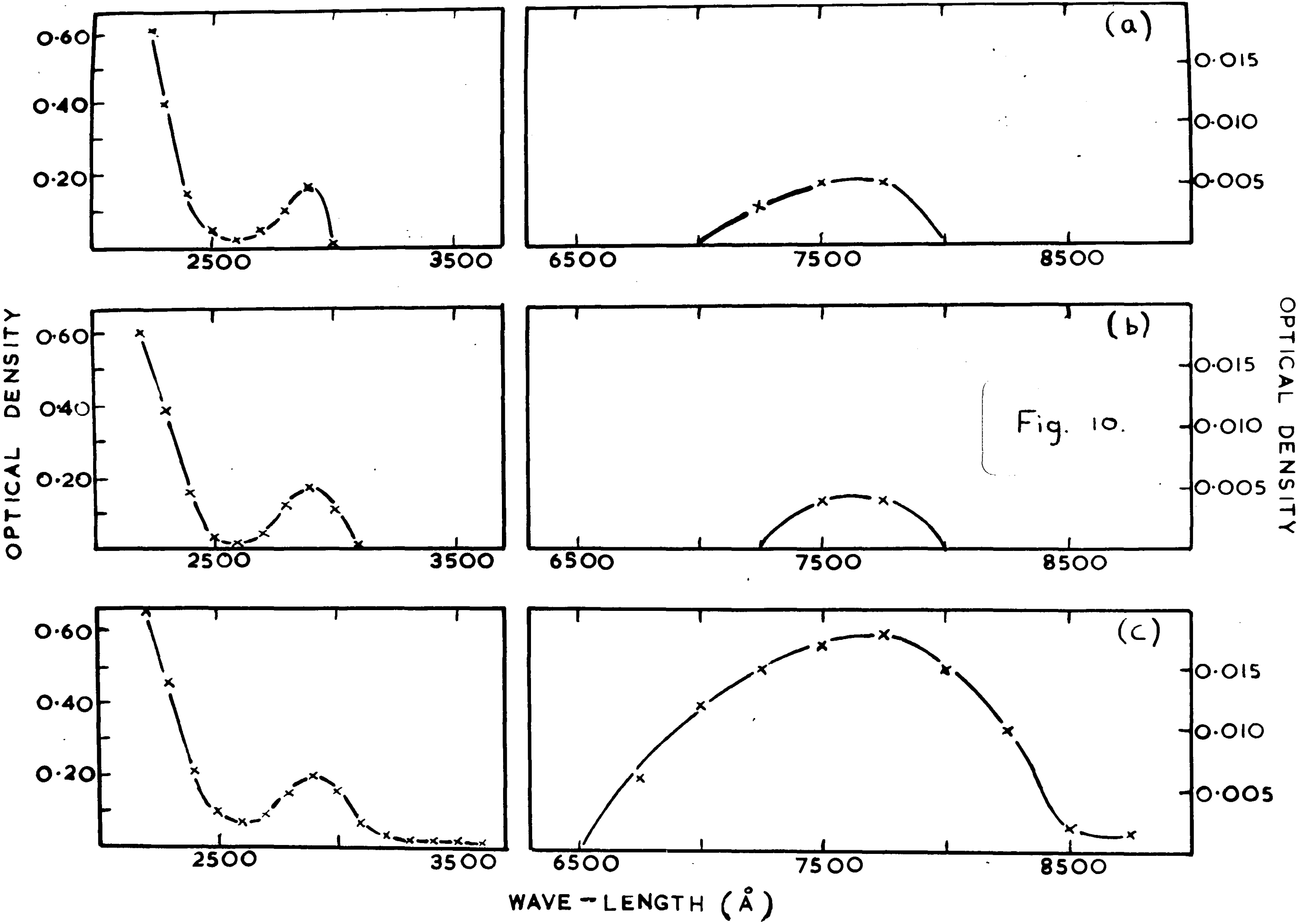

(a)
(b)
(c)
0·60
0·40
0·20
0·015
0·010
0·005
2500
3500
6500
7500
8500
OPTICAL DENSITY
OPTICAL DENSITY
WAVE - LENGTH (Å)

Fig. 10.

(3) Increasing concentration of dichromate ion increases the recorded silica concentration in a linear fashion, the interference being due to the colour of the dichromate ion.

(4) Phosphate ion interferes with the estimation owing to the formation of phosphomolybdic acid.

(5) Increasing concentration of ferrous and ferric ions decreases the recorded silica concentration in a linear fashion. This interference is a result of the formation of ferric molybdate, the ferrous iron oxidising to ferric iron on precipitation of the hydroxide in the borate buffer solution.

(6) Copper ion interferes with the estimation owing to the formation of a complex, the apparent ratio of copper to silica being 12 : 1.

REMOVAL OF INTERFERING IONS.

Up till now, all solubility experiments conducted at Glasgow, have been carried out using pure silica (quartz etc.) but the work will soon be extended to the study of mine dusts. It is necessary, therefore, to obtain methods for removing these ions which have been shown to interfere with the method of analysis.

(1) Copper.

Copper ion in solutions of pH 7.5, is precipitated as the hydroxide. It should be possible, therefore, to remove copper ion from the borate buffer solution by either centrifuging or filtering the solution and work was carried out to confirm this.

The following solutions were made up, total volume being 100 ml. in each case.

(a) 20 ml. standard silica solution, 50 ml. borate buffer solution 30 ml. distilled water.

(b) 20 ml. standard silica solution, 50 ml. borate buffer solution and 30 ml. 0.01 M copper sulphate solution.

(c) 20 ml. standard silica solution, 50 ml. borate buffer solution, 4 ml. 0.01 M copper sulphate solution and 26 ml. distilled water.

50 mls. of each solution were centrifuged for 30 minutes at 3000 r.p.m. 25 ml. sample of the centrifuged solutions were taken and estimated /

estimated for silica content in the normal manner.

A further 50 ml. of solutions (a), (b) and (c) were filtered through Ford "Sterimat" pads (Grade G.S.) and 25 ml. sample of the filtered solutions estimated for silica content in the normal manner.

The results obtained (Table 2) indicate that the removal of copper ion by this method has proved successful.

It is concluded, therefore, that copper ion is successfully removed by either of the two methods, namely, by centrifuging for 30 minutes at 3000 r.p.m. or by filtering through a Ford "Sterimat" pad (Grade G.S.).

(2) Ferrous and Ferric Iron.

Various methods for the removal of iron in conjunction with phosphate have been examined. They are discussed in detail in the section on the removal of phosphate ion.

Ferrous and ferric iron, like copper, are precipitated as the corresponding hydroxide in buffer solutions of pH 7.5. It was decided to examine the possibility of removing ferrous and ferric iron by filtration. It was decided not to examine the effect of centrifuging the samples as it was thought that this method would not be successful as the hydroxide precipitate is partly colloidal.

The /

TABLE 2.

REMOVAL OF COPPER ION

SOLUTION	SILICA CONTENT (Mg.)	
	(a) Centrifuging	(b) Filtering
(a)	0.125	0.125
(b)	0.125	0.125
(c)	0.125	0.125

The following solutions were made up, the total volume being 50 ml. in each case.

(a) 10 ml. standard silica solution, 25 ml. borate buffer solution and 15 ml. distilled water.

(b) 10 ml. standard silica solution, 25 ml. borate buffer solution and 15 ml. 0.01 M ferric sulphate solution.

(c) 10 ml. standard silica solution, 25 ml. borate buffer solution, 2 ml. 0.01M ferric sulphate solution and 13 ml. distilled water.

(d) 10 ml. standard silica solution, 25 ml. borate buffer solution and 15 ml. 0.01 M ferrous sulphate solution.

(e) 10 ml. standard silica solution, 25 ml. borate buffer solution, 2 ml. 0.01 M ferrous sulphate solution and 13 ml. distilled water.

The solutions were filtered through Ford "Sterimat" pads (Grade G.S.) and, then, 25 ml. samples of each solution estimated for silica content in the normal manner.

The result obtained (Table 3) indicate that simple filtration is sufficient to remove ferrous and ferric ion from the solution.

It is concluded that ferrous and ferric ion is successfully removed by filtration.

(3) Phosphate.

Various methods have been suggested for the removal of phosphate interference. These include precipitation with magnesia mixture; calcium /

TABLE 3.

REMOVAL OF FERROUS AND FERRIC ION

SOLUTION	SILICA CONTENT (mg.)
(a)	0.125
(b)	0.125
(c)	0.125
(d)	0.125
(e)	0.125

calcium chloride and calcium carbonate; calcium chloride and ammonium hydroxide; or calcium chloride and a sodium borate-sodium hydroxide mixture.

Other methods of treatment involve the destruction of the preformed phosphomolybdic acid by the addition of citric acid (64) oxalic acid (65), or tartaric acid (66). The use of sodium fluoride is said to mask iron and phosphate interference.

Another method which could be used is the classical basic acetate method of qualitative analysis. The advantage of using this method would be that iron, chromium and phosphate could be removed in one treatment.

It was decided, therefore, to investigate the possibility of using any of the above methods:

(a) "Basic" acetate method.

This was the first method investigated, as by this method iron, chromium and phosphate can be removed in the one treatment.

However, after removing the interfering ions by this method, it was found, on estimating for silica, that no molybdenum blue complex developed and it was concluded that either (a) silica was also removed; or (b) acetate ion interfered with the estimation. It was decided to examine the second of these two possibilities.

The possible effect of acetate ion was examined by the method described /

described previously and it was found that acetate ion did not interfere with the estimation.

However, the concentration of acetate ion present in solution after basic acetate treatment is much greater than that examined and it was thought that acetate ion may interfere in the estimation due to its action as a buffer solution. It was decided, therefore, to examine this possibility.

A silica estimation of a sample which had undergone acetate treatment was carried out in the normal manner and the pH of the solution determined. The pH of the solution was found to be 5.0 and, therefore, β - silicomolybdic acid is not formed as formation occurs only in solution of pH < 2.5 (59). This difficulty could be overcome by using more acid solution of ammonium molybdate. However, when the number of equivalents of acid per gram-ion of molybdate is greater than 10, the reaction becomes impracticably slow.

This buffering effect will occur in the other precipitation methods mentioned and, therefore, it is concluded that precipitation methods are unsuitable, due to the combined buffering action of the borate solution and the solution used for phosphate removal.

(b) "Masking" methods.

A detailed study of the various methods employing the use of reagents which destroyed the preformed phosphomolybdic acid complex was /

was undertaken.

The following solutions were made up:-

(a) 4 ml. standard silica solution, 25 ml. borate buffer solution, made up to 43 ml. with distilled water.

(b) 4 ml. standard silica solution, 25 ml. borate buffer solution, 9 ml. 0.01 M potassium dihydrogen phosphate solution, made up to 43 ml. with distilled water.

(c) Five solutions containing 4 ml. standard silica solution, 25 ml. borate buffer solution and 9 ml. 0.01 M potassium dihydrogen phosphate solution.

Silica estimations were carried out on the above solutions in the normal manner, with the following variation. After the yellow coloration had been allowed to develop for 4 minutes, 5 ml. of one of the following solutions were added to sample (c).

(i) 10% tartaric acid
(ii) 10% citric acid
(iii) 10% oxalic acid
(iv) 10% ammonium citrate
(v) 10% ammonium tartrate

The results obtained are shown in table 4 and they indicate that these methods do not remove phosphate interference.

Varying strengths of solution of these reagents were experimented with, /

TABLE 4.

ESTIMATION OF DISSOLVED SILICA IN PRESENCE OF PHOSPHATE ION.

SOLUTION	SILICA CONTENT (mg.)					
	Control	Tartaric Acid	Citric Acid	Oxalic Acid	Ammonium Citrate	Ammonium Tartrate
(a)	0.100	-	-	-	-	-
(b)	0.025	-	-	-	-	-
(c)	-	0.010	0.025	0.015	0.025	0.015

with, but the results obtained indicated that interference by phosphate ion was not removed by these methods.

This is contrary to the results obtained by other workers and it is concluded that this may be the result of an effect caused by the borate buffer solution.

The use of sodium fluoride for the removal of iron and phosphate interference was also investigated and was found to be unsuccessful.

It may be possible, however, to remove phosphate ion by passing the solution through an ion-exchange resin and it is suggested that work on this field be carried out.

However, it may become necessary, if all methods of phosphate removal fail, to conduct solubility experiments in another solvent.

(4) Dichromate.

Dichromate ion in solutions of pH 7.5 is partly precipitated as chromic hydroxide, but filtering or centrifuging the solution does not ensure complete removal of the interfering ion.

It was decided, therefore, to estimate silica in presence of dichromate using a "blank" solution to determine the effect of the dichromate ion. This method is preferred to methods of removing the dichromate ion by precipitation, as silica may also be removed by these methods.

The following solutions were made up and their silica content determined /

determined.

(a) 4 ml. standard silica solution, 25 ml. borate buffer solution diluted to 43 ml. with distilled water.

(b) 4 ml. standard silica solution, 25 ml. borate buffer solution, 10 ml. 0.01 M potassium dichromate solution made up to 43 ml. with distilled water.

(c) 25 ml. borate buffer solution, 10 ml. 0.01 M potassium dichromate solution made up to 43 ml. with distilled water.

(d) as for (b).

(e) 4 ml. standard silica solution, 1 ml. 0.01 M potassium dichromate solution, 25 ml. borate buffer solution made up to 43 ml. with distilled water.

(f) as for (e).

For solutions (d) and (f), 2 ml. of $\overline{N}$. sulphuric acid were added in place of 5% ammonium molybdate solution.

The results obtained are shown in Table 5 and they indicate that it is possible to estimate silica in presence of dichromate ion by the molybdenum blue method, provided a "blank" estimation is carried out.

The following procedure is recommended:-

A 5 ml. sample is taken diluted to 7 ml. with distilled water and the estimation carried out at the same time as the silica estimation.

2 ml. of 0.02 $\overline{N}$ sulphuric acid are added in place of ammonium molybdate solution /

TABLE 5.

ESTIMATION OF DISSOLVED SILICA IN PRESENCE OF DICHROMATE ION.

SOLUTION	SILICA CONTENT (mg.)	
	Uncorrected	Corrected
(a)	-	0.10
(b)	0.16	0.10
(c)	0.06	-
(d)	0.06	-
(e)	0.11	0.10
(f)	0.01	-

solution and only 1 ml. of "reducing" solution added. The colorimeter reading obtained is subtracted from that obtained for the silica estimation and the true silica content determined.

Summary.

Methods of removing iron and copper interference and for estimating silica in presence of dichromate ion are described.

Various methods for the removal of phosphate ion have been investigated, but none have been found successful. This is thought to be the result of an effect produced by the borate buffer solution.

Part II. Determination of Free Silica by Infra-red Spectroscopy.

Introduction.

The accurate determination of the free silica content of mine dust is important from the point of view of obtaining a true correlation between the pathogenicity of a dust and its free silica. Many methods, both chemical and physical, have been employed but the majority of these methods have been found to be inaccurate.

The chemical methods of analysis consist of a series of operations designed to remove from the material under examination all minerals except quartz and correction factors for the attack of the reagents employed on the quartz have to be applied. The methods involve a long series of operations and mechanical losses can be very high.

The two main physical methods of analysis are by differential thermal analysis and by X-ray diffraction. These methods only estimate crystalline material and, as airborne silica dust contains a high percentage of amorphous material (67, 68), they tend to give low results.

The purpose of this investigation is to try to develop a new method of analysis using infra-red spectroscopy.

The atoms of a solid do not remain at rest but are continually in vibration. The frequencies of these vibrations are within the range of 10^{13} to 10^{14} cycles per second which is the same order of magnitude /

magnitude as the frequencies of infra-red radiation. These intra-molecular vibrations occur at certain frequencies depending on the grouping (e.g. C-H, C-O, C=O.) and if substances are irradiated by a succession of monochromatic bands of infra-red radiation, these radiated frequencies which correspond to the intra-molecular vibrational frequencies may be absorbed. It is possible, therefore, by plotting the percentage of radiation absorbed by a substance against the incident wavelength to state that a molecule contains certain groupings e.g. C=O. The use of infra-red spectroscopy as an analytical tool has been developed, with a great degree of success, in the field of organic chemistry; but its use in inorganic chemistry has been neglected.

The absorption of infra-red radiation by silicate minerals was first observed by Coblentz (69) as early as 1906. He obtained infra-red absorption spectra of many silicates using slices about 0.1 mm. thick, and observed that they absorbed infra-red radiation having wavelengths greater than 9 μ. This work was confirmed in the 1930's by Schaeffer et al. (70) and Matossi and Kruger (71), who used the same technique as Coblentz.

Barnes (72) has shown that the infra-red absorption spectra of a solid could be obtained by using a thin film of powder, provided that the particle size of the powder was less than the wavelength of the infra-red radiation. When the particle size was greater than the incident /

incident wavelength, refraction of the infra-red rays occurred. This technique was first applied to various clays and silicate minerals by Keller and Pickett (73). The absorption spectra obtained by them are poorly defined as a result of large particle scattering but subsequent work by Hunt et al. (74) using particles having diameters less than 5 micron, gave well defined absorption spectra of various silicates.

Launer (75) has shown that infra-red spectra can be used to characterise the type of silicon - oxygen group, and states that the region of strongest absorption tends to shift towards shorter wavelengths as the ratio of silicon to oxygen increases.

From a study of the results of the above workers, it is noticed that free silica has absorption bands at 12.5 μ and 12.85 μ which are not shown by the various silicates, and therefore it should be possible to determine the free silica content of a mine dust by infra-red spectroscopy.

However, the powder technique used by previous workers is not suitable for quantitative work, and therefore a new technique must be evolved.

Dolinsky (76) has developed a technique for the infra-red analysis of solids insoluble in nonpolar solvents based on suspending the solid in a viscous aluminium stearate-carbon tetrachloride mixture. It was decided to try to adapt this method to the silica problem.

On the basis of the above discussion, it was decided to develop work on the following lines.

(1) Qualitative study of the problem.

(2) The development of a quantitative method of analysis.

(3) The comparison of this method with

(a) an established chemical method and

(b) an established physical method.

The methods chosen for this comparison are

(a) Chemical method - Shaw - Skinner semi-micro method.

(b) Physical method - Differential Thermal Analysis.

Description of Apparatus.

The instrument used throughout this work was a "double-beam" infra-red spectrophotometer described by Brownlie (77). The spectrophotometer is of the Littrow type, the optical system being basically similar to that of the instrument by Baird Associates. A Schwarz thermopile is used in place of a bolometer in the receiving system.

As previous experience has shown that the instrument loses its sensitivity when used as a double beam instrument, it was decided to use it as a single beam instrument throughout this work.

I - QUALITATIVE STUDY OF THE PROBLEM.

The infra-red absorption spectra of the following free and combined silica samples were obtained.

(a) Quartz.

(b) Cristobalite.

(c) Tridymite.

(d) Vitreosil.

(e) Olivine.

(f) Willemite.

(g) Kaolin.

(h) Mica.

All samples had an average particle size of 1 micron. This is essential as large particles tend to cause refraction of the infra-red beam and erroneous results.

Experimental Procedure.

A sample of the material under test was mixed with Nujol (liquid paraffin) to form a Nujol "mull" and its infra-red absorption spectrum obtained. The spectrum of pure Nujol was also obtained and the absorption spectrum of the unknown found by comparison.

It was found necessary (as shown later), as the work progressed, to abandon the use of Nujol as a dispersion agent in favour of a "cyclo"hexane - aluminium stearate mixture.

Absorption /

Absorption spectra of magnesium oxide and calcium carbonate were also obtained at a later date. These results will be discussed at this stage for the sake of continuity.

Results and Discussion of Results.

The spectra obtained are shown diagramatically in Fig. 11-14. The height of the line is an indication of the intensity of absorption at that wavelength.

(1) Nujol. Fig. 11-1.

A study of Fig. 11-1 shows that Nujol absorbs strongly at 3.44 μ, 3.51 μ. 6.84 μ, and 7.26 μ. An absorption band of medium intensity occurs at 13.9 μ.

(2) "cyclo"Hexane Fig. 11-2.

"cyclo"Hexane absorbs strongly at the following wavelengths, 3.44 μ, 3.72 μ, 3.79 μ, 6.88 μ, 7.95 μ, 11.05 μ, and 11.6 μ. Absorption bands of medium intensity occurs at 7.4 μ, 9.65 μ and 9.85 μ, and weak absorption occurs at 2.51 μ, 2.87 μ, 2.97 μ, 3.14 μ, 4.25 μ, 4.40 μ, 4.60 μ, 4.68 μ, 4.83 μ, 5.00 μ, 5.32 μ, 5.44 μ, and 8.64 μ.

(3) Aluminium stearate Fig. 11-3.

Aluminium stearate has absorption bands of medium intensity at 6.35 μ and 6.85 μ, and a weak absorption band at 10.25 μ.

(4) Quartz Fig. 12-1.

Quartz absorbes strongly between 7.70 μ and 11.70 μ. Absorption bands /

FIG. 11.

INFRA-RED ABSORPTION SPECTRA

1 - Nujol.

2 - "cyclo"Hexane.

3 - Aluminium stearate.

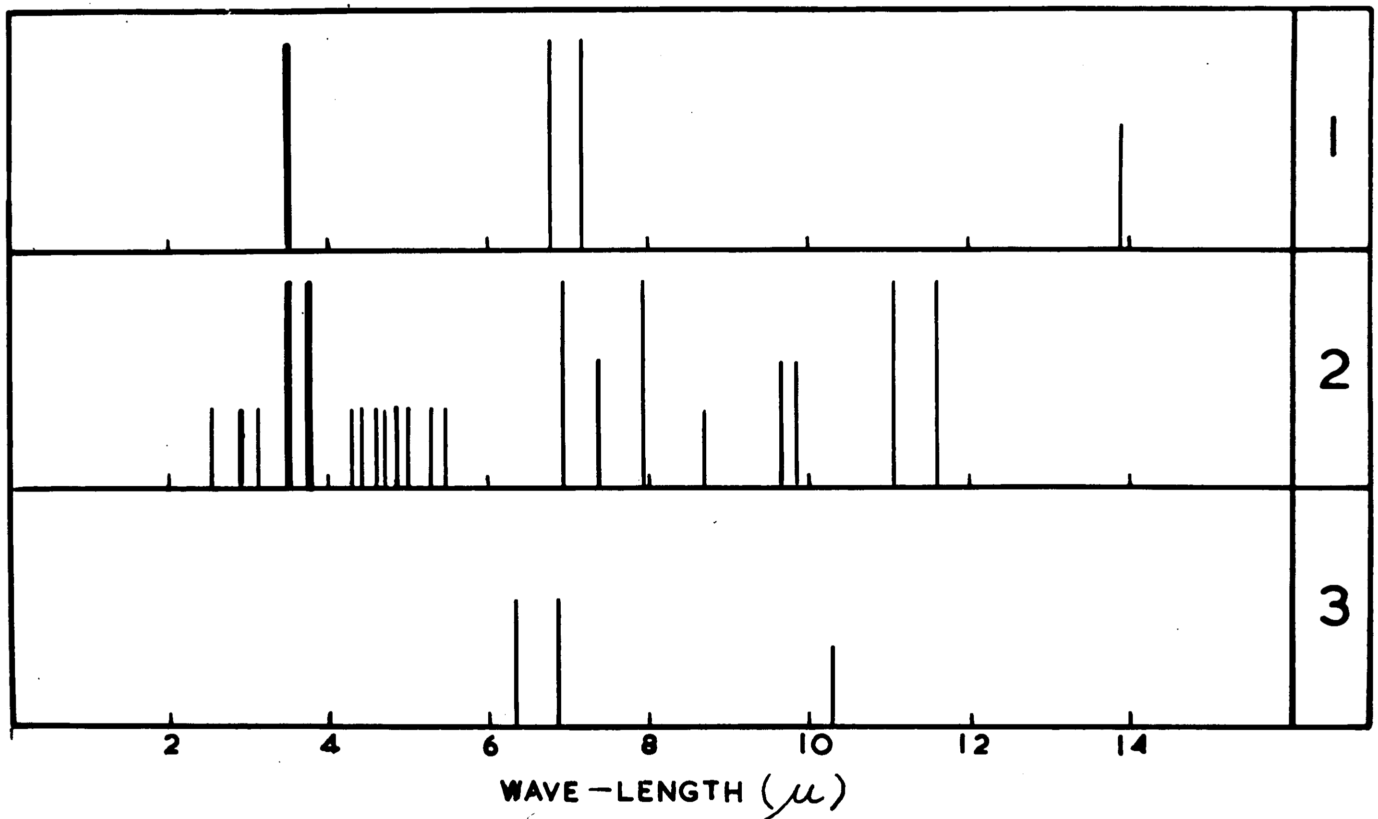


Fig. 11.

bands of medium intensity occur at 12.5 μ and 12.85 μ, and weak absorption bands occur at 5.95 μ and 6.30 μ.

(5) Cristobalite, Tridymite and Fused Silica Fig. 12-2, 3, 4.

These substances absorb strongly between 7.70 μ and 11.70 μ. A broad absorption band of medium intensity occurs at 12.50 μ (cf Quartz) and bands of weaker intensity occur at 5.95 μ and 6.30 μ.

(6) Olivine Fig. 13-1.

Strong absorption occurs in the wavelengths 9.85 μ - 11.90 μ. Olivine shows weak absorption characteristics at 6.10 μ and 13.10 μ.

(7) Willemite Fig. 13-2.

Willemite absorbs strongly between 10.00 μ and 11.55 μ. Weak absorption bands occur at 8.25 μ, 8.60 μ, 9.00 μ, 9.15 μ and 9.50 μ.

(8) Kaolin Fig. 13-3.

Kaolin exhibits strong absorption characteristics between 8.95 μ and 10.95 μ. Absorption bands of medium intensity occurs at 14.60 μ while weak absorption bands occur at 6.00 μ, 7.45 μ and 13.35 μ.

(9) Mica Fig. 13-4.

Mica absorbs strongly in the region 9.30 μ - 10.80 μ. An absorption /

FIG. 12.

INFRA-RED ABSORPTION SPECTRA

1 - Quartz.

2 - Cristobalite.

3 - Tridymite.

4 - Fused silica.

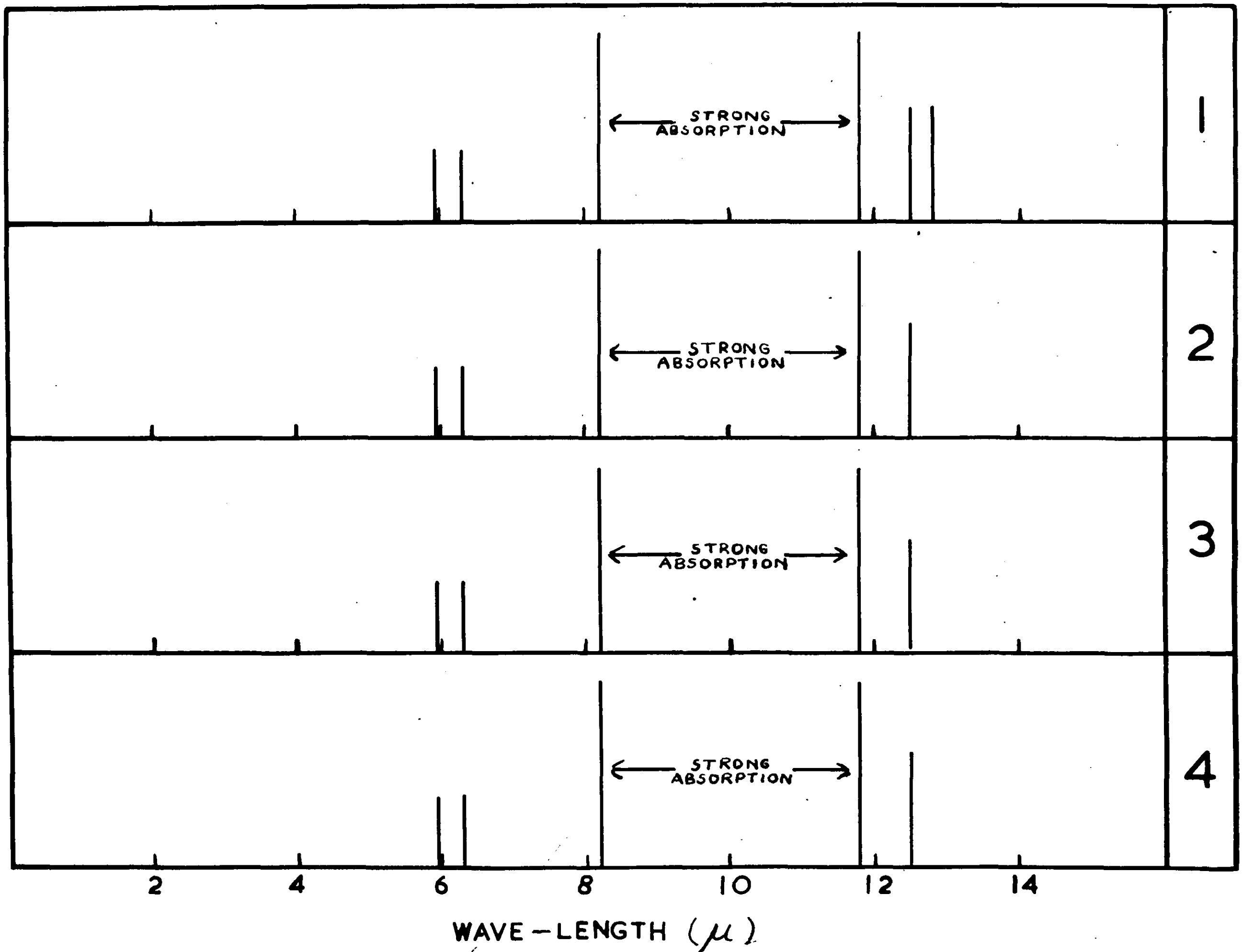

1
2
3
4
STRONG ABSORPTION
STRONG ABSORPTION
STRONG ABSORPTION
STRONG ABSORPTION
2
4
6
8
10
12
14
WAVE-LENGTH (μ)

Fig. 12.

FIG. 13.

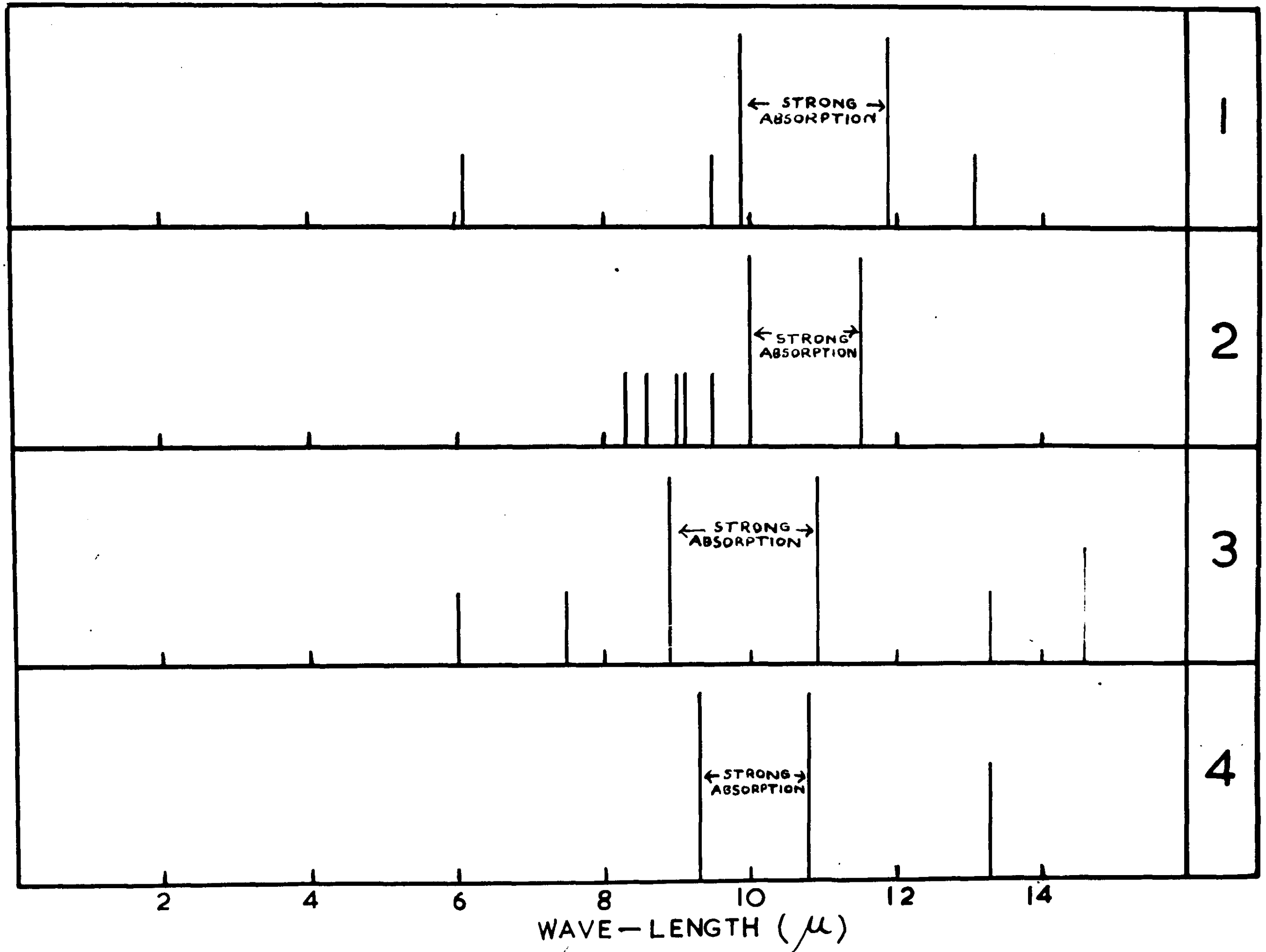
INFRA-RED ABSORPTION SPECTRA

1 - Olivine.

2 - Willemite.

3 - Kaolin.

4 - Mica



1
2
3
4
← STRONG → ABSORPTION
← STRONG → ABSORPTION
← STRONG → ABSORPTION
← STRONG → ABSORPTION
2
4
6
8
10
12
14
WAVE—LENGTH (μ)

Fig. 13.

absorption band of medium intensity occurs at 13.30 μ.

(10) Magnesium oxide Fig. 14-1.

An absorption band of medium intensity occurs at 14.45 μ. The compound exhibits weak absorption characteristics at 7.00 μ, 8.85 μ, 9.40 μ, 10.0 μ and 11.8 μ.

(11) Calcium carbonate Fig. 14-2.

Calcium carbonate has a strong absorption band at 6.80 μ. Absorption of medium intensity occurs between 6.95 μ and 7.40 μ, while weak absorption bands occur at 6.50 μ, and between 8.70 μ and 10.05 μ.

Conclusions.

From a study of the above absorption spectra and of the spectra in the literature (74, 75), it is seen that quartz has absorption maxima at 12.50 μ and 12.85 μ, while silicates have no absorption maxima at these wavelengths. It should be possible, therefore, to estimate quartz, in the presence of silicates, at the above wavelengths, namely 12.50 μ and 12.85 μ.

A study of the spectra obtained for the various forms of free silica shows that all forms (quartz, cristobalite, tridymite and fused silica) have an absorption maximum at 12.50 μ but that only quartz has an absorption maximum at 12.85 μ. From this, it could be concluded that the estimation of quartz in the presence of the other forms of free /

FIG. 14.

INFRA-RED ABSORPTION SPECTRA

1 - Magnesium oxide.

2 - Calcium carbonate.

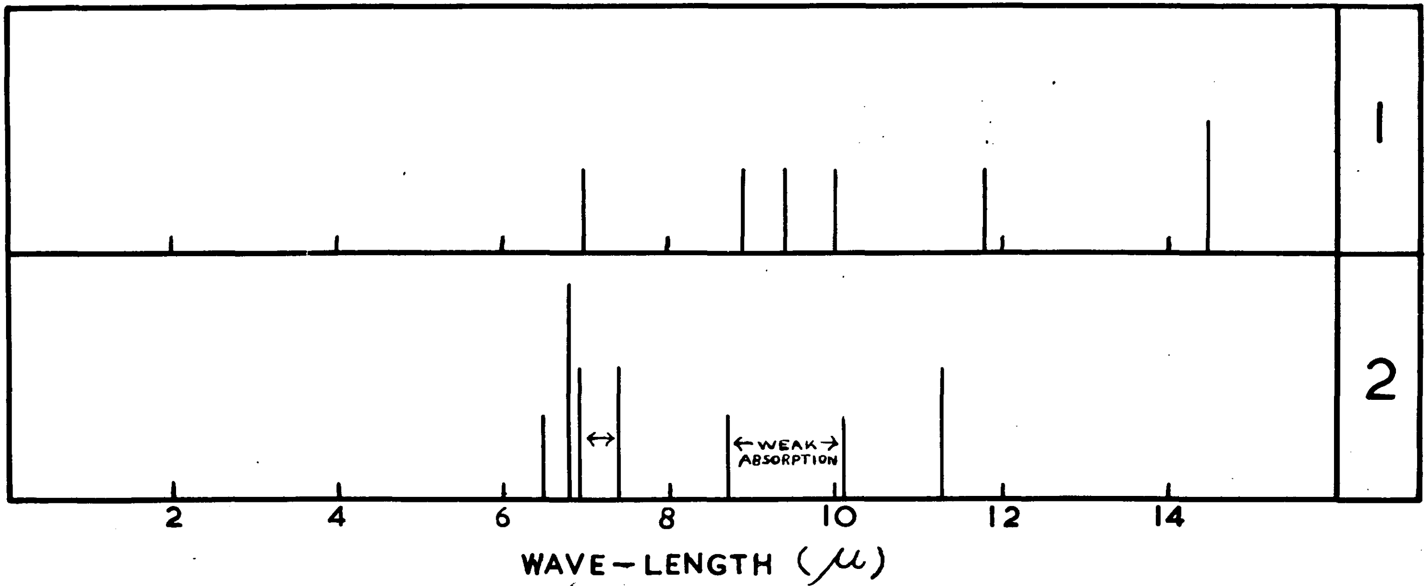


Fig. 14.

free silica could be carried out by this method. However the absorption band at 12.50 µ shown by cristobalite, tridymite and fused silica is broad and overlaps the 12.85 µ absorption band of quartz. It is only possible, therefore, to differentiate between free and combined silica by this method.

Magnesium oxide and calcium carbonate have no absorption bands in the 12.50 µ region and therefore, they can be used as diluents in standard mixtures for calibration purposes.

II - DEVELOPMENT OF A QUANTITATIVE METHOD OF ANALYSIS.

The following conditions must be observed for a quantitative estimation of silica by infra-red spectroscopy.

(1) The particle size of the material under test must be 1 micron or less.

(2) The material under test must be uniformly dispersed in the dispersion medium.

(3) A cell of uniform thickness must be used.

To ensure that the first condition is obeyed, the material under test is ground for 18 hours in a mechanical agate mortar. The particle size of the material, after grinding is less than 1 micron.

Conditions 2 and 3 must be developed simultaneously.

Preliminary Work.

The first stage in the development of a quantitative method was an attempt to place the Nujol method on a quantitative basis, the method being preferred to that of Dolinsky (76) as a result of its relative simplicity. The following procedure was adopted:-

> The material under test (1 g.) and Nujol (25 ml.) were placed in a 250 ml. "Quickfit" flask and heated to 100°C with constant shaking. The flask was then cooled and glass beads (25 ml.) added. The contents of the flask were /

were then shaken for 1 hour on a "Microid" flask shaker.

The material was then ready for analysis.

The material was heated and shaken to ensure the complete dispersion of the solid in the liquid media.

Much work was done on this method but it was eventually abandoned as a result of the tendency of the silica particle to aggregate.

A detailed study of the method of Dolinsky (76) was now undertaken. In the original method, Dolinsky used a 1% solution of aluminium stearate in carbon tetrachloride or carbon disulphide as the dispersion agent. However, the use of carbon tetrachloride is precluded as it absorbs strongly in the 12.5 μ region. It was decided, on account of its relatively high volatility, not to use carbon disulphide.

It was necessary, therefore, to find another solvent and, after a study of absorption spectra, it was decided to use "cyclo"hexane. However, a 1% solution of aluminium stearate did not give a solution of sufficient viscosity and, on examination, it was found that a 4% solution of aluminium stearate in "cyclo"hexane was required. This dispersion agent, as shown earlier, has no absorption bands in the 12.5 μ region. The preparation of samples for analysis is as follows:-

The material under test (1 g.), aluminium stearate (1 g.) and "cyclo"hexane (25 ml.) are placed in a 250 ml. "Quickfit" flask and heated to boiling, with constant shaking. The flask /

flask is allowed to cool, and glas beads (25 ml.) are then added. The flask is then shaken for 1 hour on a "Microid" flask shaker. The material is now ready for analysis.

Development of Cell.

The use of standard liquid absorption cells was investigated, but they were found to be unsuitable. This was because the highly viscous nature of the liquid used led to difficulties in filling and cleaning the cells. Various modification of the standard liquid cell were also investigated and were found to be unsuitable.

In qualitative work, the substance under test is placed between two rock salt plates and the development of this type of cell for quantitative work was examined.

It is necessary, in order to adapt this type of cell to quantitative work, to ensure that a uniform cell thickness is obtained. It was decided, therefore, to insert amalgamated lead strips of known thickness between the rock salt plates. The procedure adopted is as follows:-

Two lead strips (0.007 in. thick) were placed lengthwise at opposite ends of a rock salt plate. The sample is placed in the middle of the rock salt plate and the second rock salt plate placed into position on top. Care must be /

be taken to ensure complete exclusion of air bubbles from the cell.

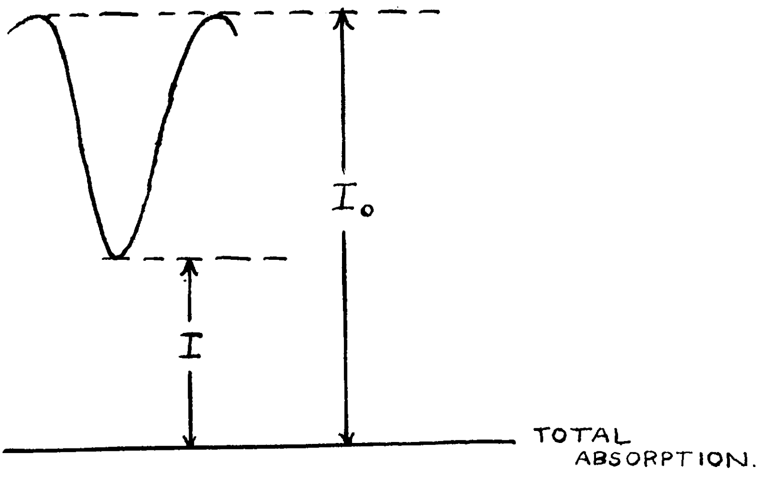
The rock salt plates are 1 inch square and the lead "spacers" 1 inch by 0.1 inch. The cell is easily mounted and cleaned.

The development of the method had now reached the stage where it was possible to place it on a sound quantitative basis. However, before calibration curves could be obtained, it was essential to find the effect of time of shaking the material.

Effect of Time of Shaking.

Samples were prepared in the prescribed manner, the time of shaking being different in each case. The amount of absorption taking place was calculated by the base-line technique.

The concentration of material present in a sample is proportional to the amount of radiation absorbed by the sample. This is obtained from the infra-red spectrum as follows:-



Concentration of material present $\propto \log_{10} \frac{I_o}{I}$

The results obtained are shown in Fig. 15 and a study of this diagram shows that, shaking for 1 hour, ensures that stable conditions are attained.

Calibration Curves.

A series of experiments on a sample of pure quartz were conducted in order to determine the accuracy of the method.

The results obtained are shown in Table 6. A study of the results shows marked variations from sample to sample. This may be due to differences in cell thickness but a study of the results shows that the results appeared in sets of marked reproducibility. It was noticed that the variations were between samples analysed on different days and that experiments carried out on the same day were repeatable. It was concluded, therefore, that the variations may be as a result of daily variations in the sensitivity of the instrument.

It was decided, therefore, to examine the absorption spectra of benzene obtained at different times using a standard liquid cell of known thickness.

The results obtained are shown in Table 7 and they confirm the conclusion reached above, that the variations in the results obtained are a result of variations in the sensitivity of the instrument and not as a result of variations in cell thickness.

This /

FIG. 15.

EFFECT

OF

TIME OF SHAKING

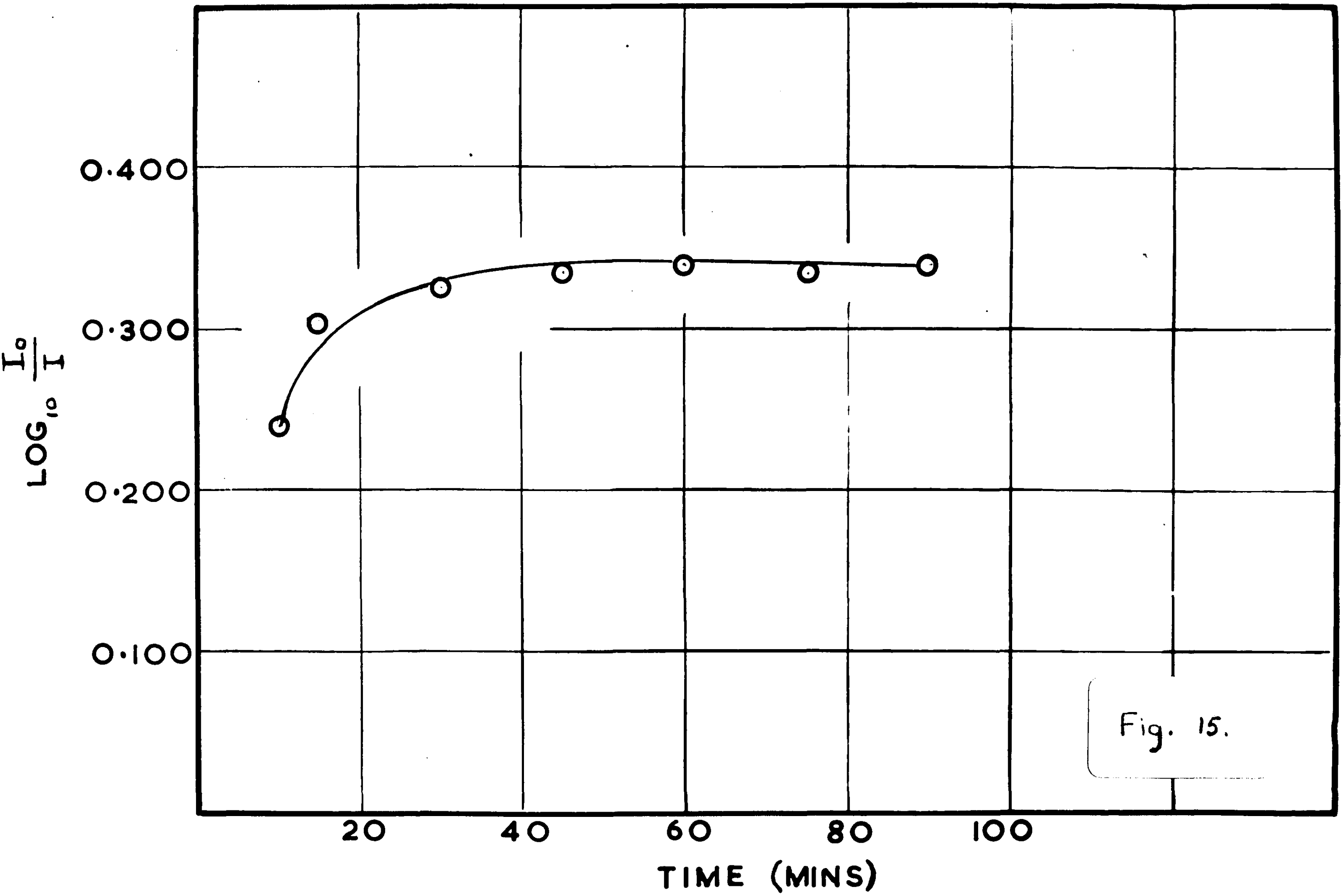


Fig. 15.

0·400
0·300
0·200
0·100
$\mathrm{LOG}_{10}\ \frac{I_o}{I}$
20
40
60
80
100
TIME (MINS)

TABLE 6.

REPRODUCIBILITY TESTS.

Run	$\log_{10} \frac{I_o}{I}$
1	0.3064
2	0.3061
3	0.3033
4	0.3064
5	0.3407
6	0.3473
7	0.3454
8	0.3949
9	0.3980
10	0.3986

TABLE 7.

REPRODUCIBILITY TESTS.

Wavelength (µ)	$\text{Log.}_{10} \frac{I_o}{I}$		
	Run 1	Run 2	Run 3 +
3.22	0.6049	0.6095	0.7048
4.42	0.0293	0.0364	0.0371
5.06	0.3512	0.3689	0.3986
5.50	0.5088	0.5412	0.5673
6.52	0.2276	0.2689	0.2145
6.76	0.6338	0.7630	0.7851
7.17	0.1927	0.1776	0.2045
8.02	0.0381	0.0390	0.1422
8.50	0.1929	0.1824	0.2035
9.65	0.6752	0.7720	0.8090
11.80	0.1294	0.1284	0.1394
12.98	0.1003	0.0889	0.1176

+ To ensure that the results obtained were not due to personal error, Run 3 was carried out by another worker.

This result, of necessity, precludes any attempt to obtain calibration curves and to place the method on a normal quantitative footing. However, as the method appeared promising it was decided to compare the unknown sample with standard mixtures containing known amounts of silica. If the various samples were examined one after the other, variations in the sensitivity of the instrument would be discounted.

Standard mixtures of magnesium oxide and quartz, containing 0,10, 20, 30, 40, 50, 60, 70, 80, 90, and 100% of quartz were prepared and the amount of radiation absorbed, at 12.5 μ, by each sample obtained in the normal manner.

It was found that the accuracy of the method decreased rapidly below 50% silica concentration, so that only samples containing more than 50% of silica can be estimated. However, if a sample contains less than 50% of silica, it can be mixed with pure silica and its silica content determined. The procedure adopted is as follows. The absorption spectrum for the unknown sample is obtained and the amount of radiation absorbed, at 12.5 μ, measured, giving an indication of the silica content, say 65%. Spectra for standard mixtures containing 60% and 70% of silica are then obtained and the silica content of the sample obtained to within ± 5% by comparison. For /

For samples containing less than 50% of silica, 0.5 grams of unknown are mixed with 0.5 grams of pure quartz and the mixture analysed in the normal manner.

III - COMPARISON OF THE METHOD WITH ESTABLISHED METHODS.

It was decided to compare the method with the Shaw-Skinner semi-micro method and with differential thermal analysis. (For details of these methods, see Appendix at end of section).

The samples used for this work were supplied by Dr. G. Nagelschmidt of the Safety in Mines Research Establishment, Sheffield, and were part of a scheme on chemical and physical analysis of dust set up by the Medical Research Council.

Samples.

The following samples were used. The reference numbers are taken from Dr. Nagelschmidt's index.

(a) X. 1072 - Pure Madagascar quartz.

(b) X. 1876 - Kaolin.

(c) X. 2043 - A mixture of X. 1072 and X. 1876 containing 67% of quartz.

(d) X. 2431 - Mica.

(e) X. 2478 - A mixture of X. 1876 and X. 2431.

(f) X. 2479 - A mixture of X. 1072, X. 1876 and X. 2431 containing 14% quartz.

(g) X. 2480 - A mixture of X. 1072, X. 1876 and X. 2431 containing 48.4% quartz.

Experimental Procedure.

Sample under test (1 g.), aluminium stearate (1 g.) and "cyclo"hexane (25 ml.) were placed in a 250 ml. "Quickfit" flask and the flask heated to boiling with constant shaking. The flask was then cooled, glass beads (25 ml.) added, and shaken for 1 hour on a "Microid" flask shaker. The sample was now ready for analysis by infra-red spectroscopy. Each analysis was carried out in duplicate.

Samples of standard mixtures were also analysed and the amount of silica in the unknown obtained by comparison.

0.5 grams of sample and 0.5 grams of pure quartz were taken for the analysis of samples containing less than 50% of free silica.

Duplicate analysis on each sample were also carried out using the Shaw-Skinner semi-micro method and differential thermal analysis.

Results and Discussion of Results.

The results obtained are shown in Table 8.

A study of these results indicates that infra-red spectroscopy gives a more accurate result than either the Shaw-Skinner method or differential thermal analysis. However, it must be stressed that the accuracy of the method is lessened as a result of the procedure which has to be adopted because of the variations in the sensitivity of the instrument. It is thought that if the method were developed on /

TABLE 8.

ESTIMATION OF FREE SILICA CONTENT.

Sample	Actual free silica content %	Free silica content % by		
		Shaw-Skinner	D.T.A.	I.R.
X. 1072	100.0	88.2	60.9	100.0
X. 1876	0.0	9.0[+]	0.0	0.0
X. 2043	67.0	65.5	31.0	68.0
X. 2431	0.0	4.2[+]	0.0	0.0
X. 2478	0.0	0.7	0.0	0.0
X. 2479	14.0	16.4	5.1	15.0
X. 2480	48.4	47.0	23.0	50.0

[+] While the other methods confirm the figure given by Dr. Nagelschmidt, the Shaw-Skinner method gives a positive result. This positive result has also been obtained by other workers. The reason for this result is not clear.

on a completely stabilised instrument, enabling calibration curves to be obtained, the accuracy of the method would be within the limits ± 2%, as it was observed that, on a series of samples analysed on the above instrument on the same day, this accuracy was obtained.

Conclusions.

(1) A quantitative method for the analysis of silicious dusts by infra-red spectroscopy has been developed.

(2) The method appears to give more accurate results than the established methods and, while it is essential that more work be done before the method is established, it seems that it may answer the problem of determining the silica content of airborne mine dust.

Note. With mine dusts containing coal dust, it may be necessary to ash the sample before analysis as the organic matter present may interfere in the estimation.

IV - EFFECT OF CALCIUM CARBONATE ON THE ESTIMATION OF SILICA BY INFRA-RED SPECTROSCOPY.

Workers at the National Coal Board, Central Research Establishment, Cheltenham, in a recent investigation on the possibility of determining free silica in limestone dusts by infra-red spectroscopy observed that the presence of calcium carbonate led to consistently high results (78). The investigation was abandoned for this reason. However, as calcium carbonate has no absorption bands in the 12.5 µ region, it was decided to investigate this problem.

Experimental Procedure.

Samples containing,

(a) 50% mixture of magnesium oxide and quartz;

and (b) 50% mixture of calcium carbonate and quartz;

were analysed in the normal manner.

Results.

The results obtained are as follows:-

(a) % quartz :- 50%

(b) % quartz :- 50%

Conclusion.

It is concluded, therefore, that calcium carbonate does not interfere with the determination of silica by infra-red spectroscopy. This result is expected as calcium carbonate (as shown earlier) has

no /

no absorption bands in the 12.5 μ region. It is suggested that the erroneous results obtained by the other workers are a result of the aggregation of the silica particles. They used a Nujol "mull" method and, as has been shown previously, aggregation of the silica particles is an inherent fault of this method.

SECTION A.

APPENDIX.

(1) Shaw-Skinner Semi-micro Method (79).

Reagents.

(a) Hydrochloric acid, dilute - 2.5% by volume. 2.5 ml. of concentrated acid are diluted to 100 ml. with distilled water.

(b) Hydrochloric acid, dilute - 5% by volume, 5 ml. of concentrated acid are diluted to 100 ml. with distilled water.

(c) Sulphuric acid, dilute - 10% by volume. 10 ml of concentrated acid are diluted to 100 ml. with distilled water.

(d) Sulphuric acid, dilute - 25% by volume. 25 ml. of concentrated acid are diluted to 100 ml. with distilled water.

(e) Lunge solution - 37 g. anhydrous sodium carbonate (A.R.) and 10 g. sodium hydroxide (A.R.) are dissolved in distilled water, diluted to 1 litre and stored in a polythene bottle.

Experimental Procedure.

The dried sample (0.15 g.) is heated to boiling with 2.5% hydrochloric acid solution (9 ml.) in a platinum basin covered with a watch glass. This treatment is to remove any carbonates. The liquid, after cooling, is decanted into a 15 ml. centrifuge tube which is then centrifuged for 15 minutes at 3,000 r.p.m. The clear supernatent liquid is carefully decanted off and the solid washed back into the platinum dish with the minimum amount of distilled water. The contents of the dish are then evaporated to dryness.

After /

After cooling, 25% sulphuric acid solution (6 ml.) is added and the uncovered dish heated on a sand bath at 200°C until white fumes are just visible. The operation normally takes approximately 45 minutes. The contents of the dish are then allowed to cool, distilled water (30 ml.) added, the liquid stirred, and centrifuged as before. The residue is then washed back into the dish, the liquid evaporated to dryness, and the sulphuric acid treatment repeated. The contents of the dish are again allowed to cool, distilled water (30 ml.) added and the liquid transferred to centrifuge tubes. The dish and its contents are then washed with distilled water (5 ml.) and the liquid transferred to the centrifuge tubes. The purpose of this wash is to remove as much of the sulphuric acid as possible and, thus, reduce the amount of Lunge solution required at the next stage. After the liquid has been centrifuged, the solid matter is again washed back into the dish and the liquid evaporated to dryness. Methyl red indicator (1 drop) is added to the residue and then, Lunge solution added dropwise until the indicator changes colour. It is advisable to cover the dish during this operation as effervescence may occur. After neutralisation, Lunge solution (9 ml.) is added in excess, and the covered dish is heated until the liquid boils. After cooling, the supernatent liquid is centrifuged, and the residue again washed back into the dish and evaporated to dryness. Concentrated hydrochloric acid (15 ml.) is then added /

added to the covered dish and the liquid boiled for 5 minutes. After cooling, distilled water (15 ml.), which can with advantage be used to wash down the watch glass, is added to the liquid and the liquid decanted and centrifuged in the normal manner. The residue is returned to the dish and, after evaporation to dryness, is again neutralised with Lunge solution. Lunge solution (4 ml.) is added and the liquid heated to boiling. After cooling, the liquid is decanted and centrifuged. The residue is then washed back into the dish and evaporated to dryness. Concentrated hydrochloric acid (6 ml.) is then added to the residue, and the liquid boiled for 5 minutes. After cooling, distilled water (6 ml.) is added and the liquid filtered through a small (7 cm.) Whatman No.540 paper. The dish is finally cleaned with a small piece of cotton wool twisted round the end of a glass rod. The cotton wool is then added to the filter paper. (On ignition, the cotton wool leaves no weighable residue.) The paper is then washed twice with 5% hydrochloric acid solution and 4 times with distilled water. It is then transferred to a weighed platinum crucible and dried in an oven at 105°C. After drying, the crucible is placed at the front of a muffle furnace, which is heated to 800°C at its centre, for 10 minutes, when it is moved into the centre of the furnace and ignited to constant weight (Residue A). The residue is finally treated with 10% sulphuric acid (6 drops) and 40% hydrofluoric acid (5 ml.) and gently heated to dryness. The crucible /

crucible is then ignited to constant weight (Residue B).

Calculation.

The residue (A) consists of the free silica and some undecomposed silicates, which are assumed to be potash felspar. The loss in weight caused by the hydrofluoric acid treatment is due to the volatilisation of the free silica and the silica combined in these silicates. The final residue (B) consists, therefore, of the non-silicious portion and after ignition is in the form of alumina. On the macro scale, it would be possible to estimate this and obtain a figure for the amount of felspar actually present. On the semi-micro scale, however, this is not possible, but the amount of alumina multiplied by 2.01 gives a very close estimate of the amount of felspar. The calculation is, therefore, as follows -

If A is the weight of the total residue and B is the weight of residue remaining after the hydrofluoric acid treatment, then the percentage of free silica present in the material is equal to (A - 2.01B) X 100/weight of material taken. To correct for the loss of quartz by solution in alkali, the final figure is multiplied by 100/92.

$$\% \text{ FREE SILICA} = \frac{(A-2.01B)}{\text{WT. OF MAT. TAKEN}} \times \frac{100}{92}$$

(2) Differential Thermal Analysis. (80).

The differential thermal analysis method depends on the measurement

of /

of the heat effect in the phase change $\alpha \rightleftharpoons \beta$ quartz which occurs at 573°C. The temperature of the test material is measured relative to that of an adjacent inert material by thermocouples. The evolution or absorption of heat in the test material causes a difference in temperature between it and the inert material which produces a difference in E.M.F. between the thermocouple junctions. The experimental results are obtained from measurements of this difference in E.M.F., the difference in E.M.F. having a direct relationship to quartz content.

Outline of Apparatus.

The apparatus used is similar to that described by Roberts (67) and is described in detail by Dempster (68). It consists of

(a) Specimen Cell.

This cell is a thin walled refractory container with two similar compartments into which are packed the test and inert materials in which the thermocouples are embedded.

(b) Refractory Block.

The specimen cell fits into a refractory block. This block is made in two halves and when assembled is cylindrical in shape except for one square end which locates the block in the furnace tube.

(c) Furnace.

The furnace is a refractory tube, round which the heating element is wound, in a square aluminium case packed with asbestos wool.

Experimental Procedure.

A weighed amount of test sample is carefully packed into the 'one-wire' cell compartment and a weighed sample of fine inert material is packed into the other. The inert material used was finely ground chromatographic alumina (81) as recommended by Roberts (80). After assembly in the furnace and the connection of the thermocouple circuits, the temperature is raised to 700°C. The current is then switched off and the furnace allowed to cool. When the temperature reaches 650°C, the reading of galvanometer deflections (in cm.) is begun. This is continued at fifteen second intervals until the temperature reaches 550°C.

A thermal graph of galvanometer deflection in cm. against time is obtained and the 'peak height' calculated. The galvanometer deflections in centimetres are proportional to the E.M.F. across the galvanometer and can, therefore, since E.M.F. is proportional to the difference in temperature, be substituted for the temperature difference between the samples in the thermal curves.

The silica content of the material is determined from calibration curves of 'peak height' against concentration of silica.

The measurement of 'peak area', in place of 'peak height', is claimed to give a more accurate result. The measurement of 'peak height' was used in this work, as it is easier to measure.

SECTION B.

SOME SORPTION PROPERTIES OF SILICIOUS DUSTS.

Part I. The Adsorption of Amino-Acids and Dipeptides on Finely divided Silica.

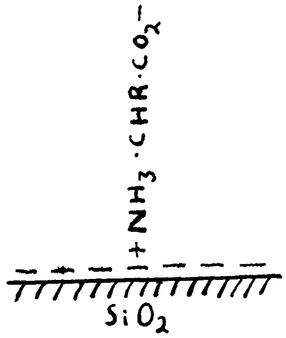
Introduction.

The adsorption of proteins and organic colloids on quartz and montmorillonite clays has been found, by many workers, to take place according to a polar mechanism.

It has been shown that silica particles in aqueous suspension are negatively charged (82). Amino-acids in solution exist in the form of the zwitterion (or dipolar ion) thus:-

$$^{+}NH_3 \cdot CHR \cdot CO_2^{-}$$

The adsorption of amino acids in solution on silica has, therefore, a polar mechanism, adsorption taking place through the positively charged amino group in the following manner.



An extensive study of the adsorption of amino-acids and dipeptides on finely divided silica has been carried out by Watson (83) and his results /

results confirm the above statement.

Watson obtained adsorption isotherms for various amino-acids and dipeptides and the results he obtained indicated, as would be expected, that the extent of adsorption decreased with increasing temperature. However, the adsorption isotherms obtained for dl-leucylglycine were an exception to this rule. He found that the extent of adsorption at 37°C was greater than that at 25°C, while adsorption at the higher temperature 50°C and 65°C is considerably lower than that at 25°C. The result is unexpected and requires some explanation. It was decided, therefore, to repeat, in greater detail, the work of Watson over the temperature range 25°C - 50°C in an attempt to explain the above results. It was also decided, for the sake of completeness and for the purpose of comparison, to study the adsorption characteristics of the parent substances, glycine and dl-leucine, and the isomer glycyl-dl-leucine.

Adsorbent.

The adsorbent used throughout this work was a finely divided powder supplied by Messrs. Colin Stewart Ltd. under the trade-name M.S.C. This dust was chosen as it could be obtained easily and; also, it has been shown by King et al. (84) that a similar silica dust from the same source had a high pathogenicity.

The material contained 93% silica, the impurities being in the form of aluminium and ferric oxides. However, the dust has the same adsorption /

adsorption characteristics as pure quartz dust (83).

The apparent surface area of the material, as determined by the method of Lea and Nurse (85), is claimed by the suppliers to be 10,800 sq. cm. per gm. However, as the various methods of determining surface area give widely differing results, it was decided to plot all adsorption results on a gram basis i.e. moles $\times 10^{-5}$/gm. of adsorbent.

Preparation of Solutions.

Standard solutions (0.005M - 0.07M) of the following amino-acids and dipeptides were prepared.

A - Amino-acids.

(1) glycine

(2) dl-leucine

B - Dipeptides.

(1) glycyl-dl-leucine

(2) dl-leucylglycine

Experimental Procedure.

A - Amino-acids.

Finely divided silica (2g.) was weighed into a 50 ml. "Quickfit" adsorption tube and standard amino-acid solution (12.5 ml.) added. This procedure was carried out with seven tubes, standard amino-acid solution, in the range 0.005M - 0.07M, being used with increasing concentration along the set of tubes. The tubes were then rotated at 30 r.p.m. /

30 r.p.m. in a thermostatic water bath at 37°C for 48 hours. At the end of this period, the suspension was centrifuged at 3,500 r.p.m. for 10 minutes and then filtered through a Ford "Sterimat" pad (Grade G.S.). The filtrate was then analysed (For method of analysis see Appendix at end of section) and the amount of amino-acid adsorbed (moles x 10^{-5}/gm. of adsorbent) plotted against equilibrium concentration of the solution (moles x 10^{-2}/litre).

This procedure was repeated for a range of temperatures between 25°C and 50°C (25°, 27°, 30°, 32.5°, 37°, 40°, 45°, 50°C).

B - Dipeptides.

The procedure used for dipeptides was identical with that used for the amino-acids, except that the amount of adsorbent used for each test was increased to 4 grams. This was necessary as the extent of adsorption of the dipeptides was found to be very low.

Results and Discussion of Results.

The results obtained are shown in tables 9-12.

(1) Glycine (Table 9).

The results obtained confirm and amplify the work of Watson (83), the extent of adsorption decreasing with increasing temperature. The amount of glycine adsorbed reaches a constant maximum (8.51 x 10^{-5} moles/gram).

(2) dl-Leucine (Table 10).

The /

TABLE 9.

Adsorption of Glycine on Finely divided Silica

25°C		27°C		30°C		32.5°C	
Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.
0.701	4.992	0.541	3.621	0.541	3.190	0.541	2.801
1.090	8.231	0.911	6.143	0.911	5.503	0.911	5.014
1.714	8.484	1.581	8.520	1.581	8.523	1.581	8.490
2.246	8.520	1.986	8.531	1.986	8.509	1.986	8.512
2.824	8.518	2.992	8.518	2.992	8.515	2.992	8.509
3.504	8.515	3.722	8.522	3.722	8.510	3.722	8.514
5.107	8.509	5.046	8.519	5.046	8.521	5.046	8.521
37°C		40°C		45°C		50°C	
0.701	3.090	0.541	2.391	0.541	2.101	0.701	1.982
1,090	5.181	0.911	3.984	0.911	3.614	1.090	3.574
1.714	7.664	1.581	6.787	1.581	5.989	1.714	5.400
2.246	8.498	1.986	8.044	1.986	7.553	2.246	6.983
2.824	8.501	2.992	8.517	2.992	8.504	2.824	8.514
3.504	8.520	3.722	8.524	3.722	8.496	3.504	8.523
5,107	8.496	5.046	8.520	5.046	8.519	5.107	8.517

TABLE 10.

Adsorption of dl. - Leucine on Finely divided Silica.

25°C		27°C		30°C		32.5°C	
Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.
0.715	1.792	0.521	1.091	0.521	0.994	0.521	0.732
1.265	3.201	1.132	2.494	1.132	2.141	1.132	1.594
1.817	4.156	1.511	3.110	1.511	2.892	1.511	2.147
2.408	4.201	2.231	4.206	2.231	4.152	2.231	3.175
2.926	4.189	2.772	4.221	2.772	4.194	2.772	3.830
3.762	4.204	3.332	4.215	3.332	4.220	3.332	4.218
37°C		40°C		45°C		50°C	
0.715	0.814	0.521	0.441	0.521	0.323	0.715	0.320
1.265	1.466	1.132	1.013	1.132	0.735	1.265	0.584
1.817	2.030	1.511	1.360	1.511	0.996	1.817	0.821
2.408	2.641	2.231	2.003	2.231	1.460	2.408	1.143
2.926	3.257	2.772	2.392	2.772	1.774	2.926	1.410
3.762	4.221	3.332	2.925	3.332	2.431	3.762	1.837

The results obtained for the adsorption of leucine shows that the extent of adsorption decrease with increasing temperature. The amount of leucine adsorbed reaches a constant maximum (4.20×10^{-5} moles/gram).

(3) Glycyl-dl-leucine (Table 11).

The results obtained are similar to the results obtained by Watson, increasing temperature decreasing the amount of dipeptide adsorbed. The amount of dipeptide adsorbed reaches a constant maximum (1.60×10^{-5} moles/gram).

(4) dl-Leucylglycine (Table 12).

The results obtained confirm and amplify the work of Watson. Adsorption increased with increasing temperature between 25°C and 40°C. Above 40°C, the adsorption behaviour falls back into the normal form with adsorption decreasing with increasing temperature.

The isotherms, also, indicate multilayer formation, the extent of adsorption at the first "flat" being 1.50×10^{-5} moles/gram, and, that of the second "flat" 3.00×10^{-5} moles/gram. From the simple numerical ratio of these two adsorption values, it may be deduced that 1.50×10^{-5} moles/gram represents a unimolecular layer, and 3.00×10^{-5} moles/gram, a bimolecular layer.

The abnormal temperature effect is shown graphically in Fig. 16, the adsorption of a 0.005M solution of dl-leucylglycine in

moles /

TABLE 11.

Adsorption of Glycyl-dl.-leucine on Finely divided Silica.

25°C		27°C		30°C		32.5°C	
Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.
0.521	0.541	0.396	0.303	0.396	0.254	0.396	0.230
0.752	0.730	0.830	0.726	0.830	0.531	0.830	0.485
1.796	1.584	1.611	1.341	1.611	1.050	1.611	0.913
2.734	1.603	2.446	1.610	2.446	1.557	2.446	1.341
3.470	1.624	3.203	1.606	3.203	1.601	3.203	1.600
4.250	1.598	3.752	1.597	3.752	1.604	3.752	1.594
5.370	1.606	4.865	1.594	4.865	1.589	4.865	1.606
37°C		40°C		45°C		50°C	
0.521	0.232	0.396	0.154	0.396	0.100	0.521	0.132
0.752	0.346	0.830	0.283	0.830	0.242	0.752	0.170
1.796	0.801	1.611	0.560	1.611	0.435	1.796	0.665
2.734	1.170	2.446	0.846	2.446	0.663	2.734	0.558
3.470	1.534	3.203	1.153	3.203	0.861	3.470	0.704
4.250	1.612	3.752	1.290	3.752	1.007	4.250	0.963
5.370	1.604	4.865	1.622	4.865	1.344	5.370	1.154

TABLE 12.

Adsorption of dl. - Leucylglycine on Finely divided Silica.

25°C		27°C		30°C		32.5°C	
Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.	Equilibrium Concentration M. x 10^{-2}/L.	Adsorption M. x 10^{-5}/G.
0.507	0.241	0.363	0.180	0.363	0.232	0.363	0.304
1.039	0.453	0.993	0.532	0.993	0.654	0.993	0.825
1.806	0.746	1.612	0.829	1.612	1.021	1.612	1.350
2.696	1.130	2.456	1.284	2.456	1.484	2.456	1.504
3.708	1.651	3.218	1.504	3.218	1.521	3.218	1.950
4.413	1.556	3.935	1.510	3.935	1.870	3.935	2.631
6.848	2.980	4.865	2.562	4.845	3.034	4.845	2.998
37°C		40°C		45°C		50°C	
0.507	0.706	0.507	0.901	0.363	0.121	0.396	0.112
1.039	1.420	1.039	1.572	0.993	0.303	0.830	0.213
1.806	1.501	1.806	1.723	1.612	0.461	1.612	0.390
2.696	2.253	2.696	2.060	2.456	0.580	2.466	0.574
3.708	2.925	3.708	2.992	3.218	0.902	3.222	0.816
4.413	3.071	4.413	3.101	3.935	1.083	3.752	1.044
5.263	2.997	5.263	3.040	4.845	1.153	4.865	1.180

FIG. 16.

EFFECT OF TEMPERATURE
ON THE ADSORPTION OF

0.005M. dl-LEUCYLGLYCINE

ON SILICA

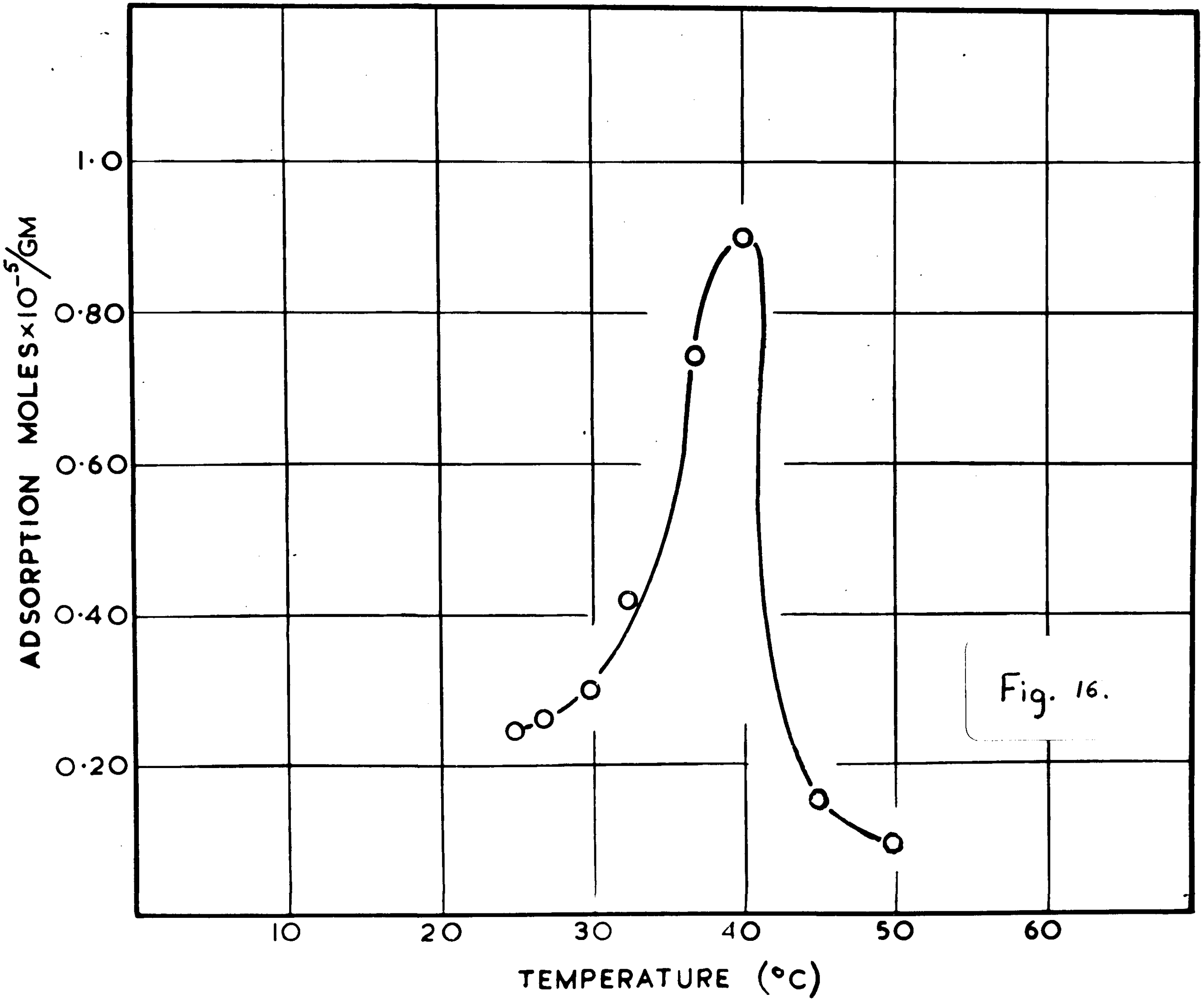

1·0
0·80
0·60
0·40
0·20
ADSORPTION MOLES×10⁻⁵/GM
10
20
30
40
50
60
TEMPERATURE (°C)

Fig. 16.

moles x 10^{-5}/gram being plotted against temperature. An explanation of these abnormal results is required.

Adsorption is an exothermic process and, therefore, it is to be expected that an increase in temperature would cause a decrease in adsorption. This statement has been confirmed by studies on the adsorption of gases on solid.

Bartell et al. (86) have stated that in adsorption from solutions, temperature affects not only the adsorption process but also the solubility of the adsorbate. They state that - "Since solubility and adsorption are different manifestation of the escaping tendency of the solute, adsorption should be greater if the solubility is smaller". In adsorption from solutions, therefore, the solubility effect will be an additional factor. If the adsorbate has a positive temperature coefficient of solubility, both the temperature and solubility effects will work together and adsorption will decrease. If, on the other hand, the adsorbate has a negative temperature coefficient of solubility, the two effects will combat each other and adsorption may increase or decrease depending on which factor is predominant.

The above statement may explain the results obtained for dl-leucylglycine and, therefore, it was decided to determine the temperature coefficients of solubility for the four substances.

Solubility Experiments.

Tubes containing water and glycine were rotated at 30 r.p.m. in a thermostatic water bath at 20°C, and 37°C, for 24 hours. The concentration of glycine in water was then determined gravimetrically.

The above procedure was repeated for dl-leucine, glycyl-dl-leucine and dl-leucylglycine.

The results obtained are shown in Table 13. The results obtained for glycine and dl-leucine agree essentially with those in the literature (87,88). A study of the results shows that dl-leucylglycine has a positive temperature coefficient of solubility and, therefore, the concept of Bartell does not explain the results obtained.

It is seen, also, that glycyl-dl-leucine has a negative temperature coefficient of solubility and this compound, according to Bartell, could be expected to show abnormal adsorption characteristics. On the basis of Bartell's argument, the fact that this compound shows normal adsorption characteristics could be explained by the fact that the temperature effect predominates.

Of the four dipeptides examined by Watson (83), only dl-leucylglycine exhibits abnormal adsorption characteristics and, if dl-leucylglycine was the only one which had a positive temperature coefficient of solubility, a possible explanation of the above results might be obtained. However, glycylglycine (also, examined by Watson) has a positive /

TABLE 13.

SOLUBILITIES IN WATER.

Temperature °C	Solubility (Moles/Litre)			
	Glycine	dl-leucine	Glycyl-dl-leucine	dl-leucylglycine
20°	3.003	0.0716	0.6131	0.1273
37°	4.042	0.0891	0.5929	0.1396

positive temperature coefficient of solubility (89), and, therefore, no explanation of the above results can be obtained through the temperature coefficient of solubility.

Another explanation of the abnormal results obtained for dl-leucylglycine must be sought and the following explanation is put forward. It is suggested that two types of adsorption occur; Type A occurring between 25°C and 40°C, and Type B above 40°C. It may be that physical or Van der Waals adsorption occurs below 40°C and chemisorption or activated adsorption above 40°C, or vice-versa. While there is no definite evidence pointing to this fact, it seems, on the basis of the results obtained, to be the most logical explanation.

Conclusions.

(1) Glycine, dl-leucine and glycyl-dl-leucine exhibit normal adsorption characteristics on finely divided silica, the extent of adsorption decreasing with increasing temperature.

(2) The extent of adsorption of dl-leucylglycine on finely divided silica increased with increasing temperature between 25°C and 40°C. Above 40°C, the compound exhibits normal adsorption characteristics i.e. the extent of adsorption decreases with increasing temperature. It is suggested that this is a result of a change in the type of adsorption.

Part II - The Inhibition of Adsorption of Amino-acids on finely divided Silica.

Introduction.

Heffernan (37) has observed that the presence of alumina inhibited the adsorption of amino-acids on silica, the effect being explained by the fact that alumina in aqueous media has a positive charge and will compete, therefore, with the amino-acid. As a result of this observation, the possibility of using some harmless organic material to inhibit the adsorption of amino-acids on silica occurred to several workers.

Engel and Holzapfel (90) studied the adsorption of sugars on quartz and they found that galactose was more strongly bound to the quartz surface than the other sugars. They also found that the bulk of the material adsorbed from milk by quartz surfaces consisted of galactose and glucose, and that no protein was adsorbed. Further work indicated that galactose inhibited the adsorption of protein material on quartz surfaces, only glycine showing high adsorption characteristics in the presence of galactose.

However, Engel and Holzapfel conducted their experiments in neutral solutions only. Since Watson (83) had found that adsorption of amino-acids by finely divided silica varied markedly with change in pH, it was decided to study the effect of galactose on the adsorption /

adsorption of amino-acids on finely divided silica over the pH range 2 - 11.

The amino-acids studied, represented the three main groups of amino-acids.

$$NH_2 \cdot CHR \cdot COOH$$

basic ($R = (CH_2)_nNH_2$), neutral (R = alkyl), acidic ($R = (CH_2)_nCOOH$)

Adsorbent.

Finely divided silica dust, marketed by Messrs. Colin Stewart, Ltd., under the trade-name M.S.C., was used throughout this work.

Preparation of Solutions.

0.02M solutions were prepared from galactose, and from the following amino-acids; (a) dl-alanine; (b) aspartic acid; (c) glutamic-acid; and (d) lysine.

Experimental Procedure.

Finely divided silica dust (2 g.) was weighed into a 50 ml. "Quickfit" adsorption tube. 0.02M galactose solution (12.5 ml.) was then added and the solution made up to 25 ml. with distilled water. Ten tubes were prepared in this way, and their pH adjusted by the addition of N hydrochloric acid or N sodium hydroxide solution, giving a pH range of 2 - 11 along the set of tubes. The tubes were then rotated at 30 r.p.m. in a thermostatic water bath at 25°C for 24 hours. At the end of this period, the suspension was centrifuged at 3,500 r.p.m. for /

for 10 minutes, and then filtered through a Ford "Sterimat" pad (Grade G.S.). The filtrate was then analysed (for method of analysis see Appendix at end of section) and the amount of galactose adsorbed determined. The adsorption in moles x 10^{-5}/gram of adsorbent was plotted against pH.

The above procedure was repeated with dl-alanine, aspartic acid, glutamic acid and lysine.

Tests were also conducted in the above manner using solutions containing:-

(a) 12.5 ml. of 0.02M galactose solution and 12.5 ml. of 0.02M dl-alanine solution.

(b) 12.5 ml. of 0.02M galactose solution and 12.5 ml. of 0.02M aspartic acid solution.

(c) 12.5 ml. of 0.02M galactose solution and 12.5 ml. of 0.02M glutamic acid solution.

(d) 12.5 ml. of 0.02M galactose solution and 12.5 ml. of 0.02M lysine solution.

In each case, the adsorption in moles x 10^{-5}/gram of adsorbent was plotted against pH.

Results.

The results obtained are shown graphically in Figs. 17 - 20.

Discussion of Results.

A - Adsorption from simple solutions.

(1) Galactose (Fig. 17a).

From a study of graph 17a, it is seen that maximum adsorption

(1.38 moles /

FIG. 17.

ADSORPTION OF dl-ALANINE
AND GALACTOSE ON SILICA.

(a) Separately.

(b) Competitively.

ALANINE — GALACTOSE

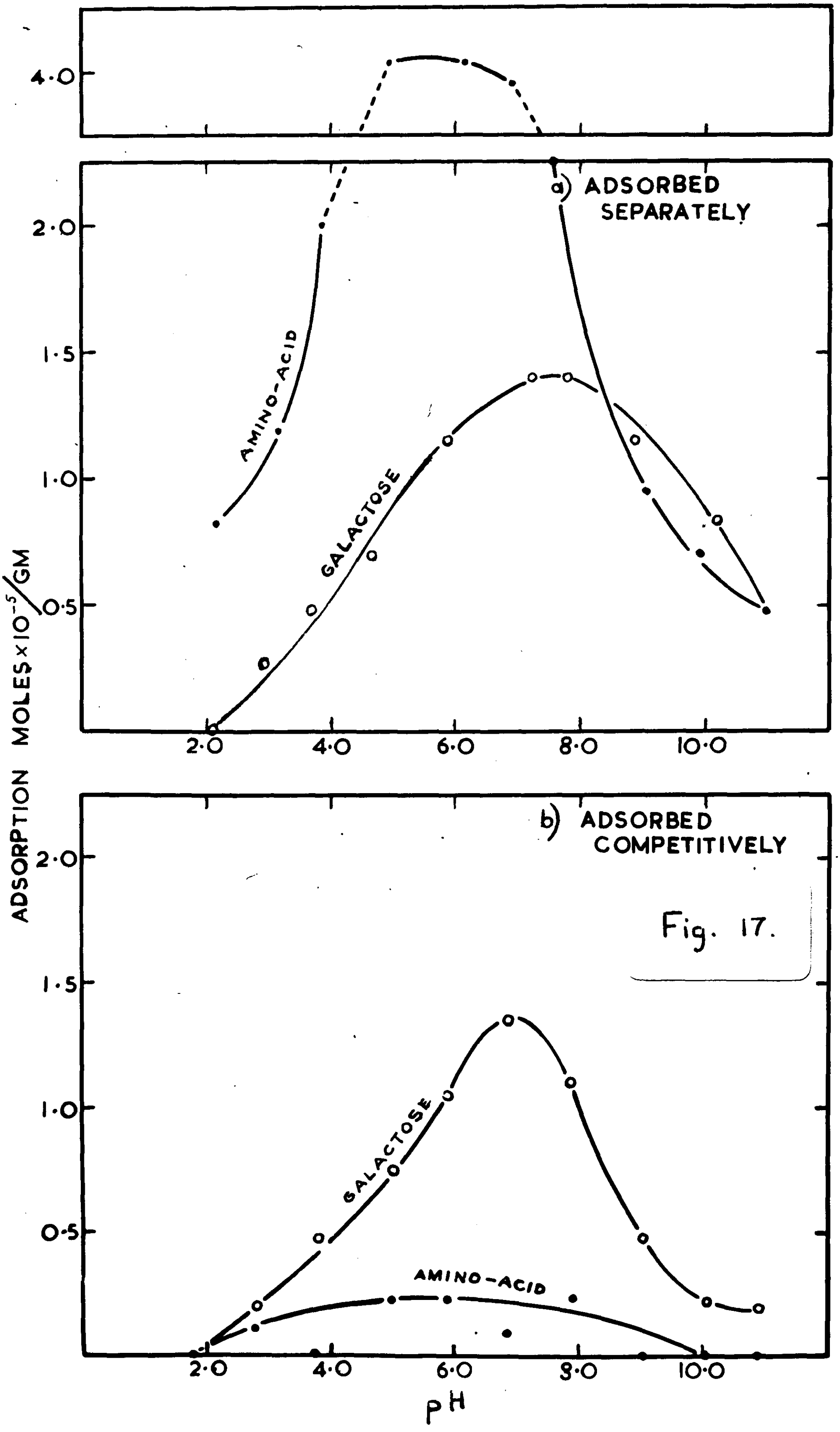


Fig. 17.

(1.38 moles x 10^{-5}/gram) occurs between pH 7 and pH 8.

(2) dl-Alanine (Fig. 17a).

Maximum adsorption (3.98 moles x 10^{-5}/gram) occurs between pH 4.8 and pH 6.8 and the results obtained, confirm the work of Watson.

Maximum adsorption occurs at the isoelectric pH of the amino-acid. This is to be expected, as, at this pH, the acid is mainly in the dissociated form (B)

$$\underset{(A)}{NH_2 \cdot CHMe \cdot COOH} \rightleftharpoons \underset{(B)}{{}^{+}NH_3 \cdot CHMe \cdot COO^{-}}$$

Increased acidity and increased alkalinity shifts the equilibrium towards the uncharged form (A) and adsorption, therefore, decreases as shown by the results.

(3) Lysine (Fig. 18a).

The results obtained confirm the work of Watson, maximum adsorption (1.80 moles x 10^{-5}/gram) occurring between pH 5 and pH 6.

(4) Glutamic and Aspartic Acids (Fig. 19(a) & Fig. 20(a).

The adsorption curves of glutamic and aspartic acids over the pH range are shown in Figs. 19(a) & 20(a). It is observed that maximum adsorption occurs as follows:-

	Maximum Adsorption (moles x 10^{-5}/g.)	pH	Isoelectric pH
Glutamic Acid	1.35	4 - 6	3.08
Aspartic Acid	1.96	5 - 7	2.98

The /

FIG. 18.

ADSORPTION OF LYSINE
AND GALACTOSE ON SILICA

(a) Separately.

(b) Competitively.

LYSINE — GALACTOSE

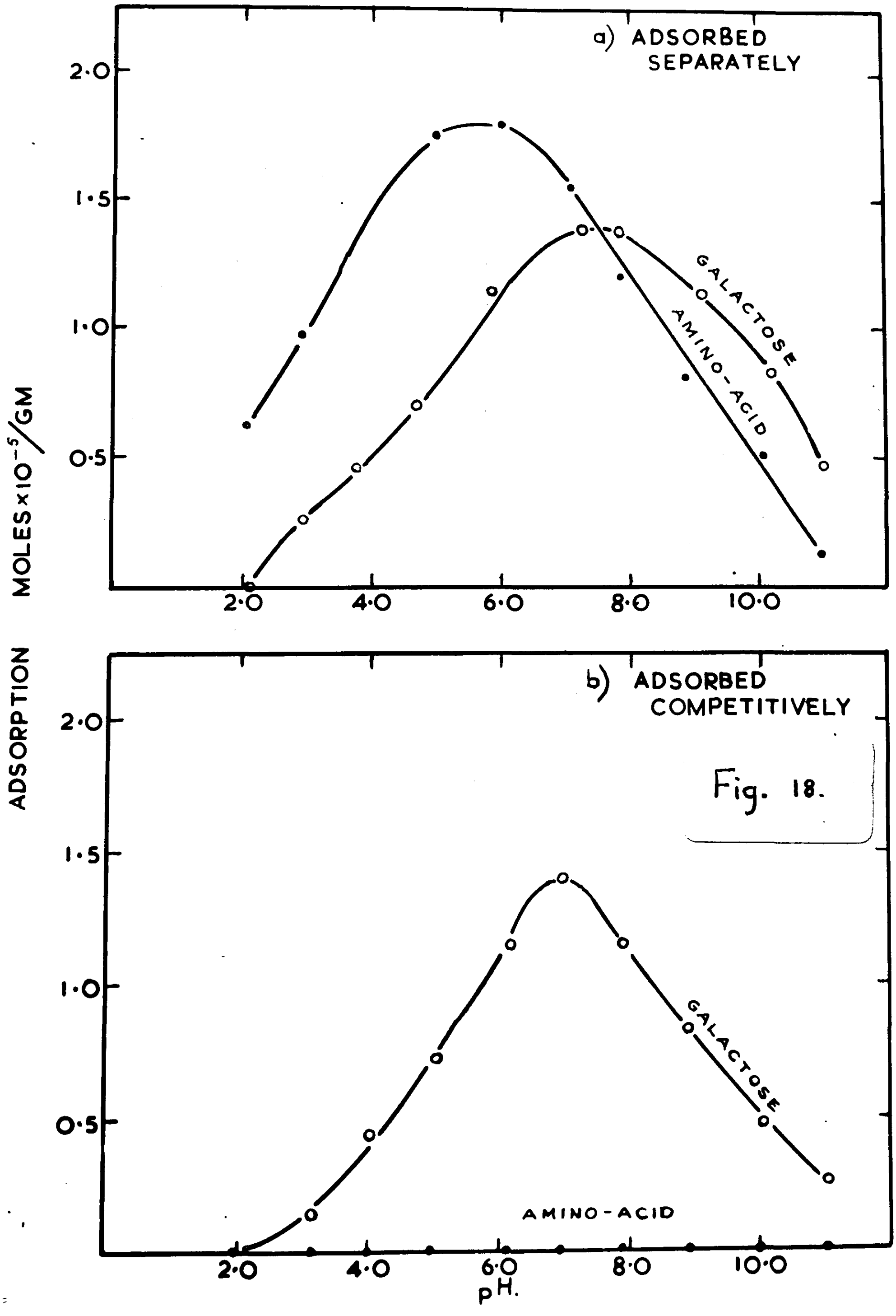


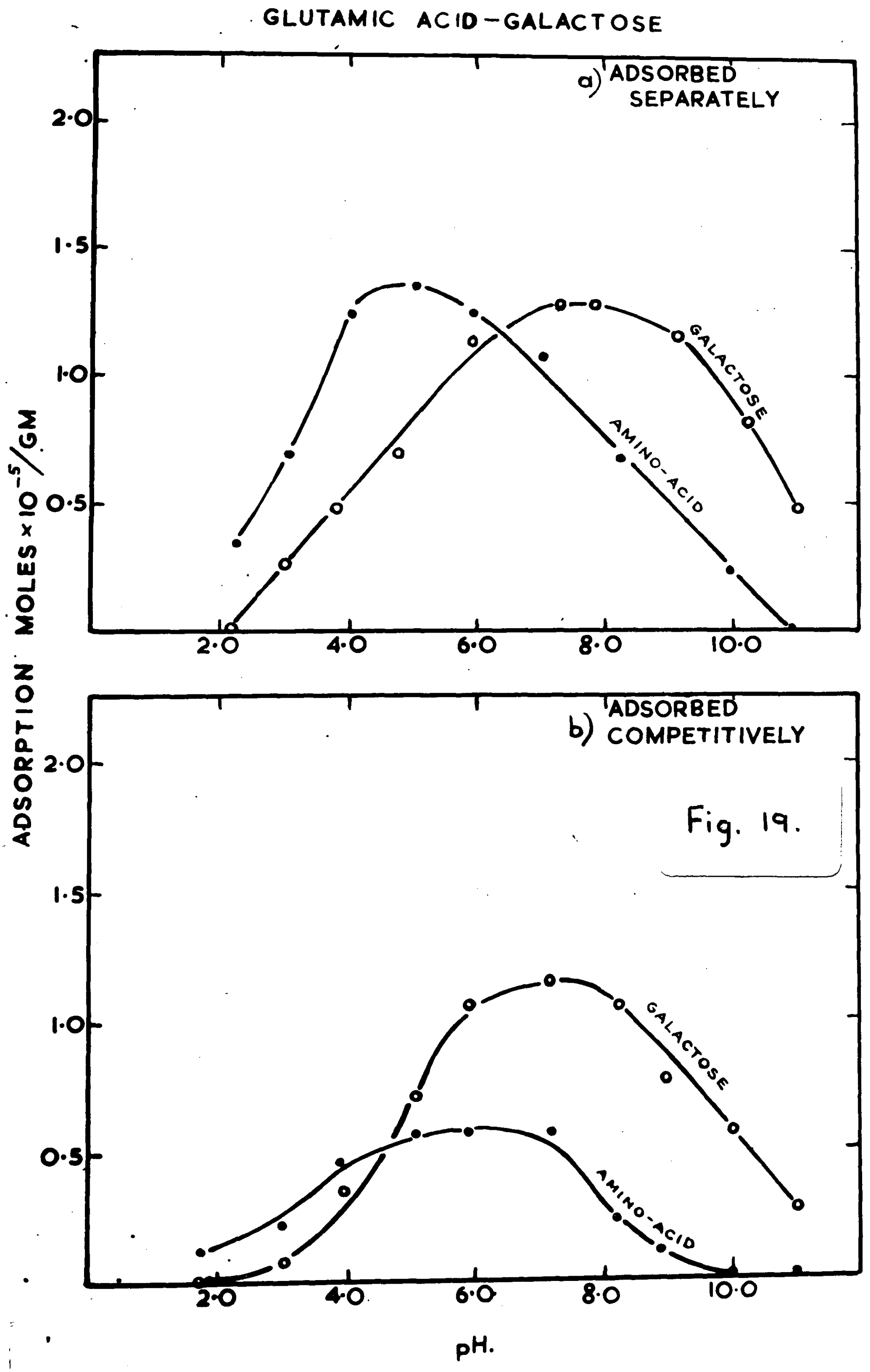
Fig. 18.

FIG. 19.

ADSORPTION OF GLUTAMIC ACID AND GALACTOSE ON SILICA.

(a) Separately.

(b) Competitively.



GLUTAMIC ACID – GALACTOSE

Fig. 19.

FIG. 20.

ADSORPTION OF ASPARTIC ACID AND GALACTOSE ON SILICA.

(a) Separately.

(b) Competitively.

ASPARTIC ACID-GALACTOSE

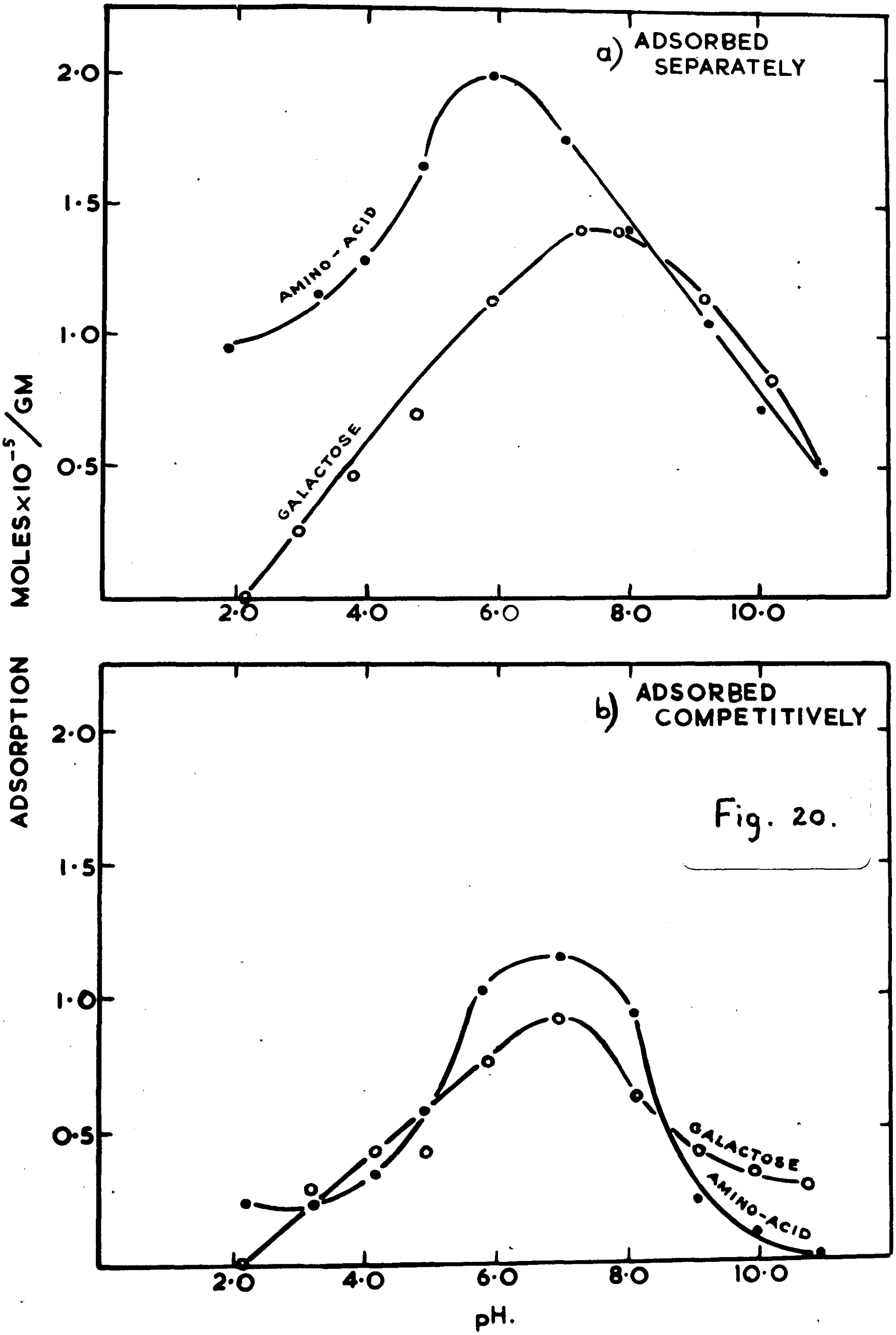


Fig. 20.

The maximum adsorption does not occur at the isoelectric pH of the acid (Contrast the alkyl substituted α - amino-acids (83).) This can be explained in the following manner. Verwey (91) (Table 14) has shown by his work on the electrical double layer of oxidic substances, that the negative zeta-potential on the surface of a silica particle in suspension decreases as the hydrogen ion concentration is increased, and becomes weakly positive for suspensions in 0.1N hydrochloric acid.

The zeta-potential of the silica particles is low at the isoelectric point and the amount of amino-acid adsorbed is, therefore, low. As the pH increases, dissociation of the positively charged NH_3 group into its uncharged amino (NH_2) form increases, but any immediate decrease in adsorption is probably more than counterbalanced by the increase in the negative charge on the silica particles. Thus, adsorption increases until a balance is attained at the point of maximum adsorption. Thereafter, the amount adsorbed decreases with increasing pH as a result of the formation of the uncharged amino form.

B - Adsorption in presence of galactose.

(1) dl-Alanine (Fig. 17(b)).

A study of graph 17(b) shows that the adsorption of dl-alanine is almost completely suppressed over the pH range 2 - 11. The results /

TABLE 14.

(after Verwey)

ZETA-POTENTIAL OF SILICA IN SUSPENSION

Zeta-potential (mv.) in			
10^{-4}N.H.Cl.	10^{-3}N.H.Cl.	10^{-2}N.H.Cl.	0.1N.HCl.
-56	-37	-20	weakly positive

results indicate that galactose is adsorbed preferentially throughout the pH range, adsorption being almost the same as when galactose is in solution alone. (cf. Fig. 17(a)).

It is concluded, therefore, that the adsorption of simple α- amino-acids (R - alkyl) on finely divided silica is almost completely suppressed in the presence of galactose.

(2) Lysine (Fig. 18b).

A study of graph 18(b) shows that the adsorption of lysine is completely suppressed over the pH range 2 - 11. It is also shown that galactose is adsorbed preferentially throughout the pH range, the extent of adsorption being almost the same as when galactose is in solution alone.

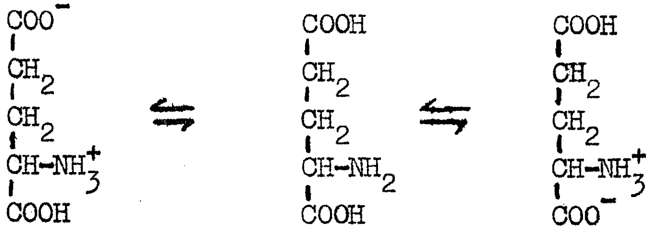
It is concluded, therefore, that the adsorption of diamino carboxylic acids on finely divided silica is completely suppressed in the presence of galactose.

(3) Glutamic Acid (Fig. 19(b)).

Graph 19(b) shows that the adsorption of glutamic acid in the presence of galactose is still considerable. At the maximum point, it is approximately 41% of the maximum adsorption attained when glutamic acid is in solution alone.

This is contrary to the results obtained for the two previous types of amino-acid studies, and may be explained in the following manner /

manner. The abnormality is probably due to the combined effect of both carboxyl groups on the amino group, thus:-



$$\begin{array}{l}\mathrm{COO^-}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH{-}NH_3^+}\\ |\\ \mathrm{COOH}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH{-}NH_2}\\ |\\ \mathrm{COOH}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH{-}NH_3^+}\\ |\\ \mathrm{COO^-}\end{array}$$

The electropositive character of the molecule is then still strong enough to prevent complete suppression of the adsorption of glutamic acid, and to suppress, to a certain extent, the adsorption of galactose.

The amount of galactose adsorbed is, at the maximum point, approximately 82% of the maximum adsorption attained when galactose is alone in solution.

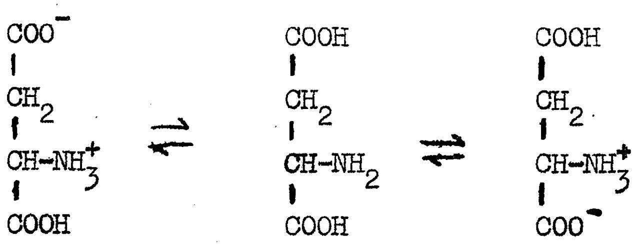
(4) <u>Aspartic Acid (Fig. 20(b))</u>.

As a result of the abnormalities shown by glutamic acid, it was decided to study the adsorption of another dicarboxylic amino-acid on finely divided silica. Aspartic acid was chosen.

From a study of graph 20b, it is seen that the adsorption of aspartic acid in the presence of galactose is still considerable, and at the maximum point is approximately 58% of the maximum adsorption attained when aspartic acid is alone in solution.

The explanation given for glutamic acid can be applied in this /

this case also, as a study of the structures shows.



$$^{-}OOC-CH_2-CH(NH_3^+)-COOH \rightleftharpoons HOOC-CH_2-CH(NH_2)-COOH \rightleftharpoons HOOC-CH_2-CH(NH_3^+)-COO^-$$

(A) (B) (C)

The suppression of the adsorption of aspartic acid in the presence of galactose is less than that for the adsorption of glutamic acid (42% as opposed to 59%). This is probably a result of the greater part played in the equilibrium by form (A) since the second carboxylic group is not so far removed from the amino group.

This electropositive character, therefore, prevents complete suppression of the adsorption of aspartic acid and suppresses to a certain extent the adsorption of galactose. The amount of galactose adsorbed at the maximum point is approximately 65% of the maximum adsorption attained when galactose is alone in solution.

Aspartic acid suppresses the adsorption of galactose to a greater extent than glutamic acid (35% as opposed to 18%) and this is a result of the greater electropositive character of aspartic acid as compared to glutamic acid.

It is concluded, therefore, that the adsorption of dicarboxylic α-amino-acids on finely divided silica is not successfully suppressed by /

by galactose for the reasons stated above.

Conclusions.

(1) The adsorption of dl-alanine on finely divided silica is almost completely suppressed in the presence of galactose.

It is concluded, therefore, that the adsorption of simple α-amino-acids (with R = alkyl) on finely divided silica is almost completely suppressed in the presence of galactose.

(2) The adsorption of lysine on finely divided silica is completely suppressed in the presence of galactose. This leads to the conclusion that the adsorption of diamino-carboxylic acids on finely divided silica is completely suppressed in the presence of galactose.

(3) The adsorption of aspartic and glutamic acids on finely divided silica is not successfully suppressed in the presence of galactose.

It is concluded, therefore, that the adsorption of dicarboxylic α-amino-acids on finely divided silica is not successfully suppressed in the presence of galactose.

(4) On the basis of the above results, it may be concluded, that galactose, if present in body fluids in contact with silica and proteins, would be only partially successful in suppressing interaction of the protein side-chain groupings with the silica surfaces.

SECTION B.

APPENDIX.

The methods of analysis used in determining the amounts of amino-acid and galactose adsorbed by finely divided silica are described below.

(1) Estimation of Amino-acid.

Amino-acid content is determined by a modification of the semi-micro Kjeldahl method of Hitchcock and Belden (92). This method depends on the destructive oxidation of the amino-acid with concentrated sulphuric acid forming ammonium sulphate which can be estimated readily. The ammonium sulphate is treated with strong caustic soda solution, liberating ammonia which is absorbed in a known volume of standard acid solution. The standard acid solution is then back-titrated with standard alkali solution, and the amount of ammonia liberated determined.

The standard amino-acid solutions are analysed before and after adsorption.

Reagents.

(1) Sulphuric acid - concentrated solution.

(2) Potassium sulphate - micro - analytical reagent.

(3) Selenium - Analar reagent.

(4) Copper sulphate - micro - analytical reagent.

(5) Caustic soda solution - A solution containing 500 g. sodium hydroxide (A.R.) and 120 g. sodium thiosulphate (A.R.) made up to 500 ml. with distilled water.

(6) /

(6) Hydrochloric acid - 0.1N. solution.

(7) Sodium hydroxide (A.R.) - 0.1N. solution.

(8) Methyl red - 1 g. of free acid dissolved in 60 ml. of ethanol and diluted to 1 litre with distilled water.

Experimental Procedure.

A volume of the amino-acid solution containing approximately 5 mg. of nitrogen is accurately measured into a Pyrex combustion tube. Concentrated sulphuric acid (2 ml.), potassium sulphate (1 g.), copper sulphate (50 mg.) and selenium (10 mg.) are added to the solution and the mixture heated gently until all the water has been boiled off. The solution was then heated strongly for approximately 20 minutes. At the end of this period, decomposition of the amino-acid is complete and the solution is green in colour. The solution is then cooled and transferred to the steam distillation apparatus. Concentrated caustic soda solution (5 ml.) is added to the solution and the ammonia liberated is steam-distilled into 0.1N hydrochloric acid (5 ml.). The excess hydrochloric acid is back-titrated with 0.1N sodium hydroxide solution using methyl red as an indicator.

Blank analysis on the reagents in distilled water are carried out at regular intervals.

The observed accuracy of the above method is ± 0.05%.

(2) Estimation of Galactose.

The /

The galactose content of the solutions, before and after adsorption, was determined by the method of Okey (93). This method depends on the reaction between sugars and picric acid in the presence of sodium carbonate, which produces a reddish-brown coloration.

Reagents.

(1) Picric acid (A.R.) - saturated solution.

(2) Sodium carbonate (A.R.) - 20% solution.

Experimental Procedure.

The solution under test (1 ml.), saturated picric acid solution (2 ml.) and 20% sodium carbonate solution (1 ml.) are placed in a test tube. The tube is lightly stoppered with a tin-foiled stopper, and immersed in boiling water for 20 minutes. The tube is then cooled, the contents diluted to 20 ml. with distilled water and the galactose content determined with an EEL colorimeter using an Ilford green filter No. 404.

Calibration curves were obtained by the above method, using varying amounts of 0.01M galactose solution. It was also found necessary to obtain calibration curves for galactose in the presence of the amino acids, as it was found that they had some small influence on the estimation.

SUMMARY OF CONCLUSIONS

AND

SUGGESTIONS FOR FUTURE WORK.

(1) The Effect of various inorganic Ions on the Estimation of dissolved Silica by the Molybdenum Blue Method.

(i) The following ions did not interfere in the estimation.

Anions :- Carbonate, chloride, nitrate, and sulphate.

Cations:- Aluminium, calcium, magnesium, and manganese.

(ii) Dichromate ion interferes with the estimation as a result of its colour in solution.

(iii) Phosphate ion interferes with the estimation owing to the formation of phosphomolybdic acid.

(iv) Ferrous and ferric ions interfere with the estimation as a result of the formation of ferric molybdate, the ferrous ion oxidising to ferric ion on precipitation of the hydroxide in the borate buffer solution.

(v) Copper ion interferes with the estimation as a result of the formation of a complex, the apparent ratio of copper to silica being 12 : 1.

(vi) Methods of removing copper and iron interference and for determining dissolved silica in the presence of dichromate ion are described.

(vii) Various methods for the removal of phosphate ion interference have been investigated but they have been found to be unsuccessful. It is suggested that this effect is caused by the borate buffer solution.

It is suggested that the use of ion-exchange resins for the removal of phosphate ion should be investigated. If this method is unsuccessful, it may become necessary to conduct solubility experiments in a solvent other than borate buffer solution.

(2) Estimation of free Silica by Infra-red Spectroscopy.

(i) A qualitative study of the use of infra-red spectroscopy for the estimation of free silica has been conducted and it is concluded that the quantitative determination of free silica could be carried out by this method.

(ii) A quantitative method of analysis has been developed. It is suggested that this technique could be used in the development of infra-red spectroscopy as an analytical tool in inorganic chemistry.

(iii) A comparison of this method with two established methods (Shaw-Skinner method and differential thermal analysis) has been carried out and it is concluded that the method is potentially of greater accuracy than the established methods and that it may be an answer to the problem of determining the free silica content of mine dusts. However, work must be carried out to determine whether any other inorganic compound likely to be present in a mine dust absorbs in the 12.5 μ region. (e.g.

Carbonates /

Carbonates do not absorb in the 12.5 μ region).

Interference from any organic material present can be discounted, as organic material can be removed by combustion and the analysis carried out on the ash.

(3) Adsorption of Various Amino-acids and Dipeptides on finely divided Silica.

(i) Adsorption isotherms, in the temperature range 25° - 50°C, for glycine, dl-leucine, glycyl-dl-leucine, and dl-leucylglycine have been obtained.

(ii) Glycine, dl-leucine, and glycyl-dl-leucine exhibit normal adsorption characteristics, the extent of adsorption decreasing with increasing temperature.

(iii) The results obtained for dl-leucylglycine show that the extent of adsorption increases with increasing temperature between 25°C and 40°C. Thereafter, the compound exhibits normal adsorption characteristics, i.e. the extent of adsorption decreasing with increasing temperature.

No definite explanation of these results has been obtained. However, it is suggested that a change in the type of adsorption occurs at 40°C.

(4) The Inhibition of Adsorption of Amino-acid on finely divided Silica.

(i) /

(i) The effect of galactose on the adsorption of dl-alanine, aspartic acid, glutamic acid, and lysine on a finely divided silica powder has been investigated.

(ii) The adsorption of dl-alanine on finely divided silica is almost completely suppressed over the pH range 2 - 11. It is also shown that galactose is adsorbed preferentially throughout the pH range.

It is concluded, therefore that the adsorption of simple α-amino-acid ($NH_2 \cdot CHR \cdot CO_2H$, where R = alkyl) on silica is almost completely suppressed in the presence of galactose.

(iii) The adsorption of lysine on finely divided silica is completely suppressed over the pH range, galactose being preferentially adsorbed. It is concluded, therefore, that the adsorption of diamino carboxylic acid on silica is successfully suppressed in the presence of galactose.

(iv) The adsorption of aspartic and glutamic acids is not successfully suppressed in the presence of galactose and the adsorption of galactose is partially suppressed. This is thought to be a result of the increased electropositive character of the molecules.

It is concluded, therefore, that the adsorption of dicarboxylic amino-acid on silica is not successfully suppressed in the presence of galactose.

(v) /

(v) It is concluded that galactose, if present in body fluids in contact with silica and protein, is only partially successful in suppressing interaction of the protein side-chain groupings with the silica surfaces.

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