VOLATILE POTATO SPROUT SUPPRESSANT CHEMICALS

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SUMMARY

The object of this study was to find and develop new potato sprout suppressant chemicals. It was considered important that these chemicals should be shown to be effective under commercial conditions. In addition, the chemicals were studied to determine whether or not they were suitable for use on seed potatoes. The chemicals were evaluated as treatments applied to harvested potato tubers. Only volatile, naturally-produced chemicals were considered.

The compounds tested were, α-pinene, benzothiazole, 1,4-dimethylnaphthalene, 1, 6-dimethylnaphthalene, 2, 3-dimethylnaphthalene, citral, camphene, citronellol, coumarin, α-terpineol, naphthalene, limonene, 2-methoxy-3-ethylpyrazine, biphenyl, carvone, pulegone, camphor, vanillin, methyl salicylate and borneol.

An experimental method was designed in order that the sprout suppressant properties of these chemicals could be assessed. The method consisted of treating 10 kg tuber samples at rates between 0 and 500 mg kg^{-1}. The sprout suppressant properties of these chemical treatments were studied over periods of 12 to 14 weeks at 10°C. The tubers were held in cardboard boxes with loosely fitting lids.

From this assessment work dimethylnaphthalene was shown to be a suitable sprout suppressant. When applied at 100 mg kg^{-1} sprout growth control was as good as that obtained using tecnazene applied at the recommended rate of 135 mg kg^{-1}. Dimethylnaphthalene did not adversely affect the emergence and total yield of treated seed potato tubers.

It was decided that the sprout suppressant properties of dimethyl-naphthalene should be further investigated during the following growing season. To do this, four development experiments were carried out. They were designed to determine, (a) the best application rate, (b) the effects of application rate and airing before planting on the performance of treated seed potato tubers, (c) sprout suppression,

emergence and yield of seed potato tubers treated under typical commercial conditions and (d) sprout suppression of tubers held in long-term commercial stores. The results of these experiments confirmed that the best seed potato tuber application rate was 100 mg kg^{-1}. Treatment at this rate, with 4 to 7 weeks airing did not adversely affect emergence and total yield. Treatment at 300 mg kg^{-1} could cause a reduction in total yield. However, airing periods of 7 weeks before planting reduced the adverse effects of 300 mg kg^{-1} treatments. Dimethylnaphthalene treatment affected the size distribution of tubers grown from treated seed potato tubers. Dimethylnaphthalene treatment increased the proportion of tubers ≤ 52 mm. However, this increase was not as great as that caused by tecnazene applied at its recommended rate of 135 mg kg^{-1}. 100 mg kg^{-1} dimethylnaphthalene treatments were effective when applied to 500 kg boxes of tubers held under commercial seed potato storage conditions. Total yield of such seed was not reduced. The proportion of tubers ≤ 52 mm was however increased. Application rates up to 200 mg kg^{-1} were not sufficient to prevent sprouting under the long-term storage conditions of tubers intended for processing.

Residue analysis of tubers treated with 1, 4-dimethylnaphthalene were studied. Levels of 3 to 4 mg kg^{-1} were found in unpeeled tubers treated with 100 mg kg^{-1} 1, 4-dimethylnaphthalene. Tubers treated with 300 mg kg^{-1} 1, 4-dimethylnaphthalene had residue levels of 11 mg kg^{-1}. Airing tubers for 7 weeks caused a 30% decrease in residue levels.

Headspace concentrations of 1, 4 dimethylnaphthalene in 10 kg capacity boxes containing treated tubers were studied. The results showed that the minimum effective headspace concentration of 1, 4-dimethylnaphthalene was between 3 and 6 mg m^{-3}.

Headspace experiments demonstrated the importance of considering the minimum effective headspace concentration and relative volatility when considering the properties of new sprout suppressant chemicals.

Headspace concentrations of tecnazene and chlorpropham were determined in the air of commercial bulk potato stores. Tecnazene was present at a concentration of 0.22 mg m^{-3}, 6 hours after the tubers had been treated. Chlorpropham was present at a concentration of 0.055 mg m^{-3}, 3 days after application to the tubers.

To study headspace and residue concentrations, new analytical techniques were developed.

Trace organic vapour analyses were carried out using porous polymer adsorbent methods. Precolumn traps containing Tenax GC were used to concentrate trace organic volatiles. The volatiles were thermally desorbed from the traps before gas chromatographic analysis. Headspace samples containing known concentrations of naphthalene were used to assess the accuracy and precision of the headspace analysis method. In this way, porous polymer precolumns were shown to be accurate and precise when sampling rates greater than 1.0 cm^3 min^{-1} were used. It was important that the porous polymer precolumns were inserted into the headspace being studied and were removed immediately after sampling was completed.

The headspace analysis methods were extended for use in bulk potato stores. In these experiments sample volume was most easily measured by the time taken to sample at a sampling rate which had been predetermined in the laboratory.

A residue analysis method for 1,4-dimethylnaphthalene was developed. 1,4-dimethylnaphthalene was extracted from treated tubers using ethanol and hexane. An alumina column clean-up step was used with final analysis by gas chromatography. It was found necessary to maintain strict control over temperature and vacuum when reducing the volume of solutions containing dimethylnaphthalene in hexane. Otherwise, dimethylnaphthalene was lost through evaporation with the solvent. The analysis method was shown to be accurate, precise and had an efficiency of 84.5%.

CHEMICAL SPROUT SUPPRESSION SECTION

CHAPTER I

INTRODUCTION TO CHEMICAL SPROUT SUPPRESSION SECTION AND THESIS DESCRIPTION

The useful storage life of potato tubers is limited by sprouting. Sprouting causes a loss of material to the tubers and an accelerated loss of water through the permeable surface of the sprout. Chemicals can provide an effective means of controlling sprout growth. 38% of the storage capacity in Great Britain in 1977 was treated with sprout suppressant chemicals. In Great Britain two main chemicals are used as sprout suppressants. The most commonly used is tecnazene (1, 2, 4, 5-tetrachloro-3-nitro-benzene), which in 1977 was used on 1. 50 million tonnes of stored tubers. The other chemical, chlorpropham((3 chlorophenyl) carbamic acid 1-methylethyl ester) was used on 0. 5 million tonnes of stored tubers (Anon, 1978). Only tecnazene can be used on seed potatoes.

The aim of this project was to find and develop new potato sprout suppressant chemicals which would be effective under commercial storage conditions. The project was also intended to find whether any of these new sprout suppressants could be used on seed potatoes.

At the start of the project an immediate distinction was made between sprout suppression methods in which chemicals were applied directly to harvested tubers and methods in which chemicals were applied to the plant foliage before harvest. The study was concerned with investigating the sprout suppressant properties of chemicals applied directly to harvested tubers.

Only volatile chemicals were studied. Volatile chemicals have considerable advantages over solid inhibitors and liquid sprays or dips. Introduction of the chemical as a vapour provides an easier, more uniform means of distribution. If the chemical is sufficiently volatile it can be introduced after storage has been completed. In this way,

application can be deferred until proved necessary (e. g. during winters of higher than normal temperatures) and re-application during longer storage periods will also be possible. At the end of the storage period, residues of volatile chemicals can be readily reduced by a period of ventilation. Low residues are important as human consumption of the chemical should be minimized. The risk of possible taints will also be reduced. Low residues will help minimize any subsequent effects chemical treatment may have on the emergence and yield of seed tubers.

In this study the initial choice of chemicals was restricted to naturally produced chemicals in the belief that they would prove more acceptable from a toxicological point of view than their anthropogenic counterparts.

At the beginning of the project considerable emphasis was placed on identifying the volatile chemicals evolved by stored potato tubers. It had been shown that these volatile substances possessed sprout suppressant properties (Burton, 1952; Burton and Meigh, 1971). Most of the early research work in this project was directed towards developing the analytical methods necessary to collect and identify these compounds. However, before any of these compounds could be positively identified, the main research effort was diverted from this work, following the results of early sprout suppressant assessment experiments.

An alternative approach to finding new sprout suppressant chemicals was to assess volatile chemicals which, from the results of published studies, had known growth regulant properties. Such chemicals were studied by small scale laboratory assessment experiments, designed to predict how well the chemicals would suppress sprouting under commercial conditions. The assessment experiments were also designed to show the effect of chemical treatment on emergence and final yield of seed tubers. Using these methods, 20 naturally produced,

volatile chemicals were studied. The results showed that one of these chemicals was an effective sprout suppressant which did not affect total yield of treated seed tubers. The chemical was dimethylnaphthalene.

The main research effort was then directed towards developing dimethylnaphthalene as a sprout suppressant chemical. The development studies assessed dimethylnaphthalene in further small scale laboratory experiments and also in larger commercial scale experiments.

As a preliminary step towards assessing the toxicity of dimethylnaphthalene treatments, analytical methods were developed for measuring the amount of dimethylnaphthalene residues in treated tubers.

Trace organic vapour analysis techniques were used to determine the relationship between sprout control and chemical headspace vapour concentration. The analytical methods originally intended to collect and identify potato tuber volatiles were developed for use in these quantitative trace organic volatile studies. The accuracy and precision of these methods were extensively studied. Using these methods the headspace concentrations of volatile sprout suppressant chemicals were accurately determined above treated tubers.

This thesis consists of two distinct sections. The first section (Chapters 2, 3 and 4) is concerned with chemical sprout suppression. Chapter 2 considers the assessment experiments in which the sprout suppressant properties of 20 volatile chemicals were studied. Chapter 3 deals with the development experiments designed to fully characterise the sprout suppressant properties of dimethylnaphthalene. Chapter 4 considers the methods used in the assessment and development experiments. Questions concerning the methodology of these experiments are explained with the aid of headspace analyses.

The second section (Chapters A1 and A2) is concerned with the development of chemical analytical techniques. A short introduction precedes this second section. Chapter A1 discusses the development

of trace volatile headspace analysis techniques. Chapter A2 discusses the development of analytical techniques for determining trace residues of dimethylnaphthalene in treated tubers.

CHAPTER 2

SPROUT SUPPRESSANT ASSESSMENT EXPERIMENTS

2.1 INTRODUCTION

The sprout suppressant properties of 20 naturally produced, volatile chemicals was assessed experimentally. The compounds tested were, α-pinene, benzothiazole, 1, 4-dimethylnaphthalene, 1, 6-dimethylnaphthalene, 2, 3-dimethylnaphthalene, citral, camphene, citronellol, coumarin, α-terpineol, naphthalene, limonene, 2-methoxy-3-ethylpyrazine, biphenyl, carvone, pulegone, camphor, vanillin, methyl salicylate and borneol.

The principal aim of this chapter is to consider the sprout suppressant properties of these 20 test compounds. The chapter describes the compounds, including their relevant physical/chemical properties. It also details the assessment method and finally presents and discusses the results of the assessment experiments. The results of these experiments raise several questions concerning the assessment method itself. These points, however, are not discussed until Chapter 4.

2.1.1 THE CHOICE OF CHEMICALS

For the reasons previously stated (Chapter 1), only naturally produced, volatile chemicals were considered. The choice of which chemicals were finally selected was decided by consideration of the three main objectives of the assessment experiments.

The first and most important objective was to find new sprout suppressant chemicals which could be used under commercial conditions. The rational adopted was that of testing already established growth regulants under prescribed laboratory conditions, assuming that the laboratory method was an accurate means of predicting performance under commercial conditions. Therefore, with the exception

of 2-methoxy-3-ethylpyrazine all of the naturally produced volatile chemicals had been previously shown to be active growth regulants. Some had established sprout suppressant properties.

The second objective was to try to predict which of those chemicals found to be evolved by potatoes (as a result of any future potato volatile collection and identification experiments) were the active sprout suppressants previously shown to be present (Burton, 1952; Burton and Meigh, 1971). Therefore, included in the range of chemicals were several compounds which had already been found in potato tubers.

The third objective was to develop a suitable laboratory assessment method. Thus, any newly identified potato volatile (or indeed any other chemical) could be accurately assessed as a sprout suppressant suitable for use under commercial conditions. This objective could to some extent be achieved by including chemicals which had been previously tested for sprout suppressant activity. Thus the results of the assessment experiments could be compared with earlier reported experiments, some of which used alternative methods.

The study consisted of three assessment experiments. The following chemicals were investigated in each assessment experiment.

First assessment experiment

α-pinene	1, 4-dimethylnaphthalene
benzothiazole	citral

Second assessment experiment

camphene	naphthalene
citronellol	limonene
coumarin	2-methoxy-3-ethylpyrazine
α-terpineol	biphenyl
1, 6-dimethylnaphthalene	carvone

Third assessment experiment

α-pinene	borneol
citral	vanillin
carvone	methyl salicylate
pulegone	2, 3-dimethylnaphthalene
camphor	tecnazene

2.1.2 THE ASSESSMENT METHOD

The chemicals were assessed over a treatment period of 12 or 14 weeks at 10^{o}C. Sprout suppression was measured in terms of the mean length of the longest sprout of treated material compared to untreated and tecnazene treated controls. 10 kg batches of potatoes stored in cardboard boxes with loosely fitting lids were used. The chemicals were applied in an alumina carrier.

These somewhat arbitrary conditions were designed to accurately assess in the laboratory how each chemical would perform under typical commercial conditions (i. e. a one tonne box, etc.).

In addition it was important to know whether or not any successful new sprout suppressant would be suitable for use on seed potatoes. This was determined by comparing the performance of treated seed with untreated and tecnazene treated controls. Seed performance was measured in terms of sprout growth after airing, emergence time after planting, and final yield.

The first and second assessment experiments were carried out in the storage season 1975-76. In these experiments, the chemicals were tested over a 12 week period. They were applied at 4 application rates. The highest rate was 100 mg kg^{-1}. The remaining three application rates were placed, in theory*, at equidistant points on a logarithmic scale between 0 and 10^{3} mg per 10 kg. Due to shortage of material, 2-methoxy-3-ethylpyrazine was applied, in theory,* at equidistant points on a logarithmic scale between 0 and $10^{2.5}$ mg per 10 kg. The first assessment experiment was carried out using 2 x 10 kg batches of seed size tubers. This provided enough material to allow for a fully replicated field assessment of emergence and yield. Limited resources

* In practice, however, accurate measurement of the lower rates was not convenient. For volatile liquids, the lowest rate was restricted to the weight of one drop of liquid.

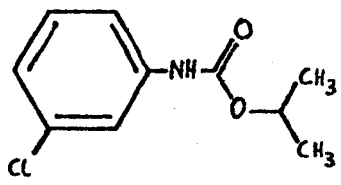
restricted the experiment to the study of four chemicals. Therefore, the chemicals chosen for this experiment were at that time considered to be those with the greatest possibility of proving successful. The second assessment experiment was carried out using 1 x 10 kg batches of ware size tubers. A further 10 chemicals were tested in this way.

The third assessment experiment was carried out in the storage season 1976-77. In this experiment the chemicals were tested over a 14 week period. They were applied at 4 application rates. The highest rate was 500 mg kg^{-1}. The remaining three application rates were placed, in theory, at equidistant points on a logarithmic scale between 0 and 500 mg kg^{-1}. 1 x 10 kg batches of tubers were used. 10 chemicals were tested.

2.1.3 PROPERTIES OF THE CHEMICALS

The following notes summarize the relevant properties of the chemicals which were assessed as sprout suppressants. The notes are also intended to explain why each chemical was studied. To provide a comparison, the properties of tecnazene and chlorpropham are also included.

Chlorpropham; (3-chlorophenyl) carbamic acid 1-methylethyl ester



$C_{10} H_{12} Cl NO_2$

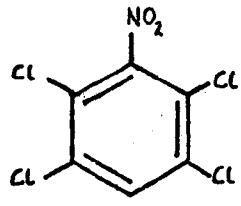
m. wt. 213.68
m. p. 40.7 - 41.1°C
b. p. 229°C

Recommended application rate, 10 - 20 mg kg^{-1} (van Vliet and Sparenberg, 1970).

Acute LD_{50}, 5,000 - 7,500 mg kg^{-1} (rats) (Martin, 1972).

Vapour pressure; 0.039 Pa (25°C), 0.006 Pa (10°C) (Liebmann and Sieber, 1964).

Tecnazene; 1, 2, 4, 5-tetrachloro-3-nitro-benzene



$C_6 H Cl_4 NO_2$

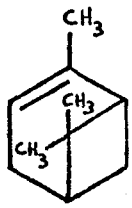
m. wt. 260.89
m. p. 98 - 101°C
b. p. 304°C

Recommended application rate, 135 mg kg^{-1} (Brown and Reavill, 1954).

Low mammalian toxicity; rats fed 57 mg kg^{-1} d^{-1} or mice fed 215 mg kg^{-1} d^{-1} suffered no ill effects (Buttle and Dyer, 1950).

Vapour pressure; 0.06 Pa (25°C) (Caseley, 1968).

α-Pinene; 2, 6, 6-trimethylbicyclo (3.1.1) hept - 2 - ene.



$C_{10} H_{16}$

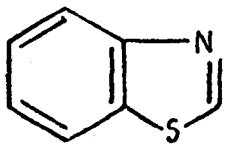
m. wt. 136.23
m. p. -55°C
b. p. 155 - 156°C

Naturally produced monoterpenoid. Identified as a volatile growth inhibitor produced by Salvia leucophylla, S. apiana, S. mellifera (Muller and Muller, 1964) and Eucalyptus camaldulensis (del Moral and Muller, 1970). Causes a 50% reduction in germination of radish seeds at a headspace concentration of 4 g m^{-3} (Asplund, 1968). Active potato sprout growth inhibitor (Dalziel, 1975).

Fatal dose 180 g orally as turpentine (Merck Index, 1976).

Vapour pressure; 588.6 Pa (25°C), 224.3 Pa (10°C) (Hawkins and Armstrong, 1954).

Benzothiazole



$C_7 H_5 NS$

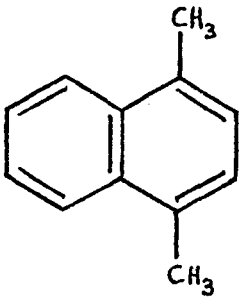
m. wt. 135.18
m. p. 2°C
b. p. 227 - 228°C

Active volatile potato sprout growth inhibitor. Complete suppression when applied at a headspace concentration between 8 and 28 mg m^{-3} (Meigh et al., 1973).

Found in potato peel (Meigh et al., 1973) and boiled potato (Buttery et al., 1970).

LD_{50}, i.v., 100 mg kg^{-1} (mice) (Merck Index, 1976).

1, 4-Dimethylnaphthalene



$C_{12}H_{12}$
m. wt. 156. 23
m. p. -18°C
b. p. 262 - 264°C

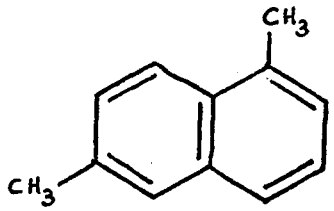
Active volatile potato sprout growth inhibitor. Complete suppression when applied at a headspace level between 0 and 14 mg m^{-3} (Meigh et al., 1973).

Found in potato peel (Meigh et al., 1973). Dimethylnaphthalene present in cooked, unpeeled potatoes (Nursten and Sheen, 1974).

1, 6-isomer, LD_{50}, 5 g kg^{-1} (rat) (Anon, 1976).

Vapour pressure (2, 7-isomer); 0. 56 Pa (25°C), 0. 09 Pa (10°C) (Osborn and Douslin, 1975).

1, 6-Dimethylnaphthalene



$C_{12}H_{12}$
m. wt 156. 23

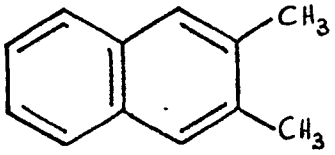
Active volatile potato sprout growth inhibitor. Complete suppression when applied at a headspace level between 0 and 16 mg m^{-3} (Meigh et al., 1973).

Found in potato peel (Meigh et al., 1973). Dimethylnaphthalene is present in cooked, unpeeled potatoes (Nursten and Sheen, 1974).

LD_{50}, 5 g kg^{-1} (rat) (Anon, 1976).

Vapour pressure (2, 7-isomer); 0. 56 Pa (25°C), 0. 09 Pa (10°C) (Osborn and Douslin, 1975).

2, 3-Dimethylnaphthalene



$C_{12}H_{12}$

m. wt. 156. 23

m. p. 102 - 104°C

b. p. 269°C

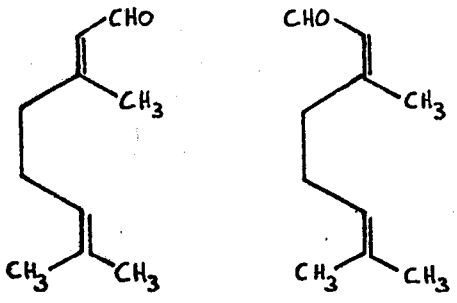
Active volatile potato sprout growth inhibitor. Causes a 64% reduction in sprout length (cf. untreated control) when applied at a headspace concentration of 7 mg m^{-3} (Meigh et al., 1973).

Dimethylnaphthalene is present in cooked, unpeeled potatoes (Nursten and Sheen, 1974).

1, 6-isomer, LD_{50}, 5 g kg^{-1} (rat) (Anon, 1976).

Vapour pressure (2, 7-isomer); 0. 56 Pa (25°C), 0. 09 Pa (10°C) (Osborn and Douslin, 1975).

Citral; 3, 7-dimethyl-2, 6-octadienal



geranial neral

Naturally produced monoterpenoid. Consists of a mixture of 2 geometric isomers (geranial and neral) when derived from natural sources (Merck Index, 1976).

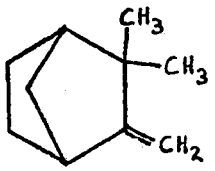
$C_{10}H_{16}O$, m. wt. 152. 24, b. p. 229°C.

Active volatile potato sprout growth inhibitor (Huelin, 1933). Complete suppression when applied at a headspace concentration between 22 and 71 mg m^{-3} (Meigh, 1969).

LD_{50}, acute oral, 4960 mg kg^{-1} (rat) (Jenner et al., 1964).

Vapour pressure; 11. 93 Pa (25°C), 3. 64 Pa (10°C) (Weast, 1978).

Camphene; 2, 2-dimethyl-3-methylenebicyclo (2. 2. 1) heptane

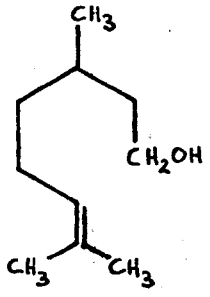


$C_{10} H_{16}$
m. wt. 136. 23
m. p. 51 - 52°C
b. p. 158 - 159. 5°C

Naturally produced monoterpenoid. Identified as a volatile plant growth inhibitor produced by Salvia leucophylla, S. apiana and S. mellifera (Muller and Muller, 1964).

LD_{50}, acute oral, >5 g kg^{-1} (rat) (Opdyke, 1975a).

Citronellol; 3, 7-dimethyl-6-octen-1-ol



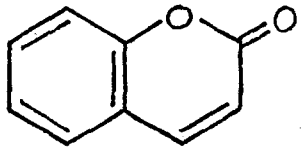
$C_{10} H_{20} O$
m. wt. 156. 26
b. p. 224. 5°C

Naturally produced monoterpenoid. Active volatile potato sprout growth inhibitor. Causes a 51% reduction in sprout length (cf. untreated control) when applied at a headspace concentration of 37 mg m^{-3} (Meigh, 1969).

LD_{50}, acute oral, 3. 5 g kg^{-1} (rat) (Opdyke, 1975b).

Vapour pressure; 2. 11 Pa (25°C), 0. 52 Pa (10°C) (Hughes and Lias, 1960).

Coumarin; 2H-1-benzopyran-2-one



$C_9 H_6 O_2$

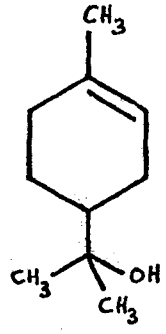
m. wt. 146.14
m. p. 68 - 70°C
b. p. 297 - 299°C

Naturally produced lactone of o-hydroxy cinnamic acid. Potent inhibitor of seed germination and growth of wheat seedlings (Rice, 1974).

LD_{50}, acute oral, 293 - 680 mg kg^{-1} (rats) (Opdyke, 1974a).

Vapour pressure; 0.13 Pa (25°C), 0.02 Pa (10°C) (Hughes and Lias, 1960).

α-Terpineol; α, α, 4-trimethyl-3-cyclohexene-1-methanol



$C_{10} H_{18} O$

m. wt. 154.26
m. p. 40°C
b. p. 220°C

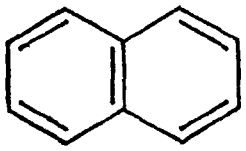
Naturally produced monoterpenoid. Active, volatile, plant growth inhibitor (Helfrich, 1962) and sprout growth inhibitor (Emilsson, 1949; Findlen, 1955; Meigh, 1969). Complete sprout suppression when applied at a headspace concentration between 64 and 125 mg m^{-3} (Meigh, 1969). Treatments at rates of 50 mg kg^{-1} (as a wax emulsion) and 75 mg kg^{-1} (incorporated in a fine soil dust) were relatively ineffective (Findlen, 1955; Edwards, 1952).

Found in fresh and cooked potatoes (Buttery et al., 1970).

LD_{50}, acute oral, 2.9 - 5.7 g kg^{-1} (rats) (Opdyke, 1974c).

Vapour pressure; 5.39 Pa (25°C), 0.98 Pa (10°C) (Hughes and Lias, 1960).

Naphthalene



$C_{10}H_8$

m. wt.	128.16
m. p.	80.2°C
b. p.	217.9°C

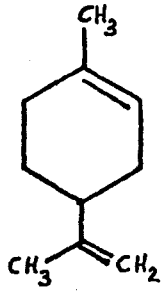
Active volatile potato sprout growth inhibitor. Causes an 80% reduction in sprout length (cf. untreated control) when applied at a headspace concentration of 54 mg m^{-3} (Meigh et al., 1973).

Found in potato peel (Meigh et al., 1973), boiled and fresh potato (Buttery et al., 1970).

LD_{50}, oral, 1780 mg kg^{-1} (rat) (Anon, 1976).

Vapour pressure; 11.22 Pa (25°C), 2.36 Pa (10°C) (Ambrose et al., 1975).

Limonene; 1-methyl-4-(1-methylethenyl) cyclohexene



$C_{10}H_{16}$

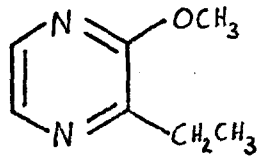
m. wt.	136.23
m. p.	-95.5°C
b. p.	175.5 - 176.5°C

Naturally produced monoterpenoid. Active, volatile plant growth inhibitor. Causes a 50% reduction in germination of radish seeds at a headspace concentration of 6 g m^{-3} (Asplund, 1968). Sprout length is reduced by 9% (cf. untreated control) when applied at a headspace concentration of 78 mg m^{-3} (Meigh, 1969).

Found in boiled potatoes (Self, 1968), cooked, peeled potatoes, cooked unpeeled potatoes and dehydrated granular potato product (Nursten and Sheen, 1974).

LD_{50}, acute oral, 4.6 - 6.0 g kg^{-1} (rat) (Opdyke, 1974b).

2-Methoxy-3-ethylpyrazine

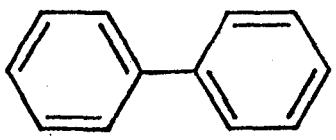


$C_7 H_{10} N_2 O$

m. wt. 138.17

Found in potato sprouts (Nursten and Sheen, 1974), and potato peel (Meigh et al., 1973). Tentatively identified in potatoes (Buttery et al., 1970). The raw earthy potato odour characteristic is attributed to this compound (Nursten and Sheen, 1974). 2-Methoxy-3-alkylpyrazines are widely distributed in the plant kingdom (Murray et al., 1970; Bramwell et al., 1969; Buttery et al., 1969).

Biphenyl



$C_{12} H_{10}$

m. wt.	154.20
m. p.	69 - 71°C
b. p.	254 - 255°C

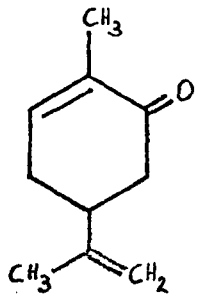
Active volatile potato sprout growth inhibitor. Causes a 58% reduction in sprout length (cf. untreated control) when applied at a headspace concentration of 16 mg m^{-3} (Meigh et al., 1973).

Found in potato peel (Meigh et al., 1973) boiled and fresh potato (Buttery et al., 1970).

LD_{50}, 2180 mg kg^{-1} (rat) (Merck Index, 1976).

Vapour pressure; 1.08 Pa (25°C), 0.21 Pa (10°C) (Hughes and Lias, 1960).

Carvone; 2-methyl-5-(1-methylethenyl)-2-cyclohexene-1-one



$C_{10} H_{14} O$

m. wt. 150. 21

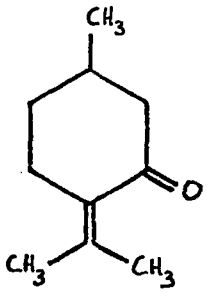
b. p. 230 - 231°C

Naturally produced monoterpenoid. Active volatile plant growth inhibitor (Helfrich, 1962) and sprout growth inhibitor (Meigh, 1969). Complete sprout suppression when applied at a headspace concentration between 9 and 26 mg kg^{-1} (Meigh, 1969).

LD_{50}, acute oral, 1640 mg kg^{-1} (rat) (Jenner et al., 1964).

Vapour pressure; 16. 60 Pa (25°C), 5. 28 Pa (10°C) (Weast, 1978).

Pulegone; 5-methyl-2-(1-methylethylidene) cyclohexanone



$C_{10} H_{16} O$

m. wt. 152. 23

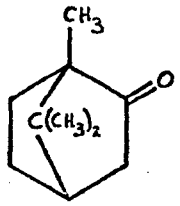
b. p. 224°C

Naturally produced monoterpenoid. Active volatile plant growth inhibitor and sprout growth inhibitor. Causes a 50% reduction in germination of radish seeds at a headspace concentration of 228 mg m^{-3} (Asplund, 1968). Complete sprout suppression when applied at a headspace concentration between 23 and 59 mg m^{-3} (Meigh, 1969).

Abs. lethal dose (chloralosed dog), 330 mg kg^{-1} (Caujolle et al., 1953).

Vapour pressure; 17. 96 Pa (25°C), 5. 47 Pa (10°C) (Weast, 1978).

Camphor; 1, 7, 7-trimethylbicyclo (2. 2. 1) heptan-2-one



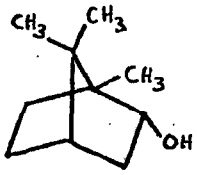
$C_{10} H_{16} O$

m. wt.	152. 23
m. p.	179. 75°C
b. p.	204°C

Naturally produced monoterpenoid. Identified as a volatile plant growth inhibitor produced by Salvia leucocphylla, S. apiana and S. mellifera (Muller and Muller, 1964). Causes a 50% reduction in germination of radish seeds at a headspace concentration of 487 mg m^{-3} (Asplund, 1968).

LD_{50}, oral, 1310 mg kg^{-1} (mice) (Horikawa, 1975).

Borneol; endo-1, 7, 7-trimethylbicyclo (2. 2. 1) heptan-2-ol



$C_{10} H_{18} O$

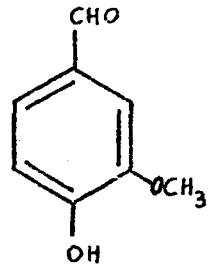
m. wt.	154. 26
m. p.	208°C
b. p.	212°C

Naturally produced monoterpenoid. Active volatile plant growth inhibitor. Causes a 50% reduction in germination of radish seeds at a headspace concentration of 3. 2 g m^{-3} (Asplund, 1968).

LD_{50}, oral, 1059 mg kg^{-1} (Horikawa, 1975).

Vapour pressure; 6. 48 Pa (25°C), 1. 65 Pa (10°C) (Timmermans, 1950).

Vanillin; 4-hydroxy-3-methoxybenzaldehyde



$C_8 H_8 O_3$

M. wt.	152.14
m. p.	80 - 81°C
b. p.	285°C

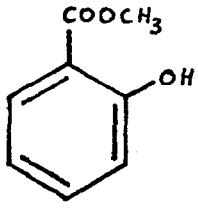
Naturally produced phenolic compound, inhibitory to seedling growth (Schreiner and Reed, 1908).

Found in potato parings (Merck Index, 1976).

LD_{50}, acute oral, 1580 mg kg^{-1} (rat) (Jenner et al., 1964).

Vapour pressure; 0.029 Pa (25°C), 0.004 Pa (10°C) (Hughes and Lias, 1960).

Methyl salicylate; 2-hydroxybenzoic acid methyl ester



$C_8 H_8 O_3$

M. wt.	152.14
m. p.	-8.6°C
b. p.	220 - 224°C

Active volatile sprout growth inhibitor. Complete suppression when applied at a headspace level between 19 and 114 mg m^{-3} (Meigh, 1969).

Found in boiled potatoes (Buttery et al., 1970).

LD_{50}, oral, 2.8 g kg^{-1} (rabbits) (Merck Index, 1976).

Vapour pressure; 15.73 Pa (25°C), 4.54 Pa (10°C) (Timmermans, 1965).

2.2 MATERIALS AND METHODS

2.2.1 GENERAL METHODS

The assessment experiment for each chemical consisted of one untreated control, four chemical treatments (at different application rates), and one tecnazene control. The treatments were applied to 2 x 10 kg potato samples in the first assessment experiment and to 1 x 10 kg potato sample in the second and third assessment experiments.

Preparation of chemicals. The chemicals were applied in an alumina solid carrier (Alumina "O", Spence and Son, Airdrie, Scotland). A 28 g screw top, glass jar, containing alumina and the test chemical was prepared for each 10 kg potato sample. 25 g of alumina was added to the jar, followed by the necessary amount of the test chemical. The jar was sealed and mixed overnight using an end-over-end shaker. Chemicals which were solids at room temperature, were warmed in their jars for 2 hours at a temperature slightly higher than their melting point. During this period the jars were shaken intermittently. Once cooled the jars were shaken on the end-over-end shaker. There was no evidence to suggest that any loss of chemical was caused by

warming the jars. This was checked by weighing jars before and after warming, and by headspace analysis (olfactory) of the warming oven. After mixing, the contents of the jars were applied to the potato samples.

Chemical application. The chemical treatments were dusted evenly over each 10 kg sample. Untreated control samples were dusted with 25 g of alumina. Tecnazene control samples were treated with Fusarex (ICI, Plant Protection, Yalding, Kent) applied at the recommended rate.

Sprout length measurement. At the end of the 12 or 14 week treatment period sprout growth in each 10 kg sample was assessed. The length of the longest sprout on 50 tubers was recorded. Every effort was made to ensure that a representative sample was taken from each box.

Sprout growth measurement after airing. Chemicals which proved to be successful sprout suppressants were then examined for their effect on the subsequent growth of treated tubers. Sprout growth following removal from the box and a period of airing was studied. The four chemical treatments, their corresponding untreated and tecnazene treated controls were used. The contents of each 10 kg box were evenly divided into 2 x 5 kg chitting trays. All sprouts were removed from the tubers at the start of the airing period. In the first and second assessment experiments the samples were constantly illuminated during the airing period. In the third assessment experiment the samples were illuminated for 16 in every 24 hours. This was due to difficulties with the temperature control room heat exchangers which were not coping with the heat generated by the chitting lights. In the first and second assessment experiments sprout growth after airing was measured in terms of the number of sprouts $\geqslant$0. 5 mm on 25 tubers from each chitting tray. In the third assessment experiment, sprout growth after airing was measured in terms of the length of the longest sprout on 25 tubers from each chitting tray.

Emergence and yield measurement. In the first assessment experiment the growth of treated tubers was further investigated by field studies

(Agronomic details 2.2.4). Four replicate plots of each treatment were used. Each plot consisted of 3 drills containing 20 tubers. 60 tubers from one chitting tray were used for each plot.

Emergence was recorded at two day intervals. Emergence for each drill of 20 tubers was measured in terms of -

(a) the mean emergence time (MET)
(b) the time to reach 25% emergence (T25)
(c) the time to reach 50% emergence (T50)
(d) the time to reach 75% emergence (T75)
(e) the total % emergence (TE)

The yield of each drill of 20 tubers was measured in terms of -

(a) yield of large size tubers, >52 mm
(b) yield of medium size tubers, >32 mm - ≤ 52 mm
(c) yield of small size tubers, >18 mm - ≤ 32 mm
(d) total yield
(e) yield of large size tubers as a percentage of total yield
(f) yield of medium size tubers as a percentage of total yield
(g) yield of small size tubers as a percentage of total yield

The tubers were graded within a few days of harvesting.

2.2.2 DETAILS OF THE ASSESSMENT EXPERIMENTS

First assessment experiment

Potato sample	cv. Record and Redskin (32 - 52 mm).
	Sample size, 2 x 10 kg.
Chemicals	α-pinene, benzothiazole, 1,4-dimethylnaphthalene, and citral.
Treatments	1 ± 0.4 mg kg^{-1}
	4 ± 0.4 mg kg^{-1}
	18 ± 0.6 mg kg^{-1}
	100 ± 0.5 mg kg^{-1}
	Untreated control (alumina only)
	120 mg kg^{-1} tecnazene (40 $\pm$ 0.5 g Fusarex per 10 kg box)

Assessment periods	Treatment time, 12 weeks (9.12.75 - 2.3.76).
	Airing time (before sprout growth measurement), 6 weeks (2.3.76 - 15.4.76).
	Airing time (before planting), 11 weeks (2.3.76 - 19.5.76).
	Time between planting and harvest, 19 weeks (19.5.75 - 29.9.76).
Observations	Length of longest sprout after treatment. Number of replicates (n) = 100.
	Number of sprouts $\geq$0.5 mm after airing, n = 100.
	Emergence time, n = 3.
	Yield, n = 3.

Second assessment experiment

Potato sample	cv. Record and Redskin (> 52 mm).
	Sample size, 1 x 10 kg.
Chemicals	camphene, citronellol, coumarin, α-terpineol, 1, 6-dimethylnaphthalene, naphthalene, limonene, 2-methoxy-3-ethylpyrazine, biphenyl, carvone.
Treatments	1 ± 0.4 mg kg^{-1}
	4 ± 0.4 mg kg^{-1}
	18 ± 0.6 mg kg^{-1}
	100 ± 0.5 mg kg^{-1}
	Untreated control (alumina only)
	120 mg kg^{-1} tecnazene (40 $\pm$ 0.5 g Fusarex per 10 kg box)
	2-methoxy-3-ethylpyrazine was applied at -
	1 ± 0.2 mg kg^{-1}
	2 ± 0.2 mg kg^{-1}
	6 ± 0.4 mg kg^{-1}
	32 ± 0.3 mg kg^{-1}
Assessment periods	Treatment time, 12 weeks (9.12.75 - 2.3.76).
	Airing time, 6 weeks (2.3.76 - 15.4.76).
Observations	Length of longest sprout after treatment. Number of replicates, (n) = 50.
	Number of sprouts $\geq$0.5 mm after airing, n = 50.

Third assessment experiment

Potato sample	cv. Record, Redskin, Maris Peer and Red Craigs Royal (32 - 52 mm).
	Sample size, 1 x 10 kg.
Chemicals	α-pinene, citral, carvone, pulegone, camphor, borneol, vanillin, methyl salicylate, 2, 3-dimethyl-naphthalene, tecnazene.
Treatments	4 ± 0.7 mg kg^{-1}
	20 ± 0.7 mg kg^{-1}
	100 ± 0.8 mg kg^{-1}
	500 ± 0.8 mg kg^{-1}
	Untreated control (alumina only)
	135 mg kg^{-1} tecnazene (45 ± 0.5 g Fusarex per 10 kg box)
Assessment periods	Treatment time, 14 weeks (30.12.76 - 5.4.77).
	Airing time, 5 weeks (5.4.77 - 11.5.77).
Observations	Length of the longest sprout after treatment. Number of observations, (n) = 50.
	Length of longest sprout after airing, n = 50.

2.2.3 MATERIALS

Chemicals. The chemicals used were of the best purity available.

Boxes and chitting trays. The 10 kg potato samples were held in 394 mm x 298 mm x 152 mm cardboard boxes with loosely fitting lids. When airing, the potato samples were held in wooden, 5 kg capacity, trays.

Temperature controlled room. The sprout suppression and sprout growth after airing experiments were conducted in a temperature controlled room at $10 \pm 0.5^{\circ}C$. Temperature was controlled by two heat exchanger units. Air inside the room was internally mixed by the heat exchanger fans which were in constant operation. A small capacity extraction fan vented air from the room.

Potato samples. cv. Record, Redskin, Maris Peer, and Red Craigs Royal were used. Visible sprouts indicated that they were no longer

dormant (Burton, 1966). cv. Redskin and Record were taken from once grown certified material. Maris Peer (F. S. 2) and Red Craigs Royal (A. A. 1) were purchased from J & E England and Son, Abernethy, Perth.

2.2.4 FIRST ASSESSMENT EXPERIMENT FIELD WORK

Once sprout growth after airing had been assessed the contents of each chitting tray were carefully covered with clear polythene and transported to the field.

The experimental plot was situated at Hattrick Farm, Bridge of Weir, Renfrewshire. It was approximately 0. 5 ha of sandy loam soil. It had been uniformly treated with FYM and received 1400 kg ha^{-1} seed potato fertilizer (Scottish Agricultural Industries) immediately before planting. Tubers were planted by hand at 300 mm spacing in drills 710 mm apart.

The experimental design consisted of four blocks, every block containing one replicate plot of each chemical treatment. Each block contained 24 independently randomized treatment plots. Each plot consisted of three drills, 6 m long. Each drill contained 20 tubers.

The experimental area was protected by guard drills. The ends of treatment plots were separated from each other by empty drills, 2 m long. This separated the plots when harvesting. Several non-experimental drills ran the length of the plot, through which the tractor passed when spraying.

Weed control was achieved by applying paraquat just before emergence plus hand-weeding when required. Captafol sprays were applied for blight prevention during August. The crop was defoliated using diquat, three weeks before harvesting.

The yield from each plot drill was harvested separately, stored in 12 kg nets and mechanically graded over 52 mm and 32 mm

riddles. Tubers $\leqslant$ 18 mm fell through the mechanical grader and were lost.

2.2.5 ANALYSIS OF RESULTS

Sprout length and sprout growth after airing data. Each chemical assessment experiment included an untreated control and a tecnazene control. All untreated control data was combined. The tecnazene control data was treated similarly, e. g. in the first assessment experiment there were 8 x 10 kg untreated controls, giving 400 sprout length measurements, which were combined. The results from the chemical treatments were compared with the combined control data. Results were expressed as mean $\pm$ standard deviation. The four chemical treatment means (i. e. 4 application rate means) were firstly compared with the untreated control mean. Significant differences between treatment means were tested by analysis of variance. The least difference between the untreated control mean and a chemical treatment mean which would be significant (L. S. D.) was calculated as,

$$\text{L. S. D.} = t_{0.05} \sqrt{\frac{s^2}{n_1} + \frac{s^2}{n_2}}$$

where; t has N - k degrees of freedom

k = number of treatments

N = total number of replicates

n_1 = number of control replicates

n_2 = number of chemical treatment replicates

s^2 = residual mean square from analysis of variance

With sprout length data, if there were significant differences between chemical treatments and untreated controls, the chemical treatments were then compared to tecnazene controls using the same statistical methods (Bailey, 1959; Parker, 1973). With sprout growth after airing data, significant differences between chemical treatments and tecnazene controls were tested, whether or not there were significant

differences between chemical treatments and untreated controls.

Emergence and yield data. The data were examined for cultivar, treatment and field block effects. Significant differences between means were tested by analysis of variance. Comparisons between treatment means were made using the Scheffé S-method for multiple comparisons (Seber, 1977). The least difference between any pair of treatment means which would be significant (L. S. D.) was calculated as,

$$\text{L. S. D.} = \sqrt{aF(0.05/a, b)} \times \sqrt{\frac{s^2}{n_1} + \frac{s^2}{n_2}}$$

where; s^2 = residual mean square from analysis of variance

n_1, n_2 = number of replicates of each mean

a = treatment degrees of freedom

b = residual degrees of freedom

2.3 RESULTS

Table 2.01. First assessment experiment. Mean sprout length of tubers treated with α-pinene and benzothiazole. Treatment time = 12 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	1 mg kg^{-1}*	4 mg kg^{-1}	18 mg kg^{-1}	100 mg kg^{-1}	120 mg kg^{-1} Tec
α-pinene	Redskin	mean	114.5	157.0[b]	113.3	117.3	114.4	28.8
		S.D.	87.3	91.2	89.9	92.1	81.0	30.8
	Record	mean	72.6	64.0	83.1	75.3	80.8	15.1
		S.D.	50.1	44.5	56.6	53.8	47.5	19.8
benzothiazole	Redskin	mean	114.5	109.8	129.8	95.0[b]	26.4[a]	28.8
		S.D.	87.3	85.6	99.5	83.4	28.3	30.8
	Record	mean	72.6	76.2	77.3	80.4	15.2[a]	15.1
		S.D.	50.1	39.9	51.6	53.9	14.3	19.8

* Application rate of chemical. Tec = tecnazene.

[a] Significantly different from corresponding untreated control mean ($p < 0.05$).

[b] Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.02. First assessment experiment. Mean sprout length of tubers treated with 1,4-dimethylnaphthalene and citral. Treatment time = 12 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	1 mg kg^{-1}*	4 mg kg^{-1}	18 mg kg^{-1}	100 mg kg^{-1}	120 mg kg^{-1} Tec
1,4-dimethyl-naphthalene	Redskin	mean	114.5	128.6	87.8[b]	39.5[a]	12.7[b]	28.8
		S.D.	87.3	101.0	69.8	44.1	14.6	30.8
	Record	mean	72.6	75.8	65.6	40.2[b]	11.4[a]	15.1
		S.D.	50.1	47.3	43.9	38.1	22.8	19.8
citral	Redskin	mean	114.5	123.4	102.1	113.0	92.1	28.8
		S.D.	87.3	99.6	87.1	80.7	73.3	30.8
	Record	mean	72.6	61.5	74.6	69.1	63.9	15.1
		S.D.	50.1	47.6	47.5	44.1	40.3	19.8

* Application rate of chemical. Tec = tecnazene.

[a] Significantly different from corresponding untreated control mean ($p < 0.05$).

[b] Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.03. Second assessment experiment. Mean sprout length of tubers treated with camphene, citronellol and coumarin. Treatment time = 12 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	1 mg kg^{-1}*	4 mg kg^{-1}	18 mg kg^{-1}	100 mg kg^{-1}	120 mg kg^{-1} Tec
camphene	Redskin	mean	144.9	157.9	133.9	122.8	152.7	49.1
		S.D.	92.5	59.7	67.3	77.0	90.5	37.5
	Record	mean	93.2	88.8	75.7[b]	93.6	70.8[b]	29.4
		S.D.	53.4	51.1	40.9	57.5	36.9	28.8
citronellol	Redskin	mean	144.9	150.1	108.3[b]	174.8[b]	115.1	49.1
		S.D.	92.5	81.0	87.7	74.1	82.7	37.5
	Record	mean	93.2	72.3[b]	73.8[b]	79.5	77.7[b]	29.4
		S.D.	53.4	37.7	50.9	47.9	40.8	28.8
coumarin	Redskin	mean	144.9	146.3	136.2	144.7	149.2	49.1
		S.D.	92.5	98.4	83.0	84.8	93.3	37.5
	Record	mean	93.2	83.7	84.5	96.8	91.6	29.4
		S.D.	53.4	56.3	54.1	46.3	55.7	28.8

* Application rate of chemical. Tec = tecnazene.

a Significantly different from corresponding untreated control mean ($p < 0.05$).

b Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.04. Second assessment experiment. Mean sprout length of tubers treated with α-terpineol, 1, 6-dimethylnaphthalene and naphthalene. Treatment time = 12 weeks, temperature = 10°C.

Chemical	Cultivar		Sprout length (mm)					
			Untreated	1 mg kg^{-1}*	4 mg kg^{-1}	18 mg kg^{-1}	100 mg kg^{-1}	120 mg kg^{-1} Tec
α-terpineol	Redskin	mean	144.9	137.4	162.2	137.6	136.5	49.1
		S.D.	92.5	91.1	88.0	80.1	73.3	37.5
	Record	mean	93.2	85.7	73.5[b]	71.8[b]	96.0	29.4
		S.D.	53.4	49.9	44.4	34.4	52.8	28.8
1, 6-dimethyl-naphthalene	Redskin	mean	144.9	131.5	160.7	102.8[b]	39.2[a]	49.1
		S.D.	92.5	76.9	102.1	66.6	36.2	37.5
	Record	mean	72.6	101.2[b]	71.0	78.6	27.7[b]	15.1
		S.D.	50.1	74.2	51.4	47.0	20.6	19.8
naphthalene	Redskin	mean	144.9	150.1	118.0	151.0	146.6	49.1
		S.D.	92.5	75.8	82.3	87.3	90.3	37.5
	Record	mean	93.2	129.4[b]	74.7[b]	99.8	109.6	29.4
		S.D.	53.4	68.3	43.8	55.0	70.5	28.8

* Application rate of chemical. Tec = tecnazene.

a Significantly different from corresponding untreated control mean ($p < 0.05$).

b Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.05. Second assessment experiment. Mean sprout length of tubers treated with biphenyl, carvone and limonene. Treatment time = 12 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	1 mg kg^{-1}*	4 mg kg^{-1}	18 mg kg^{-1}	100 mg kg^{-1}	120 mg kg^{-1} Tec
biphenyl	Redskin	mean	144.9	102.1[b]	174.6[b]	151.4	153.1	49.1
		S.D.	92.5	84.5	93.7	78.0	52.4	37.5
	Record	mean	93.2	68.7[b]	138.8[b]	125.7[b]	85.5	29.4
		S.D.	53.4	33.5	61.3	74.7	41.7	28.8
carvone	Redskin	mean	144.9	152.2	139.3	148.1	117.5	49.1
		S.D.	92.5	92.4	77.7	96.1	53.5	37.5
	Record	mean	93.2	118.0[b]	120.5[b]	129.3[b]	98.8	29.4
		S.D.	53.4	69.1	56.0	66.7	40.7	28.8
limonene	Redskin	mean	144.9	117.2[b]	107.8[b]	106.6[b]	153.3	49.1
		S.D.	92.5	70.5	71.3	69.8	72.7	37.5

* Application rate of chemical. Tec = tecnazene.

[b] Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.06. Second assessment experiment. Mean sprout length of tubers treated with 2-methoxy-3-ethylpyrazine. Treatment time = 12 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	1 mg kg^{-1}*	2 mg kg^{-1}	6 mg kg^{-1}	32 mg kg^{-1}	120 mg kg^{-1} Tec
2-methoxy-3-ethylpyrazine	Redskin	mean	144.9	148.5	179.7[b]	188.2[b]	89.5[b]	49.1
		S.D.	92.5	103.5	112.0	93.2	82.2	37.5
	Record	mean	93.2	83.2	113.6[b]	112.1[b]	91.1	29.4
		S.D.	53.4	51.7	68.2	59.0	59.4	28.8

* Application rate of chemical. Tec = tecnazene.

b Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.07. Third assessment experiment. Mean sprout length of tubers treated with α-pinene, citral and carvone. Treatment time = 14 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	4 mg kg^{-1}*	20 mg kg^{-1}	100 mg kg^{-1}	500 mg kg^{-1}	135 mg kg^{-1} Tec
α-pinene	Redskin	mean	154.4	157.4	135.7	161.0	138.7	20.6
		S.D.	81.1	94.5	62.5	72.7	70.8	23.1
	Record	mean	114.6	112.9	95.4	115.5	68.9[b]	16.3
		S.D.	73.3	71.5	65.9	70.8	52.5	20.0
citral	Redskin	mean	154.4	175.7	142.2	184.7[b]	128.3[b]	20.6
		S.D.	81.1	59.0	71.9	79.3	58.9	23.1
	Record	mean	114.6	77.6[b]	109.6	83.9[b]	102.0	16.3
		S.D.	73.3	68.7	66.3	49.1	69.3	20.0
carvone	Redskin	mean	154.4	145.0	136.6	134.6	5.9[b]	20.6
		S.D.	81.1	76.9	83.8	65.1	8.4	23.1
	Record	mean	114.6	80.3[b]	103.3	68.1[b]	4.3[b]	16.3
		S.D.	73.3	58.8	66.0	44.8	4.6	20.0

* Application rate of chemical. Tec = tecnazene.

a Significantly different from corresponding untreated control mean ($p < 0.05$).

b Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.08. Third assessment experiment. Mean sprout length of tubers treated with pulegone, camphor and borneol. Treatment time = 14 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	4 mg kg^{-1}*	20 mg kg^{-1}	100 mg kg^{-1}	500 mg kg^{-1}	135 mg kg^{-1} Tec
pulegone	M Peer	mean	287.6	280.6	270.8[b]	252.6	11.4[a]	14.3
		S.D.	34.3	50.9	51.0	32.8	25.4	27.4
	RC Royal	mean	241.0	275.1[b]	269.8[b]	238.5	3.5[a]	8.0
		S.D.	76.8	51.7	55.9	54.7	6.5	16.7
camphor	Redskin	mean	154.4	194.6[b]	191.4[b]	186.8[b]	129.7[b]	20.6
		S.D.	81.1	81.1	86.3	79.0	41.7	23.1
	Record	mean	114.6	99.9	108.9	132.4	112.4	16.3
		S.D.	73.3	70.7	83.0	65.6	56.1	20.0
borneol	Redskin	mean	154.4	150.2	158.8	129.7[b]	19.1[a]	20.6
		S.D.	81.1	76.3	76.4	54.5	41.2	23.1
	Record	mean	114.6	76.2[b]	87.0[b]	80.7[b]	11.5[a]	16.3
		S.D.	73.3	66.3	53.8	60.8	12.1	20.0

* Application rate of chemical. Tec = tecnazene.

[a] Significantly different from corresponding untreated control mean ($p < 0.05$).

[b] Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.09. Third assessment experiment. Mean sprout length of tubers treated with vanillin, methyl salicylate and 2,3-dimethylnaphthalene. Treatment time = 14 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	4 mg kg^{-1}*	20 mg kg^{-1}	100 mg kg^{-1}	500 mg kg^{-1}	135 mg kg^{-1} Tec
vanillin	Redskin	mean	154.4	183.2	135.9	148.1	146.8	20.6
		S.D.	81.1	70.8	59.9	90.3	82.1	23.1
	Record	mean	114.6	96.0	113.4	94.8	83.6[b]	16.3
		S.D.	73.3	77.8	67.2	62.9	62.7	20.0
methyl salicylate	Redskin	mean	154.4	120.3[b]	129.9[b]	152.5	41.4[b]	20.6
		S.D.	81.1	77.3	51.0	95.2	36.1	23.1
	Record	mean	114.6	84.3[b]	129.4	95.2	43.2[b]	16.3
		S.D.	73.3	62.4	72.7	71.5	56.7	20.0
2,3-dimethyl-naphthalene	Redskin	mean	154.4	157.9	119.5[b]	35.5[b]	26.2[a]	20.6
		S.D.	81.1	101.6	68.4	33.4	31.4	23.1
	Record	mean	114.6	111.6	101.0	31.7[b]	15.4[a]	16.3
		S.D.	73.3	71.8	55.7	23.7	16.7	20.0

* Application rate of chemical. Tec = tecnazene.

[a] Significantly different from corresponding untreated control mean ($p < 0.05$).

[b] Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.10. Third assessment experiment. Mean sprout length of tubers treated with tecnazene. Treatment time = 14 weeks, temperature = 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	4 mg kg^{-1}*	20 mg kg^{-1}	100 mg kg^{-1}	500 mg kg^{-1}	135 mg kg^{-1} Tec
tecnazene	Redskin	mean	154.4	141.8	99.8[b]	35.8[b]	20.3[a]	20.6
		S.D.	81.1	66.5	52.7	36.0	17.0	23.1
	Record	mean	114.6	109.8	81.9[b]	15.7[a]	11.9[a]	16.3
		S.D.	73.3	73.7	52.7	19.6	15.8	20.0

* Application rate of chemical. Tec = tecnazene.

[a] Significantly different from corresponding untreated control mean ($p < 0.05$).

[b] Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

Table 2.11. First and second assessment experiments. Mean sprout numbers ≤ 0.5 mm on tubers treated with benzothiazole, 1, 4-dimethylnaphthalene and 1, 6-dimethylnaphthalene, desprouted, then aired for 6 weeks at 10°C.

Chemical	Cultivar	Sprout numbers						
			Untreated	1 mg kg^{-1}*	4 mg kg^{-1}	18 mg kg^{-1}	100 mg kg^{-1}	120 mg kg^{-1} Tec
benzothiazole	Redskin	mean	4.1	3.9	3.4[a]	3.4[a]	3.0[b]	3.5
		S.D.	1.7	1.8	1.9	1.5	1.8	2.6
	Record	mean	2.6	2.7	2.7	2.6	2.0[b]	2.7
		S.D.	1.1	1.1	1.2	1.2	1.1	1.5
1, 4-dimethyl-naphthalene	Redskin	mean	4.1	3.5[a]	4.0	3.7[a]	3.2[a]	3.5
		S.D.	1.7	1.3	1.4	2.0	1.6	2.6
	Record	mean	2.6	2.8	3.0[a]	2.7	2.4	2.7
		S.D.	1.1	1.1	1.4	1.1	1.2	1.5
1, 6-dimethyl-naphthalene	Redskin	mean	5.5	5.5[c]	4.3[b]	4.4[b]	3.8[a]	3.3
		S.D.	1.9	1.9	1.6	1.1	1.4	1.4
	Record	mean	2.6	2.3	2.5	2.5	2.3	2.3
		S.D.	1.3	0.9	1.1	1.3	1.1	0.9

* Application rate of chemical. Tec = tecnazene.

a Significantly different from corresponding untreated control mean ($p < 0.05$).

b Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

c Significantly different from corresponding tecnazene mean ($p < 0.05$).

Table 2.12. Third assessment experiment. Mean sprout length of tubers treated with carvone, pulegone and borneol, desprouted, then aired for 5 weeks at 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	4 mg kg^{-1}*	20 mg kg^{-1}	100 mg kg^{-1}	500 mg kg^{-1}	135 mg kg^{-1} Tec
carvone	Redskin	mean	13.1	10.4[a]	9.7[a]	10.5[a]	9.7[a]	10.2
		S.D.	7.0	4.8	3.3	5.6	5.7	5.0
	Record	mean	18.6	16.7[a]	15.4	20.7	23.0[b]	17.1
		S.D.	7.0	5.9	4.7	7.1	9.9	7.7
pulegone	M Peer	mean	33.9	30.4	31.3	33.3	29.9	-
		S.D.	15.0	9.8	10.3	12.4	17.7	-
	RC Royal	mean	13.9	15.7	17.7	15.3	12.8	-
		S.D.	6.4	7.2	7.5	7.0	10.0	-
borneol	Redskin	mean	13.1	11.0	11.9	11.5	8.5[a]	10.2
		S.D.	7.0	6.1	6.6	4.7	10.1	5.0
	Record	mean	18.6	15.9[a]	16.3[a]	16.0[a]	16.3[a]	17.1
		S.D.	7.0	6.9	5.1	5.5	4.6	7.7

* Application rate of chemical. Tec = tecnazene.

a Significantly different from corresponding untreated control mean ($p < 0.05$).

b Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

c Significantly different from corresponding tecnazene mean ($p < 0.05$).

Table 2.13. Third assessment experiment. Mean sprout length of tubers treated with methyl salicylate, 2, 3-dimethylnaphthalene and tecnazene, desprouted, then aired for 5 weeks at 10°C.

Chemical	Cultivar	Sprout length (mm)						
			Untreated	4 mg kg^{-1}*	20 mg kg^{-1}	100 mg kg^{-1}	500 mg kg^{-1}	135 mg kg^{-1} Tec
methyl salicylate	Redskin	mean	13.1	13.2	12.3	11.6	14.2	10.2
		S.D.	7.0	8.6	5.4	4.8	7.8	5.0
	Record	mean	18.6	22.4[b]	17.9	19.5[c]	16.1[a]	17.1
		S.D.	7.0	9.3	6.4	7.5	6.3	7.7
2, 3-dimethyl naphthalene	Redskin	mean	13.1	12.1[c]	12.0[c]	12.8[c]	8.2[b]	10.2
		S.D.	7.0	5.7	5.6	7.3	5.4	5.0
	Record	mean	18.6	19.4	17.8	21.1[b]	20.6[c]	17.1
		S.D.	7.0	7.2	6.9	8.1	7.1	7.7
tecnazene	Redskin	mean	13.1	13.4[c]	14.0[c]	11.0[a]	8.2[b]	10.2
		S.D.	7.0	8.1	6.7	5.6	6.5	5.0
	Record	mean	18.6	21.2[b]	17.7	18.8	13.3[b]	17.1
		S.D.	7.0	9.6	8.1	7.1	8.9	7.7

* Application rate of chemical. Tec = tecnazene.

a Significantly different from corresponding untreated control mean ($p < 0.05$).

b Significantly different from corresponding untreated control mean and tecnazene mean ($p < 0.05$).

c Significantly different from corresponding tecnazene mean ($p < 0.05$).

Table 2.14. First assessment experiment. Untreated, benzothiazole (BZT), and tecnazene (Tec) treatment effects on emergence. Mean of 24 drills.

Treatment	Code	Emergence[a]			
		MET	T50	T75	TE
Untreated	A	26.8	25.0	31.0	97.3
1 mg kg^{-1} BZT	B	26.5	25.5	31.8	90.4
4 mg kg^{-1} BZT	C	27.5	26.4	32.8	91.7
18 mg kg^{-1} BZT	D	28.3	27.4	29.9	90.0
100 mg kg^{-1} BZT	E	27.7	26.9	29.2	87.1
120 mg kg^{-1} Tec	F	23.9	22.2	25.9	96.7
S.E.M.[b]		0.5	0.5	1.2	1.4
L.S.D.[c]		2.2	2.6	5.8	6.7
	Order[d]				
	1	F	F	F	A
	2	B	A	E	F
	3	A	B	D	C
	4	C	C	A	B
	5	E	E	B	D
	6	D	D	C	E

a Emergence in terms of total % emergence (TE) and emergence time (days) expressed as, mean emergence time (MET), and time to 50%, 75% emergence (T50, T75).

b Standard error of the mean.

c Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

d Order of treatments. Treatments (codes A - F) are placed in descending order, i.e. most beneficial effect (1) to least beneficial effect (6). When treatments have a common line, they do not differ significantly.

Table 2.15. First assessment experiment. Untreated, 1,4-dimethylnaphthalene (DMN), and tecnazene (Tec) treatment effects on emergence. Mean of 24 drills.

Treatment	Code	Emergence[a]			
		MET	T25	T50	TE
Untreated	A	27.7	22.6	26.4	91.7
1 mg kg^{-1} DMN	B	28.3	23.1	27.0	91.9
4 mg kg^{-1} DMN	C	27.6	22.4	26.3	89.6
18 mg kg^{-1} DMN	D	26.8	21.6	25.1	96.9
100 mg kg^{-1} DMN	E	26.6	21.9	25.2	92.3
120 mg kg^{-1} Tec	F	25.6	21.0	23.6	96.0
S.E.M.[b]		0.5	0.5	0.6	1.3
L.S.D.[c]		2.2		2.7	6.0
	Order[d]				
	1	F	F	F	D
	2	E	D	D	F
	3	D	E	E	E
	4	C	C	C	B
	5	A	A	A	A
	6	B	B	B	C

[a] Emergence in terms of total % emergence (TE) and emergence time (days) expressed as, mean emergence time (MET), and time to 25%, 50% emergence (T25, T50).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatments. Treatments (codes A - F) are placed in descending order, i.e. most beneficial effect (1) to least beneficial effect (6). When treatments have a common line, they do not differ significantly.

Table 2.16. First assessment experiment. Untreated benzothiazole (BZT), and tecnazene (Tec) treatment effects on yield. Mean of 24 drills.

Treatment	Code	Yield[a]						
		L	M	S	T	%L	%M	%S
Untreated	A	6.86	4.05	0.27	11.18	58.40	39.03	2.57
1 mg kg^{-1} BZT	B	6.38	3.50	0.29	10.16	58.15	38.73	3.13
4 mg kg^{-1} BZT	C	6.12	3.23	0.26	9.62	60.07	36.66	3.27
18 mg kg^{-1} BZT	D	7.56	3.27	0.20	11.04	66.28	31.70	2.02
100 mg kg^{-1} BZT	E	6.76	3.51	0.29	10.56	56.56	39.72	3.72
120 mg kg^{-1} Tec	F	5.97	5.30	0.48	11.75	46.45	48.81	4.74
S. E. M.[b]		0.26	0.16	0.02	0.32	1.31	1.24	0.23
L. S. D.[c]		1.23	0.78	0.10	1.54	6.29	5.92	1.09
	Order[d]							
	1	D	F	F	F	D	F	F
	2	A	A	B	A	C	E	E
	3	E	E	E	D	A	A	C
	4	B	B	A	E	B	B	B
	5	C	D	C	B	E	C	A
	6	F	C	D	C	F	D	D

[a] Yield (kg and as a % of total yield) of tubers >52 mm (L, %L), >32 - ≤52 mm (M, %M), >18 - ≤32 mm (S, %S) and as total yield (T).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatments. Treatments (codes A - F) are placed in descending order, i. e. highest yield (1) to lowest yield (6). When treatments have a common line, they do not differ significantly ($p < 0.05$).

Table 2.17. First assessment experiment. Untreated 1, 4-dimethylnaphthalene (DMN), and tecnazene (Tec) treatment effects on yield. Mean of 24 drills.

Treatment	Code	Yield[a]						
		L	M	S	T	%L	%M	%S
Untreated	A	7.22	3.67	0.25	11.12	62.84	34.80	2.36
1 mg kg^{-1} DMN	B	6.45	3.43	0.30	10.18	61.52	35.38	3.11
4 mg kg^{-1} DMN	C	6.12	3.47	0.24	9.82	58.49	38.79	2.72
18 mg kg^{-1} DMN	D	6.84	4.31	0.38	11.52	58.26	38.34	3.40
100 mg kg^{-1} DMN	E	6.37	4.22	0.33	10.90	55.15	41.39	3.46
120 mg kg^{-1} Tec	F	5.16	4.90	0.47	10.53	43.88	50.95	5.17
S.E.M.[b]		0.22	0.14	0.02	0.28	1.08	1.02	0.21
L.S.D.[c]		1.07	0.67	0.09	1.34	5.20	4.90	1.00
	Order[d]							
	1	A	F	F	D	A	F	F
	2	D	D	D	A	B	E	E
	3	B	E	E	E	C	C	D
	4	E	A	B	F	D	D	B
	5	C	C	A	B	E	B	C
	6	F	B	C	C	F	A	A

[a] Yield (kg and as a % of total yield) of tubers >52 mm (L, %L), >32 - ≤52 mm (M, %M), >18 - ≤32 mm (S, %S) and as total yield (T).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatments. Treatments (codes A - F) are placed in descending order, i.e. highest yield (1) to lowest yield (6). When treatments have a common line, they do not differ significantly ($p < 0.05$).

2.4 DISCUSSION

2.4.1 SPROUT SUPPRESSION

Sprout suppression results are presented in Tables 2.01 to 2.10.

Chemical and box effects

Significant differences between treatment means and untreated control means were regarded as being caused by two effects. The first effect was that considered to be due to the chemical treatment. Sprout growth control caused by tecnazene was a clear example of this chemical effect. The second effect was termed for convenience a box effect. It was so named, as deviation from the untreated control mean did not follow any particular trend attributable to chemical treatment and, therefore, was unique for the 10 kg box in question.

Box effects were considered to be due to several factors. The most important factors were, (a) unrepresentative 10 kg potato samples, (b) the position of the boxes in the temperature controlled room, and (c) anomalous chemical headspace concentrations within the boxes.

Each assessment experiment used c. 1000 kg of tubers. It was, therefore, difficult to ensure that each 10 kg box contained a representative sample of the 1000 kg bulk. The principal variations were those of tuber size and tuber health. Within the specified size grades, some 10 kg samples tended to have a large proportion of tubers whose size was at the upper or lower limits of that grade. As the results show, tuber size affected the length of the longest sprout. Some samples contained diseased tubers. Before storing at 10°C, the potatoes were held at 12°C for a period of 4 weeks to ensure adequate wound healing. They were thoroughly sorted when filling the 10 kg boxes. However, disease symptoms did develop in some boxes. Dry rot and bacterial soft rot were observed, along with terminal blackening of some sprouts, presumably caused by *Rhizoctonia solani*. In most cases, sprout length

measurement from diseased tubers was avoided. However, it is highly probable that the presence of tuber diseases (particularly Rhizoctonia solani) did affect the mean sprout length of some 10 kg potato samples. Generally, box effects occurred more often in the second assessment experiment. In this experiment there was a greater variation in tuber size as all tubers were graded simply as >52 mm. There was also less tubers per 10 kg sample and therefore, fewer tubers to choose from if some rots had developed in a box. It was for these reasons that seed size tubers were used in the following third assessment experiment.

The position of the boxes in the temperature controlled room could cause significant box effects (Hruschka and Koch, 1964). For example, boxes placed near heat exchanger units could experience greater variations in temperature compared to boxes placed further away. Most boxes were stacked in pairs. It was possible for sprout growth to raise the lid of the uppermost box, exposing the tubers to different environmental conditions compared to the lower box.

Anomalous headspace concentrations within the boxes (Chapter 4) could be caused by the box itself or the position of the box in the termperature controlled room. For example, boxes placed near heat exchanger fans could lose a greater amount of volatile chemical by dissipation into the surrounding air. Variation in box construction, e. g. the fitting of its lid, could also affect the headspace concentration of the volatile chemical within the box.

Box effects could be caused by these factors acting either individually or collectively. Box effects could also be caused by interaction between the chemical treatment and these factors, e. g. the beneficial or antagonistic effect chemical treatment may have on disease control which in turn could affect sprout growth.

Control samples for every chemical were combined in order to help eliminate significant differences between control means and

treatment means which were caused by box effects.

Box effects did not alter sprout growth to the same extent that chemical effects did. Sprout growth reduction caused by, for example, treatment with tecnazene, was immediately apparent whenever the 10 kg box was opened. As this was the degree of sprout suppression being asked of the test chemicals, box effects did not affect the main objective of the experiments. They did, however, reduce the sensitivity of the experiments. This made it less possible to attribute smaller significant differences in sprout growth to chemical effects.

Performance of chemical sprout suppressants

Benzothiazole and dimethylnaphthalene were successful sprout suppressants. Benzothiazole applied at 100 mg kg^{-1} caused a similar degree of sprout suppression as the tecnazene control. Of the dimethylnaphthalenes applied at 100 mg kg^{-1}, the 1, 4 isomer was the most effective, and the 2, 3 isomer least. At 100 mg kg^{-1} the 1, 4 isomer was better than the tecnazene control, the 1, 6 isomer was as good as the tecnazene control and the 2, 3 isomer not as good as the tecnazene control.

In the first and second assessment experiments all other chemicals were ineffective at application rates up to 100 mg kg^{-1}. For this reason, the highest application rate was increased to 500 mg kg^{-1} in the third assessment experiment.

When applied at 500 mg kg^{-1}, carvone suppressed sprouting to a greater extent than the tecnazene control. Pulegone and borneol applied at 500 mg kg^{-1} were as good as the tecnazene control. Methyl salicylate applied at 500 mg kg^{-1} caused a significant reduction in sprout growth which was not as good as the tecnazene control.

Box effects most probably are the reason for all other significant differences between untreated control and chemical treat-

ment means. This is particularly so in the second assessment experiment. However, it is possible that some trends worthy of consideration are being masked by box effects. For example, it is possible that at low concentrations some of the chemicals could be causing stimulation of sprout growth, as shown by carvone in the second assessment experiment, pulegone and camphor in the third assessment experiment. The growth promoting-inhibiting properties of 2-methoxy-3-ethylpyrazine are also worthy of some further more sensitive investigations.

Tecnazene was included in the third assessment experiment to check whether or not tecnazene behaved differently when applied in an alumina carrier compared to the kaolin carrier used in commercial formulations (Fusarex). The results showed that there was no difference.

In terms of cost, residue levels, and effective removal from treated seed, 100 mg kg^{-1} was considered the highest rate at which a sprout suppressant chemical could be used commercially. Therefore, although carvone, pulegone and borneol were all effective sprout suppressants at 500 mg kg^{-1}, only benzothiazole and dimethylnaphthalene showed promise of being commercially viable.

2.4.2 SPROUT GROWTH AFTER AIRING

The results are presented in Tables 2.11, 2.12 and 2.13.

In these assessment experiments all sprouts were removed from the tubers at the start of the airing period. After airing, sprout growth was assessed.

In the first assessment and second assessment experiments, the number of sprouts $\geqslant$0.5 mm was recorded. Sprout numbers on each tuber would help assess field performance. Sprout numbers per tuber influence the number of aerial stems, an increase in which normally results in a greater number of tubers (Burton, 1966). Sprout numbers

on treated tubers were compared with untreated control tubers. All chemical treatments including tecnazene had little effect on cv. Record. Sprout numbers of cv. Redskin were decreased by all chemical treatments including tecnazene. Benzothiazole had the greatest effect. Sprout numbers decreased with increasing chemical application rate. (These results could also be interpreted as an effect caused by the size of sprout removed at the start of the airing period, i. e. untreated control and low chemical application rates had larger sprouts removed, causing an increase in sprout numbers, cf. higher application rates and tecnazene controls).

In the third assessment experiment no facilities were available to assess field performance. Sprout length after airing was considered a better estimate of how the chemical treatments would affect subsequent emergence and total yield of treated seed. Comparisons with an untreated control desprouted at the start of the airing period showed that pulegone did not significantly affect subsequent sprout growth. There was a trend amongst all the other chemicals for increased application rates to decrease subsequent sprout growth. Tubers treated with tecnazene at 500 mg kg^{-1} showed significantly less sprout growth than the tecnazene controls (135 mg kg^{-1}).

2.4.3 EMERGENCE AND YIELD

A difficulty concerning the controls arose during sprout growth after airing and field assessments. It concerned the question of using a realistic control against which chemical treatments could be compared. The tubers were stored under conditions which promoted sprout growth. As a consequence, untreated control tubers had large sprouts. Clearly, planting tubers with such long sprouts could not provide realistic controls both from a plant physiological and a practical point of view. In general, presprouted seed will emerge faster than unsprouted seed. Similarly, desprouting immediately before planting will result in delayed emergence (Toosey, 1964). Although under normal commercial conditions such long sprouts would not occur, any large sprouts which are

present will most probably be removed during handling before planting. Therefore, assuming there were no chemical treatment effects, if the potatoes were planted immediately after removal from their boxes, it could reasonably be expected that (a) the presprouted untreated controls would emerge first, the chemical treatments would, therefore, appear to delay emergence, (b) even if this were not so, uniform planting of tubers with such long sprouts was neither practical nor relevant from a commercial point of view, and (c) desprouted untreated controls would emerge last, the chemicals would, therefore, appear to stimulate emergence. It was considered that the best solution would be to use desprouted untreated and desprouted tecnazene controls which were aired before planting. The airing period ensured adequate sprout regrowth before planting. In this way, the effects of one sprout removal on tuber yield could be minimized. Airing under constant illumination would give short sturdy sprouts (Toosey, 1964). The airing period allowed a valid comparison with tecnazene, as it is recommended that a period of airing should follow tecnazene treatment before planting (Dalziel and Duncan, 1975).

When the experiment started in December, a 12 week treatment period followed by 6 weeks airing before planting was intended. Unfortunately weather conditions delayed planting by 5 weeks, thus extending the airing period to 11 weeks.

The effects of benzothiazole and 1, 4-dimethylnaphthalene treatments on emergence and yield are presented in Tables 2.14, 2.15, 2.16 and 2.17. In considering the results, most attention was paid to comparisons between 100 mg kg^{-1} application rate, untreated control and tecnazene control (i. e. treatments A, E and F in the emergence and yield results tables).

In the following analysis, unless stated, all comparisons concern chemical treatment at 100 mg kg^{-1}.

Emergence

The first and most important result was that both benzothiazole and 1, 4-dimethylnaphthalene do not show large differences in emergence compared to untreated or tecnazene treated controls.

Benzothiazole did not differ significantly from, (a) MET, T50 and T75 of the untreated control, and (b) T75 of the tecnazene control. However, MET and T50 were significantly greater for benzothiazole compared to the tecnazene control. Benzothiazole significantly decreased TE compared to both untreated and tecnazene treated controls. Although not statistically significant, the lower application rates of benzothiazole also reduced total emergence compared to untreated and tecnazene treated controls.

In terms of MET, T25, T50 and TE, 1, 4-dimethylnaphthalene did not differ significantly from the untreated or tecnazene treated controls. T75 was not assessed for 1, 4-dimethylnaphthalene as three control drills did not reach 75% emergence. This also accounts for the lower TE of untreated controls in the 1, 4-dimethylnaphthalene experiment.

Tecnazene controls had significantly shorter MET and T50 compared to untreated controls. This was attributed to a better level of disease control due to the fungicidal properties of tecnazene (Brown and Reavill, 1954). The eleven week airing period would have helped minimize any growth retarding effects caused by treatment with tecnazene (Beveridge et al., 1976).

Yield

The first and most important result was that total yield of benzothiazole and 1, 4-dimethylnaphthalene did not differ significantly from the total yield of untreated or tecnazene treated controls.

With the exception of % small, benzothiazole did not differ significantly from the untreated control.

1, 4-dimethylnaphthalene did not differ significantly from the untreated control in terms of large, medium, small and total yield. However, it was significant that % large was less with % medium and % small greater, than the untreated control.

There was a significantly higher yield in medium, small, % medium and % small of tecnazene treated controls compared to untreated controls. This effect was accompanied with a corresponding significant decrease in large and % large yield. These results were, therefore, in agreement with earlier findings (Beveridge et al., 1976). Neither benzothiazole nor 1, 4-dimethylnaphthalene showed such a marked tendency towards increasing the yield of smaller sized tubers.

2.5 CONCLUSIONS

The principal conclusion was that benzothiazole and 1, 4-dimethylnaphthalene were successful sprout suppressants when applied at 100 mg kg^{-1}. At this application rate, both chemicals did not delay emergence or decrease yield. There was no marked tendency for either chemical to increase the yield of smaller sized tubers, as was shown by tecnazene treatments.

CHAPTER 3

DIMETHYLNAPHTHALENE DEVELOPMENT EXPERIMENTS

3.1 INTRODUCTION

As was seen in Chapter 2, benzothiazole and 1, 4-dimethylnaphthalene were shown to be successful sprout suppressants. Applied at 100 mg kg^{-1}, they achieved a similar level of control as the recommended application rate of tecnazene. Comparing treated with untreated seed, there was no evidence to suggest that there were large significant differences in emergence, yield and size distribution within yield.

At this stage in the project it was decided that further studies should be devoted to dimethylnaphthalene only. The reason for this choice was due to many factors. Perhaps the most compelling was that of limited time and resources. These dictated that only one chemical could be fully studied. The properties of benzothiazole and 1, 4-dimethylnaphthalene were, therefore, compared to determine which chemical was best. Dimethylnaphthalene was chosen for the following reasons. The assessment experiment results had shown that 1, 4-dimethylnaphthalene was a more active sprout suppressant than benzothiazole. Benzothiazole had also significantly reduced total emergence although this had not been reflected in any reduction of final yield. Benzothiazole is reasonably toxic. It has a low LD_{50} of 100 mg kg^{-1}. It was the most toxic of all the compounds assessed. It is probable that even without any restriction in resources, benzothiazole would have been precluded from further development studies for this reason. Toxicological data on dimethylnaphthalene was not available at the time. However, consideration of naphthalene (LD_{50}, 1780 mg kg^{-1}) suggested that dimethylnaphthalene would at least be less toxic than benzothiazole. Although dimethylnaphthalene is a polynuclear aromatic compound no published evidence of carcinogenic potential could be found. Dimethylnaphthalene was also marginally less expensive than benzothiazole. Finally, although somewhat subjectively, the chemicals' odours were assessed. Comparisons were made between

tecnazene, nonanol, chlorpropham, 1, 4-, 1, 6-dimethylnaphthalene and benzothiazole. It was considered that of these chemicals, benzothiazole in particular had an unpleasant strong odour.

Dimethylnaphthalene was studied in four development experiments. Some headspace and residue studies were also included. The development experiments had three main objectives. The first objective was to confirm the sprout suppressant properties of dimethylnaphthalene and establish the minimum application rate. The second objective was to measure the effect of dimethylnaphthalene treatment on the subsequent growth of treated seed. The third objective was to assess the performance of dimethylnaphthalene under commercial storage conditions. The aim of this chapter is to detail the objectives, methods and results of the four development experiments. In so doing the sprout suppressant properties of dimethylnaphthalene can be more fully described.

In this chapter "dimethylnaphthalene" refers to an isomeric mixture.

3.1.1 FIRST DEVELOPMENT EXPERIMENT

Storage season 1976-77. The aim of this experiment was to confirm the sprout suppressant properties of dimethylnaphthalene and assess its effect on the subsequent growth of treated seed.

As tecnazene is the only commercially available sprout suppressant suitable for use on seed potatoes, many of the assessment criteria were designed to compare the performance of dimethylnaphthalene with tecnazene. The most notable effects of tecnazene on the performance of seed potatoes can be summarized as follows. Tecnazene is an effective sprout suppressant when applied at 135 mg kg^{-1}. Unless aired before planting, treated tuber emergence will be delayed and final yield can also be reduced. The minimum recommended airing period at 10 - 12°C is 6 - 8 weeks. Treatment with tecnazene will affect the size distribution of the final yield, with a marked increase in yield of smaller sized tubers

(Dalziel and Duncan, 1975; Beveridge et al., 1976; Dalziel, 1978). Largely circumstantial evidence also suggests that application rates exceeding the recommended rate, caused by uneven application, will cause a complete loss in emergence of some tubers, with a corresponding reduction in final yield.

Much of the first development experiment was designed to find out whether or not dimethylnaphthalene would have similar effects on treated seed. A 99% pure mixture of dimethylnaphthalene isomers was used as only the isomeric mixture could be used economically on a commercial scale. Dimethylnaphthalene treatments were compared to untreated and tecnazene treated (135 mg kg^{-1}) controls. The temperature was 10°C. Dimethylnaphthalene was applied at two rates, 100 mg kg^{-1} and 300 mg kg^{-1}. From the assessment experiment results (2.4.1), 100 mg kg^{-1} was considered to be the best minimum recommended application rate. 300 mg kg^{-1} represented an excess application rate which could arise from accidental uneven dusting of tubers. Five treatment - airing time combinations were studied, i.e. (1) 74 - 39 (74 days treatment, 39 days airing), (2) 85 - 28, (3) 96 - 17, (4) 109 - 4, (5) 116 - 0. The tubers were desprouted before airing. Emergence and yield of 3 of the treatment - airing time combinations were studied by a fully replicated field experiment.

3.1.2 SECOND DEVELOPMENT EXPERIMENT

Storage season 1976-77. The aim of this experiment was to find the best minimum application rate for the 99% pure, isomeric mixture of dimethylnaphthalene. From the first assessment experiment (2.4.1) it appeared that the minimum recommended application rate for 1,4-dimethylnaphthalene could be less than 100 mg kg^{-1}. Dimethylnaphthalene was applied at 300 mg kg^{-1}, 200 mg kg^{-1}, and in theory, at 7 equidistant points on a linear scale between 0 and 200 mg kg^{-1}. Dimethylnaphthalene treatments were compared to untreated and tecnazene treated controls. The tuber samples were treated for 14 weeks at 10°C. Sprout growth

after airing for 5 weeks was also measured.

3.1.3 THIRD DEVELOPMENT EXPERIMENT

Storage season 1976-77. The aim of this experiment was to assess the performance of dimethylnaphthalene under commercial conditions. Dimethylnaphthalene was applied to two 500 kg batches of seed potatoes. The 500 kg batches were stored in a typical 500 kg box, seed potato store. After treatment the tuber samples followed the normal husbandry practices adopted by the seed potato grower. Dimethylnaphthalene (100 mg kg^{-1}) was compared to untreated and tecnazene treated (135 mg kg^{-1}) controls. The treatment period was 14 weeks. Emergence and yield of the treated tubers was measured. Field performance was also compared to seed tubers treated with half the recommended rate of tecnazene, estimated at 68 mg kg^{-1}. This half rate was the application rate used each year by the seed potato grower.

3.1.4 FOURTH DEVELOPMENT EXPERIMENT

Storage season 1977-78. The aim of this experiment was to assess the performance of dimethylnaphthalene in commercial, long-term ware potato stores. Performance in two stores was studied. One was held at 7 - 8°C and the other at 10°C. Dimethylnaphthalene was applied to 500 kg batches of potatoes, at three application rates, 100 mg kg^{-1}, 150 mg kg^{-1} and 200 mg kg^{-1}. Treatments were compared to an untreated control and chlorpropham treated material. The treatment time was 27 weeks.

3.1.5 RESIDUE AND HEADSPACE EXPERIMENTS

Storage seasons 1976-77, 1977-78. As a first step towards assessing the toxicity of dimethylnaphthalene, residue levels in treated tubers were determined from tubers in the first and second development experiments. Further residue studies were conducted during the following season.

Headspace experiments were conducted to determine the headspace concentration of dimethylnaphthalene under which adequate sprout suppression could be achieved. In this way the feasibility of applying dimethylnaphthalene directly through potato store air ducts could be assessed.

3.2 MATERIALS AND METHODS

3.2.1 FIRST DEVELOPMENT EXPERIMENT

Materials and methods were the same as those used in previous assessment experiments. Treatment and airing conditions were identical to the third assessment experiment (2.2.1). Sample size, 2 x 10 kg, was the same as the first assessment experiment (2.2.1), allowing 4 replicate field plots for each treatment - airing time combination. cv. Maris Peer and Red Craigs Royal were used. The plot size of cv. Maris Peer treatments was three drills of 20 tubers. The plot size of cv. Red Craigs Royal was 3 drills of 17 tubers. A 99% pure dimethylnaphthalene isomeric mixture was used (Aldrich, Gillingham, England).

3.2.1.1 First development experiment details

Potato sample	cv. Maris Peer and Red Craigs Royal (32 - 57 mm). Sample size, 2 x 10 kg.
Chemical	dimethylnaphthalene isomer mixture.
Treatments	Untreated control (25 g alumina). 100 $\pm$ 0.2 mg kg^{-1} dimethylnaphthalene (25 g alumina). 300 $\pm$ 1.0 mg kg^{-1} dimethylnaphthalene (75 g alumina). 135 mg kg^{-1} tecnazene (45 $\pm$ 0.5 g Fusarex per 10 kg box).
Assessment periods	The following assessment periods were adopted for each treatment - airing combination.

Combination	Assessment period (days)		
	Treatment time[a]	Airing time[b]	Airing time before planting[c]
1	74	39	50 (7 weeks)
2	85	28	-
3	96	17	28 (4 weeks)
4	109	4	-
5	116	0	8 (1 week)

[a] Treatment time before sprout length measurement. Treatment date, 30.12.76.

[b] Airing time before sprout length measurement.

[c] Airing time before planting. Planting date 3.5.77.

Time between planting and harvest was 22 weeks (3.5.77 - 5.10.77).

The tubers were graded immediately after harvest.

Observations

Length of the longest sprout after treatment, n = 100.

Length of the longest sprout after airing, n = 100.

Emergence time, n = 3.

Yield, n = 3.

3.2.1.2 Field experiment details

Once sprout growth after airing had been assessed the contents of each chitting tray were carefully covered with clear polythene and transported to the field.

The experimental plot was situated at Hattrick Farm, Bridge of Weir, Renfrewshire. It was approximately 0.25 ha of sandy loam soil. It had been uniformly treated with FYM and received 1400 kg ha^{-1} seed potato fertilizer (Scottish Agricultural Industries) immediately before planting. 10% aldicarb granules were applied at planting. Tubers were planted by hand at 230 mm spacing in drills 710 mm apart.

The experimental design consisted of four blocks, every block

containing one replicate plot of each treatment - airing time combination. Each block contained 24 independently randomized treatment plots, with the constraint that alternative plots in both directions were of different cultivars. Each plot consisted of 3 drills, which in the case of cv. Maris Peer were 4.6 m long, containing 20 tubers per drill and for cv. Red Craigs Royal were 4 m long, containing 17 tubers per drill. (Due to larger seed size cv. Red Craigs Royal treatments contained fewer tubers).

The experimental area was protected by guard drills. The experimental plan was designed in order that the sides and ends of each cv. Maris Peer plot were adjacent to plots containing cv. Red Craigs Royal (and vice versa). At harvest, the plots were distinguished by tuber colour. With the exception of one blight spray (accidental tractor application), all chemical control was achieved using a knapsack hand-spray. Non-experimental tractor passes were therefore not included in the design.

Weed control was achieved using paraquat and monolinuron plus hand-weeding when required. As the chemicals were applied using a hand-sprayer, application was delayed until 5% emergence and emerged plants were avoided. Captafol sprays were applied for blight prevention. The crop was mechanically defoliated 2 weeks before harvesting.

The yield from each plot drill was harvested separately, stored in 12 kg nets and mechanically graded over 52 mm and 32 mm riddles. Tubers $\leqslant$18 mm fell through the mechanical grader and were lost.

3.2.1.3 Analysis of results

Sprout length after treatment and airing data

Results were expressed as mean $\pm$ standard deviation. Significant differences between means were tested by analysis of variance. The least difference between a pair of means which would be significant

(L. S. D.) was calculated as:-

$$\text{L. S. D.} = t_{0.05} \sqrt{\frac{s^2}{n_1} + \frac{s^2}{n_2}}$$

where; t has N - k degrees of freedom.

k = number of treatments

N = total number of replicates

n_1, n_2 = number of replicates of each mean

s^2 = residual mean square from analysis of variance

Using this analytical procedure (Parker, 1973; Bailey, 1959), the following comparisons were analysed for significant differences.

(a) Same chemical treatment, different treatment length. The mean of each untreated, dimethylnaphthalene and tecnazene treatment was compared to its corresponding 116 day treatment.

(b) Different chemical treatments, same treatment length. The mean of each dimethylnaphthalene and tecnazene treatment was compared to the untreated control of corresponding treatment length.

(c) Different chemical treatments, same treatment length. The mean of each dimethylnaphthalene treatment was compared to the tecnazene treatment of corresponding treatment length.

Emergence and yield data

The data were examined for cultivar, chemical treatment, airing time and field block effects. Significant differences between means was tested by analysis of variance. Comparisons between treatment means were made using the Scheffé S-method for multiple comparisons (Seber, 1977). The least difference between any pair of treatment means which would be significant (L. S. D.) was calculated as:-

$$L.S.D. = \sqrt{aF(0.05/a, b)} \times \sqrt{\frac{s^2}{n_1} + \frac{s^2}{n_2}}$$

where; s^2 = residual mean square from analysis of variance

n_1, n_2 = number of replicates of each mean

a = treatment degrees of freedom

b = residual degrees of freedom

3.2.2 SECOND DEVELOPMENT EXPERIMENT

Methods and materials were identical to those used in the third assessment experiment (2.2.1). A 99% pure dimethylnaphthalene isomer mixture was used. The results were analysed by the same method used in the third assessment experiment (2.2.5). Chemical treatments were compared to combined untreated and combined tecnazene control data from the third assessment experiment.

3.2.2.1 Second development experiment details

Potato sample	cv. Record and Redskin (32 - 52 mm).	
	Sample size, 1 x 10 kg.	
Chemical	dimethylnaphthalene isomer mixture.	
Treatments	26 ± 0.2 mg kg^{-1}	125 ± 0.4 mg kg^{-1}
	51 ± 0.1 mg kg^{-1}	150 ± 0.1 mg kg^{-1}
	75 ± 0.6 mg kg^{-1}	176 ± 0.5 mg kg^{-1}
	100 ± 0.1 mg kg^{-1}	201 ± 0.2 mg kg^{-1}
	Untreated control	299 ± 0.1 mg kg^{-1}
	135 mg kg^{-1} tecnazene (45 ± 0.5 g Fusarex per 10 kg box)	
	All treatments and untreated control included a 25 g alumina solid carrier.	
Assessment periods	Treatment time, 14 weeks (30.12.76 - 4.4.77).	
	Airing time, 5 weeks (4.4.77 - 11.5.77).	
Observations	Length of the longest sprout after treatment, n = 50.	
	Length of the longest sprout after airing, n = 50.	

3. 2. 3 THIRD DEVELOPMENT EXPERIMENT

Dimethylnaphthalene (100 mg kg^{-1}) was compared to untreated and tecnazene treated controls. The treatments were applied to 2 x 500 kg batches of seed tubers. 500 kg boxes were lined with brown paper. The chemical treatments were evenly dusted over the tubers as the boxes were filled. When full, the top was covered with brown paper. The boxes were stored for 14 weeks, without temperature control, in a typical commercial seed potato store (Ross Seed Potatoes, Forfar, Scotland). At the end of the treatment period, each pair of 500 kg samples were combined and the tubers graded. They were then stored in 50 kg hessian sacks, until planting 4 weeks later.

The 1000 kg tuber samples were planted in three large plots placed side by side. The rest of the field was planted out with seed grown from the same stock but treated with half the recommended application rate of Fusarex. This was estimated as 68 mg kg^{-1} tecnazene. These tubers were included in the experiment.

Emergence and yield were estimated in a 75 m long section taken from the middle of each plot. A 75 m long section running across the field was marked off. Emergence for each plot was measured in 10 x 75 m long drills. Emergence was measured at four day intervals. Yield was measured by hand-digging 3 x 5 m lengths from the same drills used to determine emergence. The 75 m section across the field was evenly divided into three blocks. The 3 x 5 m lengths were taken, one from each block. Emergence for each 75 m drill length and yield of each 5 m drill length were measured in the same terms as the first assessment experiment (2. 2. 1). Harvested tubers were stored at c. 12°C, and then graded at the same time as the first development experiment.

Emergence and yield results were analysed by the same method used in the first development experiment (2. 2. 5). Emergence was analysed for treatment effects. Yield was analysed for treatment and

field block effects.

3.2.3.1 Third development experiment details

Potato sample	cv. Arran Pilot (32 - 57 mm).
	Sample size, 2 x 500 kg.
Chemical	dimethylnaphthalene isomer mixture.
Treatments	Untreated (1.25 kg alumina per 500 kg sample).
	100 mg kg^{-1} dimethylnaphthalene (1.25 kg alumina).
	135 mg kg^{-1} tecnazene (4.5 g kg^{-1}, Fusarex).
	68 mg kg^{-1} tecnazene (half recommended rate of Fusarex).
Assessment periods	Treatment time, 14 weeks (20.12.76 - 25.3.77).
	Time between grading and planting, 4 weeks (25.3.77 - 21.4.77).
	Time between planting and harvest, 19 weeks (21.4.77 - 29.8.77).
Observations	Length of the longest sprout, visual assessment
	Emergence time, n = 10.
	Yield, n = 30.

3.2.4 FOURTH DEVELOPMENT EXPERIMENT

Dimethylnaphthalene treatment was compared to untreated and chlorpropham treated controls. A 99% pure mixture of dimethylnaphthalene isomers was used. The treatments were applied to 500 kg batches of ware tubers. The tubers were stored in 500 kg boxes (not lined with brown paper). The tubers were evenly dusted as the 500 kg boxes were being filled. The tubers were stored alongside ware tubers intended for long-term storage. The long-term stored tubers were intermittently treated with chlorpropham (10 - 20 mg kg^{-1}). The experimental tubers were, in theory, removed when chlorpropham was being applied. The length of the longest sprout was measured on tubers taken 300 mm from the top of each box.

3.2.4.1 Fourth development experiment details

Storage conditions	4,000 tonne, bulk store (Cadbury Schweppes Foods Ltd., Catterick Bridge, England).
	Storage temperature, 7 - 8°C.
	Frequent ventilation.
	3,000 tonne, box store (United Biscuits Ltd., Thirsk, England).
	Storage temperature, 10°C.
	Less frequent ventilation as the bulk store.
Potato sample	cv. Pentland Dell (Bulk store)
	cv. Record (Box store).
	Sample size, 500 kg.
Treatments	Untreated (1.25 kg alumina).
	100 mg kg^{-1} dimethylnaphthalene.
	150 mg kg^{-1} dimethylnaphthalene.
	200 mg kg^{-1} dimethylnaphthalene.
Assessment periods	Treatment time, 27 weeks (13.12.77 - 21.6.78).
Observations	Length of the longest sprout, n = 100.

3.2.5 RESIDUE AND HEADSPACE EXPERIMENTS

The residue experimental methods and materials are detailed in Chapter A2. Headspace experimental methods are detailed in Chapter A1.5.

3.3 RESULTS

Table 3.01. First development experiment. Mean sprout length of tubers treated for periods of 74, 85, 96, 109 and 116 days. Treatments = untreated, dimethylnaphthalane (DMN) and tecnazene (Tec), cv. Maris Peer, temperature = 10°C.

Treatment		Sprout length (mm)				
		74 days	85 days	96 days	109 days	116 days
Untreated	mean	194.3[a]	233.5[a]	259.0[a]	315.0[a]	357.3
	S.D.	30.2	38.7	56.0	70.8	62.7
100 mg kg^{-1} DMN	mean	45.5[abc]	18.3[ab]	4.0[bc]	2.6[bc]	2.7[bc]
	S.D.	49.8	36.5	12.4	2.7	2.9
300 mg kg^{-1} DMN	mean	5.2[bc]	4.2[bc]	3.2[bc]	1.7[bc]	0.9[bc]
	S.D.	20.2	22.2	15.7	2.8	1.1
135 mg kg^{-1} Tec	mean	25.8[ab]	13.2[ab]	14.3[ab]	11.1[b]	6.1[b]
	S.D.	35.2	32.3	27.4	10.8	5.3
*100 mg kg^{-1} DMN	mean	19.7[ab]	12.1[abc]	2.0[bc]		
	S.D.	24.2	15.5	3.3		
	n	74	91	97		
*300 mg kg^{-1} DMN	mean	0.9[bc]	1.2[bc]	1.2[bc]		
	S.D.	1.0	3.1	2.3		
	n	95	98	98		
*135 mg kg^{-1} Tec	mean	15.4[ab]	6.7[b]	9.1[b]		
	S.D.	18.0	9.0	14.2		
	n	89	95	95		

* mean values with anomalous sprout lengths not included. Number of sprout length measurements omitted = 100 - n.

a Same chemical treatment, different treatment length. Significantly different from 116 day treatment ($p < 0.05$).

b Different chemical treatments, same treatment length. Significantly different from untreated control mean of corresponding treatment length ($p < 0.05$).

c Different chemical treatments, same treatment length. Significantly different from tecnazene treatment mean of corresponding treatment length ($p < 0.05$).

Table 3.02. First development experiment. Mean sprout length of tubers treated for periods of 74, 85, 96, 109 and 116 days. Treatments = untreated, dimethylnaphthalene (DMN) and tecnazene (Tec), cv. Red Craigs Royal, temperature = 10°C.

Treatment		Sprout length (mm)				
		74 days	85 days	96 days	109 days	116 days
Untreated	mean	191.9[a]	233.3	241.7	271.9	250.2
	S.D.	55.5	45.9	102.4	108.7	107.2
100 mg kg^{-1} DMN	mean	4.8[b]	5.3[b]	8.2[b]	4.8[b]	9.3[b]
	S.D.	8.8	9.5	25.1	7.0	12.5
300 mg kg^{-1} DMN	mean	0.9[bc]	0.2[bc]	0.6[bc]	0.2[bc]	0.6[bc]
	S.D.	3.6	0.5	1.8	0.6	3.2
135 mg kg^{-1} Tec	mean	6.9[b]	7.5[b]	8.0[b]	8.9[b]	8.3[b]
	S.D.	10.8	15.1	16.7	12.7	10.0

[a] Same chemical treatment, different treatment length. Significantly different from 116 day treatment ($p < 0.05$).

[b] Different chemical treatments, same treatment length. Significantly different from untreated control mean of corresponding treatment length ($p < 0.05$).

[c] Different chemical treatments, same treatment length. Significantly different from tecnazene treatment mean of corresponding treatment length ($p < 0.05$).

Table 3.03. First development experiment. Mean sprout length of treated tubers, desprouted, then aired for periods of 4, 17, 28 and 39 days. Treatments = untreated, dimethylnaphthalene (DMN) and tecnazene (Tec), cv. Maris Peer, temperature = 10°C.

Treatment	Sprout length (mm)				
		4 days	17 days	28 days	39 days
Untreated	mean	3.3[a]	13.3[a]	19.7[a]	40.0
	S.D.	4.6	9.5	8.6	15.8
100 mg kg^{-1} DMN	mean	1.7[abc]	5.3[ab]	10.8[abc]	31.4[bc]
	S.D.	1.6	7.2	9.6	16.7
300 mg kg^{-1} DMN	mean	1.4[abc]	1.5[abc]	2.3[abc]	5.3[bc]
	S.D.	2.2	2.5	5.6	5.2
135 mg kg^{-1} Tec	mean	3.4[a]	5.8[ab]	7.9[ab]	16.4[b]
	S.D.	3.0	6.3	5.8	9.1

[a] Same chemical treatment, different airing time. Significantly different from 39 day airing time ($p < 0.05$).

[b] Different chemical treatments, same airing time. Significantly different from untreated control mean of corresponding airing time ($p < 0.05$).

[c] Different chemical treatments, same airing time. Significantly different from tecnazene treatment mean of corresponding airing time ($p < 0.05$).

Table 3.04. First development experiment. Mean sprout length of treated tubers, desprouted, then aired for periods of 4, 17, 28 and 39 days. Treatments = untreated, dimethylnaphthalene (DMN) and tecnazene (Tec), cv. Red Craigs Royal, temperature = 10°C.

Treatment	Sprout length (mm)				
		4 days	17 days	28 days	39 days
Untreated	mean	2.9[a]	5.5[a]	11.0[a]	17.1
	S.D.	4.5	5.7	10.0	11.8
100 mg kg^{-1} DMN	mean	2.0[ab]	2.9[ab]	9.1[c]	9.6[bc]
	S.D.	2.4	5.8	8.5	11.5
300 mg kg^{-1} DMN	mean	0.5[bc]	0.3[bc]	0.6[bc]	0.8[bc]
	S.D.	2.3	0.8	1.0	1.4
135 mg kg^{-1} Tec	mean	1.6[ab]	2.9[ab]	2.6[ab]	5.4[b]
	S.D.	1.8	3.7	3.8	7.6

[a] Same chemical treatment, different airing time. Significantly different from 39 day airing time ($p < 0.05$).

[b] Different chemical treatments, same airing time. Significantly different from untreated control mean of corresponding airing time ($p < 0.05$).

[c] Different chemical treatments, same airing time. Significantly different from tecnazene treatment mean of corresponding airing time ($p < 0.05$).

Table 3.05. First development experiment. Untreated, dimethylnaphthalene (DMN) and tecnazene (Tec) treatment effects on emergence. Mean of 72 drills.

Treatment	Code	Emergence[a]			
		MET	T25	T50	TE
Untreated	A	33.0	29.4	32.4	93.7
100 mg kg^{-1} DMN	B	35.1	31.2	35.5	92.0
300 mg kg^{-1} DMN	C	42.7	40.7	47.7	78.8
135 mg kg^{-1} Tec	D	36.8	33.1	37.6	89.1
S.E.M.[b]		0.3	0.3	0.4	0.7
L.S.D.[c]		0.5	1.2	1.5	2.7
	Order[d]				
	1	A	A	A	A
	2	B	B	B	B
	3	D	D	D	D
	4	C	C	C	C

[a] Emergence in terms of total % emergence (TE) and emergence time (days) expressed as, mean emergence time (MET), and time to 25%, 50% emergence (T25, T50).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatments. Treatments (codes A - D) are placed in descending order, i.e. most beneficial effect (1) to least beneficial effect (4). When treatments have a common line, they do not differ significantly ($p < 0.05$).

Table 3.06. First development experiment. Airing time effects on emergence. Mean of 96 drills.

Airing time	Code	Emergence[a]			
		MET	T25	T50	TE
1 week	A	41.7	38.8	43.8	85.9
4 weeks	B	37.0	33.9	38.7	89.1
7 weeks	C	32.0	28.1	32.4	91.6
S.E.M.[b]		0.2	0.3	0.3	0.6
L.S.D.[c]		0.8	0.9	1.1	2.1
	Order[d]				
	1	C	C	C	C
	2	B	B	B	B
	3	A	A	A	A

[a] Emergence in terms of total % emergence (TE) and emergence time (days) expressed as mean emergence time (MET) and time to 25%, 50% emergence (T25, T50).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of airing times. Airing times (codes A - C) are placed in descending order, i.e. most beneficial effect (1) to least beneficial effect (3). When treatments have a common line, they do not differ significantly ($p < 0.05$).

Table 3.07. First development experiment. Emergence of treatment - airing time, combinations. Treatments = untreated, dimethylnaphthalene (DMN) and tecnazene (Tec), treatment time + airing time = 18 weeks for all combinations, cv. Maris Peer, mean of 12 drills.

Treatment	Airing Time	Emergence [a]			
		MET	T25	T50	TE
Untreated (A)	1 week	33.6	31.0	32.4	99.2
	4 weeks	27.6	24.1	26.7	99.2
	7 weeks	26.1	22.7	24.7	100.0
100 mg kg^{-1} DMN (B)	1 week	37.2	33.0	36.3	100.0
	4 weeks	31.7	29.0	31.2	99.6
	7 weeks	26.8	23.0	25.3	99.2
300 mg kg^{-1} DMN (C)	1 week	44.5	41.9	45.2	95.4
	4 weeks	37.3	33.6	36.4	98.8
	7 weeks	29.8	27.1	29.7	100.0
135 mg kg^{-1} Tec (D)	1 week	36.8	33.2	36.3	99.6
	4 weeks	31.2	28.5	30.8	99.6
	7 weeks	25.9	22.7	25.3	100.0
S.E.M. [b]		0.6	0.7	0.9	1.7
L.S.D. [c]		4.1	4.7	5.9	10.7
	Order [d]				
	1	D7	A7	A7	A7
	2	A7	D7	D7	D7
	3	B7	B7	B7	C7
	4	A4	A4	A4	B1
	5	C7	C7	C7	B4
	6	D4	D4	D4	D1
	7	B4	B4	B4	D4
	8	A1	A1	A1	B7
	9	D1	B1	D1	A1
	10	B1	D1	B1	A4
	11	C4	C4	C4	C4
	12	C1	C1	C1	C1

[a] Emergence in terms of total % emergence (TE) and emergence time (days) expressed as, mean emergence time (MET) and time to 25%, 50% emergence (T25, T50).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatment - airing time combinations. Combinations (codes A1 - D7) are placed in descending order, i.e. most beneficial effect (1) to least beneficial effect (12). When combinations have a common line, they do not differ significantly ($p < 0.05$).

Table 3.08. First development experiment. Emergence of treatment - airing time combinations. Treatments = untreated, dimethylnaphthalene (DMN) and tecnazene (Tec), treatment time + airing time = 18 weeks for all combinations, cv. Red Craigs Royal, mean of 12 drills.

Treatment	Airing Time	Emergence[a]			
		MET	T25	T50	TE
Untreated (A)	1 week	42.2	38.9	44.2	77.5
	4 weeks	35.5	31.1	34.9	92.2
	7 weeks	32.8	28.6	31.5	94.6
100 mg kg^{-1} DMN (B)	1 week	40.5	36.3	41.4	86.7
	4 weeks	39.8	35.6	42.6	81.4
	7 weeks	34.1	30.3	35.9	85.3
300 mg kg^{-1} DMN (C)	1 week	52.3	52.6	66.5	47.6
	4 weeks	49.6	50.4	61.3	55.9
	7 weeks	42.6	38.2	46.8	75.0
135 mg kg^{-1} Tec (D)	1 week	46.5	43.0	47.8	80.9
	4 weeks	42.3	38.8	45.0	75.5
	7 weeks	37.6	31.9	40.1	78.9
S.E.M.[b]		0.6	0.7	0.9	1.7
L.S.D.[c]		4.1	4.7	5.9	10.7
	Order[d]				
	1	A7	A7	A7	A7
	2	B7	B7	A4	A4
	3	A4	A4	B7	B1
	4	D7	D7	D7	B7
	5	B4	B4	B1	B4
	6	B1	B1	B4	D1
	7	A1	C7	A1	D7
	8	D4	D4	D4	A1
	9	C7	A1	C7	D4
	10	D1	D1	D1	C7
	11	C4	C4	C4	C4
	12	C1	C1	C1	C1

[a] Emergence in terms of total % emergence (TE) and emergence time (days) expressed as, mean emergence time (MET), and time to 25%, 50% emergence (T25, T50).

[b] Standard error of the mean.

[c] Least difference between a pair of mean which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatment - airing time combinations. Combinations (codes A1 - D7) are placed in descending order, i.e. most beneficial effect (1) to least beneficial effect (12). When combinations have a common line, they do not differ significantly ($p < 0.05$).

Table 3.09. First development experiment. Untreated dimethylnaphthalene (DMN) and tecnazene (Tec) treatment effects on yield. Mean of 72 drills.

Treatment	Code	Yield[a]						
		L	M	S	T	%L	%M	%S
Untreated	A	11.73	2.85	0.13	14.71	79.91	19.20	0.90
100 mg kg^{-1} DMN	B	9.76	4.32	0.28	14.36	68.15	29.87	1.97
300 mg kg^{-1} DMN	C	8.19	3.67	0.28	12.14	69.06	28.72	2.21
135 mg kg^{-1} Tec	D	8.80	5.00	0.31	14.11	63.03	34.77	2.20
S. E. M.[b]		0.21	0.10	0.01	0.23	0.70	0.66	0.09
L. S. D.[c]		0.84	0.41	0.05	0.93	2.83	2.64	0.37
	Order[d]							
	1	A	D	D	A	A	D	C
	2	B	B	B	B	C	B	D
	3	D	C	C	D	B	C	B
	4	C	A	A	C	D	A	A

[a] Yield (kg and as a % of total yield) of tubers > 52 mm (L, %L), >32 - ≤ 52 mm (M, %M), >18 - ≤ 32 mm (S, %S) and as total yield (T).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatments. Treatments (codes A - D) are placed in descending order, i.e. highest yield (1) to lowest yield (4). When treatments have a common line, they do not differ significantly ($p < 0.05$).

Table 3.10. First development experiment. Airing time effects on yield. Mean of 96 drills.

Airing time	Code	Yield[a]						
		L	M	S	T	%L	%M	%S
1 week	A	8.98	3.72	0.23	12.93	70.54	27.73	1.73
4 weeks	B	9.35	4.16	0.28	13.79	68.29	29.70	2.02
7 weeks	C	10.53	3.99	0.25	14.77	71.29	26.99	1.72
S.E.M.[b]		0.18	0.09	0.01	0.20	0.61	0.57	0.08
L.S.D.[c]		0.63	0.31	0.04	0.70	2.14	2.00	0.28
	Order[d]							
	1	C	B	B	C	C	B	B
	2	B	C	C	B	A	A	A
	3	A	A	A	A	B	C	C

a Yield (kg and as a % of total yield) of tubers >52 mm (L, %L), >32 - ≤52 mm (M, %M), >18 - ≤32 mm (S, %S) and as total yield (T).

b Standard error of the mean.

c Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

d Order of airing times. Airing times (codes A - C) are placed in descending order, i.e. highest yield (1) to lowest yield (3). When airing times have a common line, they do not differ significantly ($p < 0.05$).

Table 3.11. First development experiment. Yield of treatment - airing time combinations. Treatments = untreated, dimethylnaphthalene (DMN), and tecnazene (Tec), treatment time + airing time = 18 weeks for all combinations, cv. Maris Peer, mean of 12 drills.

Treatment	Airing Time	Yield[a]			
		L	M	S	T
Untreated(A)	1 week	11.13	3.68	0.13	14.93
	4 weeks	11.60	4.03	0.22	15.85
	7 weeks	12.88	2.80	0.16	15.84
100 mg kg^{-1} DMN (B)	1 week	9.23	5.70	0.40	15.33
	4 weeks	8.49	6.05	0.41	14.95
	7 weeks	10.50	4.38	0.27	15.15
300 mg kg^{-1} DMN (C)	1 week	7.52	4.80	0.39	12.70
	4 weeks	7.11	5.89	0.52	13.52
	7 weeks	7.66	6.55	0.51	14.72
135 mg kg^{-1} Tec (D)	1 week	7.26	7.13	0.51	14.89
	4 weeks	7.18	7.20	0.49	14.87
	7 weeks	9.78	6.48	0.39	16.65
S.E.M.[b]		0.51	0.25	0.03	0.57
L.S.D.[c]		3.28	1.60	0.19	3.63
	Order[d]				
	1	A7	D4	C4	D7
	2	A4	D1	D1	A4
	3	A1	C7	C7	A7
	4	B7	D7	D4	B1
	5	D7	B4	B4	B7
	6	B1	C4	B1	B4
	7	B4	B1	D7	A1
	8	C7	C1	C1	D1
	9	C1	B7	B7	D4
	10	D1	A4	A4	C7
	11	D4	A1	A7	C4
	12	C4	A7	A1	C1

[a] Yield (kg) of tubers >52 mm (L), >32 - ≤52 mm (M), >18 - ≤32 mm (S), and as total yield (T).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatment - airing time combinations. Combinations (codes A1 - D7) are placed in descending order, i.e. highest yield (1) to lowest yield (12). When combinations have a common line, they do not differ significantly ($p < 0.05$).

Table 3.12. First development experiment. Yield of treatment - airing time combinations. Treatments = untreated, dimethylnaphthalene (DMN), and tecnazene (Tec), treatment time + airing time = 18 weeks for all combinations, cv. Maris Peer, mean of 12 drills.

Treatment	Airing time	Yield[a]		
		%L	%M	%S
Untreated (A)	1 week	74.24	24.90	0.86
	4 weeks	73.25	25.36	1.39
	7 weeks	81.14	17.85	1.02
100 mg kg^{-1} DMN (B)	1 week	60.08	37.29	2.62
	4 weeks	56.74	40.50	2.75
	7 weeks	68.48	29.67	1.85
300 mg kg^{-1} DMN (C)	1 week	59.04	37.87	3.09
	4 weeks	51.83	44.11	4.06
	7 weeks	51.91	44.62	3.47
135 mg kg^{-1} Tec (D)	1 week	48.36	48.18	3.46
	4 weeks	47.95	48.77	3.28
	7 weeks	58.49	39.13	2.39
S. E. M.[b]		1.72	1.61	0.22
L. S. D.[c]		11.07	10.35	1.44
	Order[d]			
	1	A7	D4	C4
	2	A1	D1	C7
	3	A4	C7	D1
	4	B7	C4	D4
	5	B1	B4	C1
	6	C1	D7	B4
	7	D7	C1	B1
	8	B4	B1	D7
	9	C7	B7	B7
	10	C4	A4	A4
	11	D1	A1	A7
	12	D4	A7	A1

[a] Yield (as a % of total yield) of tubers > 52 mm (%L), > 32 - ≤ 52 mm (%M) and > 18 - ≤ 32 mm (%S).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatment - airing time combinations. Combinations (codes A1 - D7) are placed in descending order, i. e. highest % yield (1) to lowest % yield (12). When combinations have a common line, they do not differ significantly ($p < 0.05$).

Table 3.13. First development experiment. Yield of treatment - airing time combinations. Treatments = untreated, dimethylnaphthalene (DMN), and tecnazene (Tec), treatment time + airing time = 18 weeks for all combinations, cv. Red Craigs Royal, mean of 12 drills.

Treatment	Airing time	Yield[a]			
		L	M	S	T
Untreated (A)	1 week	9.91	1.49	0.09	11.49
	4 weeks	13.07	2.46	0.11	15.64
	7 weeks	11.80	2.36	0.10	14.54
100 mg kg^{-1} DMN (B)	1 week	9.53	2.87	0.16	12.56
	4 weeks	10.38	3.23	0.21	13.82
	7 weeks	10.44	3.70	0.24	14.38
300 mg kg^{-1} DMN (C)	1 week	7.26	1.33	0.08	8.66
	4 weeks	8.68	1.38	0.09	10.15
	7 weeks	10.90	2.07	0.12	13.08
135 mg kg^{-1} Tec (D)	1 week	9.99	2.78	0.10	12.87
	4 weeks	8.29	3.07	0.20	11.56
	7 weeks	10.28	3.35	0.22	13.85
S.E.M.[b]		0.51	0.25	0.03	0.57
L.S.D.[c]		3.28	1.60	0.19	3.63
	Order[d]				
	1	A4	B7	B7	A4
	2	A7	D7	D7	A7
	3	C7	B4	D4	B7
	4	B7	D4	B4	D7
	5	B4	B1	B1	B4
	6	D7	D1	C7	C7
	7	D1	A7	A4	D1
	8	A1	A4	A7	B1
	9	B1	C7	D1	D4
	10	C4	A1	A1	A1
	11	D4	C4	C4	C4
	12	C1	C1	C1	C1

[a] Yield (kg) of tubers > 52 mm (L), >32 - ≤52 mm (M), >18 - ≤32 mm (S), and as total yield (T).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatment - airing time combinations. Combinations (codes A1 - D7) are placed in descending order, i.e. highest yield (1) to lowest yield (12). When combinations have a common line, they do not differ significantly ($p < 0.05$).

Table 3.14. First development experiment. Yield of treatment - airing time combinations. Treatments = untreated, dimethylnaphthalene (DMN), and tecnazene (Tec), treatment time + airing time = 18 weeks for all combinations, cv. Red Craigs Royal, mean of 12 drills.

Treatment	Airing time	Yield[a]		
		%L	%M	%S
Untreated (A)	1 week	86.50	12.77	0.74
	4 weeks	83.61	15.70	0.69
	7 weeks	80.71	18.58	0.71
100 mg kg^{-1} DMN (B)	1 week	76.02	22.66	1.32
	4 weeks	75.15	23.33	1.52
	7 weeks	72.45	25.76	1.79
300 mg kg^{-1} DMN (C)	1 week	82.69	16.34	0.97
	4 weeks	85.79	13.43	0.79
	7 weeks	83.14	15.94	0.92
135 mg kg^{-1} Tec (D)	1 week	77.40	21.83	0.77
	4 weeks	72.00	26.32	1.68
	7 weeks	74.03	24.35	1.63
S.E.M.[b]		1.72	1.61	0.22
L.S.D.[c]		11.07	10.35	1.44
	Order[d]			
	1	A1	D4	B7
	2	C4	B7	D4
	3	A4	D7	D7
	4	C7	B4	B4
	5	C1	B1	B1
	6	A7	D1	C1
	7	D1	A7	C7
	8	B1	C1	C4
	9	B4	C7	D1
	10	D7	A4	A1
	11	B7	C4	A7
	12	D4	A1	A4

[a] Yield (as a % of total yield) of tubers > 52 mm (%L), >32 - ⩽52 mm (%M) and >18 - ⩽32 mm (%S).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatment - airing time combinations. Combinations (codes A1 - D7) are placed in descending order, i.e. highest % yield (1) to lowest % yield (12). When combinations have a common line, they do not differ significantly ($p < 0.05$).

Table 3.15. Second development experiment. Mean sprout length of tubers after treatment and after airing (desprouted before airing). Treatments = untreated, dimethylnaphthalene (DMN) and tecnazene (Tec), treatment time = 14 weeks, airing time = 5 weeks, temperature = 10°C.

Cultivar	Treatment		Sprout length after treatment (mm)		Sprout length after airing (mm)	
			mean	S. D.	mean	S. D.
Redskin	Untreated		154.4	81.1	13.1	7.0
	25 mg kg^{-1}	DMN	65.2[ab]	40.1	17.6[ab]	6.9
	50 mg kg^{-1}	DMN	36.3[ab]	45.2	13.7[b]	6.6
	75 mg kg^{-1}	DMN	42.4[ab]	32.4	16.9[ab]	11.0
	100 mg kg^{-1}	DMN	11.0[ab]	23.4	14.0[b]	8.1
	125 mg kg^{-1}	DMN	12.9[ab]	21.8	16.2[ab]	7.5
	150 mg kg^{-1}	DMN	14.5[a]	15.8	18.8[ab]	7.7
	175 mg kg^{-1}	DMN	3.2[ab]	6.6	10.8[a]	5.4
	200 mg kg^{-1}	DMN	6.9[ab]	10.9	13.5[b]	6.6
	300 mg kg^{-1}	DMN	2.6[ab]	5.9	11.6	4.9
	135 mg kg^{-1}	Tec	20.6	23.1	10.2	5.0
Record	Untreated		114.6	73.3	18.6	7.0
	25 mg kg^{-1}	DMN	81.9[ab]	50.0	22.9[ab]	9.3
	50 mg kg^{-1}	DMN	35.6[ab]	25.3	27.5[ab]	11.6
	75 mg kg^{-1}	DMN	61.5[ab]	33.0	25.3[ab]	8.7
	100 mg kg^{-1}	DMN	18.7[a]	17.8	21.7[ab]	5.9
	125 mg kg^{-1}	DMN	32.0[ab]	25.5	21.5[ab]	7.9
	150 mg kg^{-1}	DMN	36.8[ab]	24.3	26.6[ab]	10.4
	175 mg kg^{-1}	DMN	5.5[ab]	11.7	19.6	7.7
	200 mg kg^{-1}	DMN	9.1[ab]	21.9	22.2[ab]	7.9
	300 mg kg^{-1}	DMN	4.0[ab]	6.9	20.3[b]	7.1
	135 mg kg^{-1}	Tec	16.3	20.0	17.1	7.7

a Significantly different from corresponding untreated control mean ($p < 0.05$).
b Significantly different from corresponding tecnazene mean ($p < 0.05$).

Table 3.16. Third development experiment. Untreated, dimethylnaphthalene (DMN), and tecnazene (Tec) treatment effects on emergence. Mean of 10 drills.

Treatment	Code	Emergence[a]			
		MET	T50	T75	TE
Untreated	A	45.0	45.2	49.3	88.1
100 mg kg^{-1} DMN	B	44.5	44.2	47.8	93.1
68 mg kg^{-1} Tec	C	44.0	43.9	48.3	92.0
135 mg kg^{-1} Tec	D	47.7	47.9	54.2	85.2
S.E.M.[b]		0.29	0.29	0.59	2.22
L.S.D.[c]		1.23	1.21	2.48	
	Order[d]				
	1	C	C	B	B
	2	B	B	C	C
	3	A	A	A	A
	4	D	D	D	D

[a] Emergence in terms of total % emergence (TE) and emergence time (days) expressed as, mean emergence time (MET), and time to 50%, 75% emergence (T50, T75).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatments. Treatments (codes A - D) are placed in descending order, i.e. most beneficial effect (1) to least beneficial effect (4). When treatments have a common line, they do not differ significantly($p < 0.05$).

Table 3.17. Third development experiment. Untreated dimethylnaphthalene (DMN), and tecnazene (Tec) treatment effects on yield. Mean of 30 drills.

Treatment	Code	Yield[a]						
		L	M	S	T	%L	%M	%S
Untreated	A	6.53	5.39	0.25	12.17	53.68	44.26	2.06
100 mg kg^{-1} DMN	B	5.16	6.63	0.37	12.15	42.20	54.72	3.08
68 mg kg^{-1} Tec	C	6.29	5.89	0.32	12.51	50.73	46.70	2.57
135 mg kg^{-1} Tec	D	5.33	6.19	0.35	11.87	45.05	52.05	2.91
S.E.M.[b]		0.21	0.21	0.02	0.26	1.43	1.37	0.15
L.S.D.[c]		0.85	0.84	0.07		5.74	5.49	0.59
	Order[d]							
	1	A	B	B	C	A	B	B
	2	C	D	D	A	C	D	D
	3	D	C	C	B	D	C	C
	4	B	A	A	D	B	A	A

[a] Yield (kg and as a % of total yield) of tubers > 52 mm (L, %L), >32 - ≤52 mm (M, %M), >18 - ≤32 mm (S, %S) and as total yield (T).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). Calculated only if analysis of variance shows significant differences between means.

[d] Order of treatments. Treatments (codes A - D) are placed in descending order, i.e. highest yield (1) to lowest yield (4). When treatments have a common line, they do not differ significantly ($p < 0.05$).

Table 3.18. Fourth development experiment. Sprout length of tubers treated with dimethylnaphthalene (DMN). Storage conditions, 6,000 tonne bulk store (7 - 8°C), 3,000 tonne box store (10°C). Treatment time = 27 weeks.

Treatment	Sprout length (mm)			
	Bulk store		Box store[a]	
	mean	S. D.	mean	S. D.
Untreated	62.2	36.0	7.5	8.7
100 mg kg^{-1} DMN	49.8	25.5	6.3	7.2
150 mg kg^{-1} DMN	29.2	12.6	13.0	11.1
200 mg kg^{-1} DMN	28.8	13.6	19.0	15.1
S. E. M.[b]	2.39		1.09	
L. S. D.[c]	9.62		4.39	

[a] All samples accidentally treated with chlorpropham (10 - 20 mg kg^{-1}).

[b] Standard error of the mean.

[c] Least difference between a pair of means which would be significant ($p < 0.05$). When treatments have a common line, they do not differ significantly.

Table 3.19. Residue levels of 1,4-dimethylnaphthalene (DMN) in unpeeled, treated tubers, cv. Maris Peer, temperature 9°C.

Treatment	Treatment period (weeks)		Residue level (mg kg^{-1})	
	treatment time	airing time	mean*	S.D.
100 mg kg^{-1} DMN	12	-	3.8	0.39
100 mg kg^{-1} DMN	12	7	2.7	0.37
100 mg kg^{-1} DMN	16	-	3.1	0.23
100 mg kg^{-1} DMN	16	1	3.2	0.01
300 mg kg^{-1} DMN	16	-	11.03	0.01
300 mg kg^{-1} DMN	16	1	11.22	0.21

* mean of duplicate samples, analytical details Chapter A2.

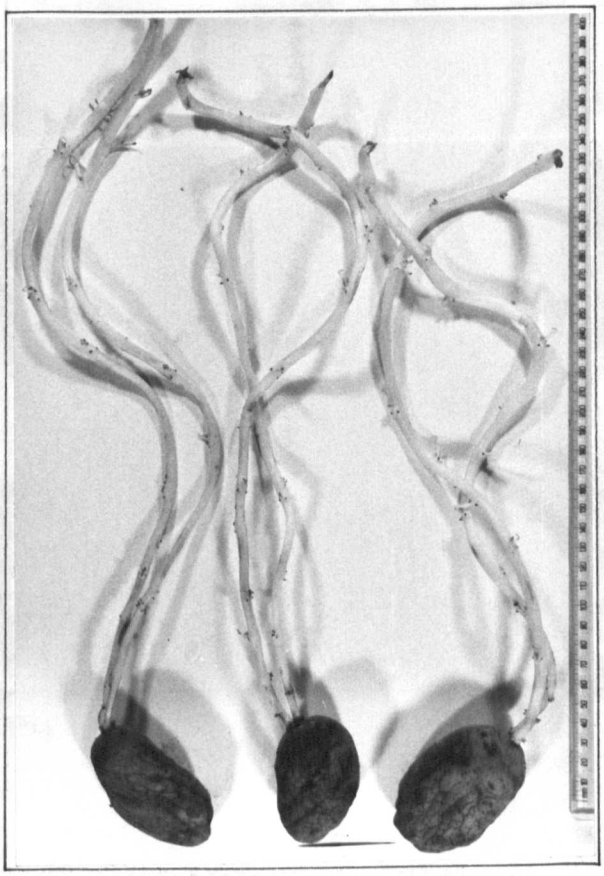
Table 3.20. Headspace concentration of 1, 4-dimethylnaphthalene (DMN) in 10 kg boxes containing treated tubers, cv. Maris Peer, sample size 5 kg, temperature 9°C.

Treatment	*Headspace concentration (mg m^{-3})				
	3 days	13 days	27 days	61 days	99 days
50 mg kg^{-1} DMN	2.6	1.5	1.1	0.6	0.3
100 mg kg^{-1} DMN	6.8	3.9	3.4	2.0	1.4
300 mg kg^{-1} DMN	10.8	10.2	6.6	6.4	3.9

* mean of duplicate boxes 3, 13, 27, 61 and 99 days after treatment, analytical details in Chapter A1. 5.1.

Plate 3.01a. First development experiment. Sprout length after 18 weeks treatment at 10°C. cv. Maris Peer.

Untreated



Dimethylnaphthalene (100 mg kg^{-1}) treated

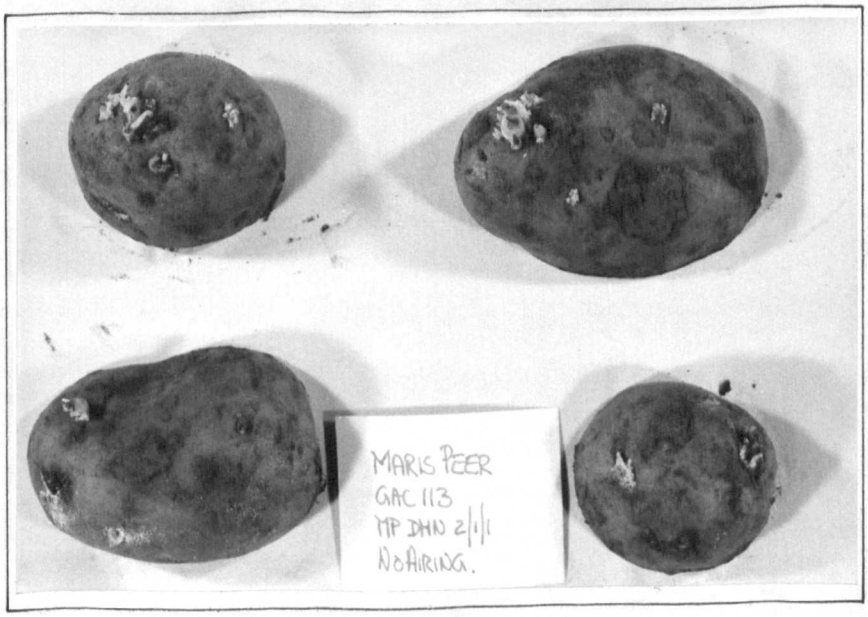


Plate 3.01b. First development experiment. Sprout length after 18 weeks treatment at 10°C. cv. Maris Peer.

Dimethylnaphthalene (300 mg kg^{-1}) treated

Tecnazene (135 mg kg^{-1}) treated

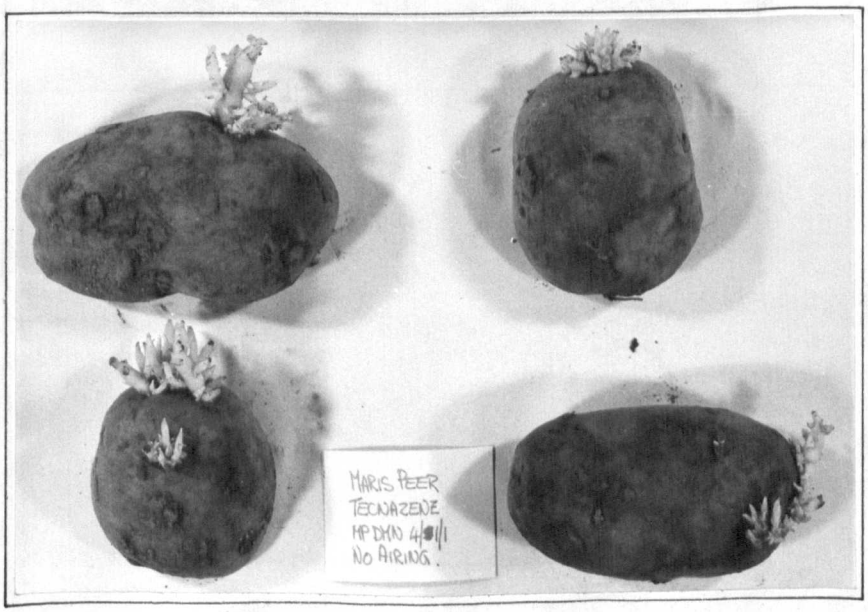


Plate 3.02a. First development experiment. Emergence of treatments 8 weeks after planting. Treatment time 116 days, airing time 8 days. cv. Maris Peer.

Untreated

Dimethylnaphthalene (100 mg kg^{-1}) treated

Plate 3.02b. First development experiment. Emergence of treatments 8 weeks after planting. Treatment time 116 days, airing time 8 days. cv. Maris Peer.

Dimethylnaphthalene (300 mg kg^{-1}) treated

Tecnazene (135 mg kg^{-1}) treated

Plate 3.03a. First development experiment. Emergence of treatments 8 weeks after planting. Treatment time 116 days, airing time 8 days. cv. Red Craigs Royal.

Untreated

Dimethylnaphthalene (100 mg kg^{-1}) treated

Plate 3.03b. First development experiment. Emergence of treatments 8 weeks after planting. Treatment time 116 days, airing time 8 days. cv. Red Craigs Royal.

Dimethylnaphthalene (300 mg kg^{-1}) treated

Tecnazene (135 mg kg^{-1}) treated

3.4 DISCUSSION

3.4.1 FIRST DEVELOPMENT EXPERIMENT

3.4.1.1 Sprout length control

The results are presented in Tables 3.01 and 3.02. When the tubers were examined after treatment, some boxes showed signs of anomalous sprout growth. In these boxes there were a few tubers which had untypically long sprouts. Such tubers were usually located in one corner of the box. With increasing treatment time this effect became more noticeable because the length of the anomalous sprouts was increasing. As the experiment progressed and more boxes were examined, it became increasingly clear that this effect was due to some factor other than chemical treatment. Two 10 kg boxes were used for each treatment. On many occasions only one box showed signs of anomalous sprouting. All chemical treatments were affected in the same way. The number of boxes showing the effect varied between each sampling date. Both cv. Maris Peer and Red Craigs Royal were affected, although cv. Maris Peer was to a much more marked extent. The possible reasons for this effect were considered to be due to the experimental method, which is discussed in Chapter 4. When sprout length after 74, 85 and 96 days' treatment was measured, a representative sample from the whole box was taken. By the time sprout length after 109 and 116 days' treatment was measured, anomalous sprout length was considered to be due to some factor other than chemical treatment. Therefore, tubers with untypically long sprouts were not included in the results. As the effect was noted more in cv. Maris Peer boxes, the results from these boxes were re-examined. Untypically long measurements were removed and the mean sprout length re-calculated. Table 3.01 presents mean sprout lengths of cv. Maris Peer including and excluding untypically long sprout measurements. It serves to show the magnitude of the effect, e.g. the mean sprout length of 100 tubers, cv. Maris Peer, treated for 85 days with 135 mg kg^{-1} tecnazene was 13.2 ± 32.3 mm. This result included 5 sprout lengths greater than 75 mm,

two of which exceeded 160 mm. When these 5 sprout lengths are excluded, the mean sprout length of 95 tubers was 6.7 ± 9.0 mm.

Sprout control by dimethylnaphthalene applied at 100 mg kg^{-1} was as good as tecnazene (135 mg kg^{-1}). At 300 mg kg^{-1}, dimethylnaphthalene sprout control was significantly better than tecnazene. For each chemical treatment, sprout control at 10°C for 116 days was not significantly different from sprout control for 74 days. These effects were shown by both cv. Maris Peer and Red Craigs Royal. Sprout control by dimethylnaphthalene can be seen in Plates 3.01a and 3.01b.

3.4.1.2 Sprout length after desprouting and airing

The results are presented in Tables 3.03 and 3.04. The samples were not treated for the same length of time (3.2.1.1). Therefore, treatment time should also be considered when comparing the effects of airing time. However, the following general comments can be made. For all treatments, sprout length increased with longer airing times. For each airing time, most chemical treatments had significantly less sprout growth compared to their corresponding untreated control. Sprout lengths of dimethylnaphthalene (100 mg kg^{-1}) treatments aired for 28 and 39 days were significantly longer than the corresponding tecnazene treatments. All of the dimethylnaphthalene (300 mg kg^{-1}) treatments had significantly less sprout growth than the corresponding untreated and tecnazene controls.

3.4.1.3 Emergence

The results are presented in Tables 3.05 - 3.08.

Untreated tubers emerged significantly faster than all the chemical treatments. Dimethylnaphthalene (100 mg kg^{-1}) treatments emerged significantly faster than tecnazene (135 mg kg^{-1}) treatments. Dimethylnaphthalene (300 mg kg^{-1}) treatments emerged significantly slower than tecnazene treatments. Total % emergence of untreated

tubers was highest of all the treatments. % emergence of dimethylnaphthalene (100 mg kg^{-1}) did not differ significantly from untreated but was significantly higher than tecnazene treated tubers. Significantly less tubers emerged when treated with dimethylnaphthalene (300 mg kg^{-1}) compared to all other treatments. % emergence of tecnazene treatments was significantly less than untreated tubers.

Treatment time should be considered when comparing airing time effects. Shorter treatment - longer airing time combinations significantly decreased emergence time and significantly increased % emergence compared to longer treatment - shorter airing time combinations.

In Tables 3.07 and 3.08 the emergence of every treatment - airing time combination are compared for each cultivar. Specific comparisons between the various treatment - airing time combinations are best made by referring to Tables 3.07 and 3.08. However, the following generalizations can be made.

Emergence of cv. Maris Peer was much better than cv. Red Craigs Royal. The emergence time of each treatment of cv. Maris Peer was in the order, 7 weeks airing time first, 4 week airing time next and one week airing time last. There were no significant differences in emergence time between all treatments of cv. Maris Peer, aired for 7 weeks. These combinations had the shortest emergence times. There were no significant differences in emergence time between untreated, dimethylnaphthalene (100 mg kg^{-1}) and tecnazene treatments of cv. Maris Peer, aired for 4 weeks. There was also no significant difference in emergence time between untreated, dimethylnaphthalene (100 mg kg^{-1}) and tecnazene treatments of cv. Maris Peer, aired for 1 week. Tubers of cv. Maris Peer, treated with dimethylnaphthalene (300 mg kg^{-1}) and aired for 4 weeks emerged in a time which was not significantly different from the time taken for all the other treatments, aired for one week. Emergence time of cv. Maris Peer treated with dimethylnaphthalene

(300 mg kg^{-1}) and aired for one week was significantly less than all other treatment - airing time combinations. There were no significant differences in total % emergence between all treatment - airing time combinations of cv. Maris Peer. % emergence did not fall below 95% for all combinations of cv. Maris Peer. The effect of one week airing time on the emergence of untreated, dimethylnaphthalene (100 and 300 mg kg^{-1}) and tecnazene treated tubers of cv. Maris Peer can be seen in Plates 3.02a and 3.02b.

Emergence of cv. Red Craigs Royal was much more severely affected by the various treatment - airing time combinations. The emergence of each treatment of cv. Red Craigs Royal was in the order, 7 weeks airing time first, 4 week airing time next, and one week airing time last. There were no significant differences in emergence time between untreated and dimethylnaphthalene (100 mg kg^{-1}) treated tubers of cv. Red Craigs Royal aired for 7 weeks and untreated tubers aired for 4 weeks. These treatment - airing time combinations had the shortest emergence airing times of cv. Red Craigs Royal. Emergence of cv. Red Craigs Royal tubers treated with tecnazene and aired for 7 weeks was significantly slower than untreated tubers aired for 7 weeks. On most occasions there was no significant difference between tecnazene and dimethylnaphthalene (100 mg kg^{-1}) treated tubers of cv. Red Craigs Royal aired for 7 weeks. Emergence of dimethylnaphthalene (100 mg kg^{-1}) treated tubers of cv. Red Craigs Royal aired for 4 weeks was on most occasions significantly slower than untreated tubers aired for 4 weeks. Emergence of cv. Red Craigs Royal tubers treated with tecnazene and aired for four weeks was significantly slower than untreated tubers aired for four weeks. There was no significant difference in emergence time between tecnazene and dimethylnaphthalene (100 mg kg^{-1}) treated tubers of cv. Red Craigs Royal, aired for 4 weeks. There was no significant difference in emergence time between untreated and dimethylnaphthalene (100 mg kg^{-1}) treated tubers of cv. Red Craigs Royal, aired for one week. On most occasions there was no significant difference in emergence

between tecnazene treated tubers of cv. Red Craigs Royal and untreated tubers aired for one week. Dimethylnaphthalene (100 mg kg^{-1}) treated tubers of cv. Red Craigs Royal aired for one week emerged significantly faster than tecnazene treated tubers aired for one week. There was significant differences in emergence time (i. e. slower) between tubers of cv. Red Craigs Royal treated with dimethylnaphthalene (300 mg kg^{-1}), aired for 7 weeks, and untreated tubers aired for 7 weeks and 4 weeks. Tubers of cv. Red Craigs Royal treated with dimethylnaphthalene (300 mg kg^{-1}), aired for four weeks or one week emerged significantly slower than all other treatment - airing time combinations. There was no significant difference in emergence time between tubers of cv. Red Craigs Royal treated with dimethylnaphthalene (300 mg kg^{-1}), aired for 4 weeks and one week. On most occasions there were no significant differences in % emergence of cv. Red Craigs Royal between untreated tubers, aired for 7 or 4 weeks and dimethylnaphthalene (100 mg kg^{-1}) treated tubers, aired for 7, 4 or 1 week. These treatment - airing time combinations of cv. Red Craigs Royal had the highest % emergence (81 - 95%). There was no significant differences in % emergence of cv. Red Craigs Royal between tubers treated with tecnazene and dimethyl naphthalene (100 mg kg^{-1}) aired for 7 or 4 weeks. % emergence of Red Craigs Royal untreated tubers aired for 7 or 4 weeks was significantly higher than tecnazene treated tubers aired for 7 or 4 weeks. There were no significant differences in % emergence of cv. Red Craigs Royal between, untreated, dimethylnaphthalene (100 mg kg^{-1}) and tecnazene treated tubers, aired for 1 week. There was no significant difference in % emergence of cv. Red Craigs Royal between untreated tubers, aired for 1 week and dimethylnaphthalene (300 mg kg^{-1}) treated tubers aired for 7 weeks. The % emergence of cv. Red Craigs Royal tubers treated with dimethylnaphthalene (300 mg kg^{-1}), aired for 4 or 1 week was significantly less than all other treatment - airing time combinations. There was no significant difference in % emergence of cv. Red Craigs Royal between tubers treated with dimethylnaphthalene (300 mg kg^{-1}) aired for 4 weeks and aired for 1 week. These treatment - airing time combinations had

the lowest % emergence of cv. Red Craigs Royal (48 - 56%). The effect of one week airing time on the emergence of untreated, dimethylnaphthalene (100 and 300 mg kg^{-1}) and tecnazene treated tubers of cv. Red Craigs Royal can be seen in Plates 3.03a and 3.03b.

The following important general points can be made. Chemical treatments delayed emergence compared to untreated controls. In most cases shorter treatments and airing periods between 4 and 7 weeks eliminated differences in emergence between untreated and chemical treated tubers. Dimethylnaphthalene (100 mg kg^{-1}) did not adversely affect emergence. Dimethylnaphthalene (300 mg kg^{-1}) significantly delayed emergence, particularly when airing times less than 7 weeks were adopted.

3.4.1.4 Yield

The results are presented in Tables 3.09 - 3.14.

The following points can be made regarding treatment and airing effects. There were no significant differences between total yield of untreated, dimethylnaphthalene (100 mg kg^{-1}) and tecnazene treated tubers. Yield of dimethylnaphthalene (300 mg kg^{-1}) treated tubers was significantly less than all the other treatments. Untreated tubers had a significantly higher yield of large and a significantly lower yield of medium and small sized tubers compared to all other treatments. Tecnazene treated tubers had a significantly lower yield of large and significantly higher yield of medium and small sized tubers compared to untreated tubers. Dimethylnaphthalene (100 mg kg^{-1}) had a significantly lower yield of large and a significantly higher yield of medium and small sized tubers compared to untreated tubers. Dimethylnaphthalene (100 mg kg^{-1}) had a significantly higher yield of large and a significantly lower yield of medium sized tubers than tecnazene treated tubers. There were no significant differences between the yield of small sized tubers of dimethylnaphthalene (100 mg kg^{-1}), tecnazene and dimethylnaphthalene (300 mg kg^{-1}) treated tubers. Dimethylnaphthalene (300 mg kg^{-1}) treated

tubers had a significantly lower yield of large and a significantly higher yield of medium and small sized tubers, compared to untreated tubers. Dimethylnaphthalene (300 mg kg^{-1}) treated tubers had a significantly lower yield of medium sized tubers compared to tecnazene treated tubers. There were no significant differences in yield of large sized tubers between dimethylnaphthalene (300 mg kg^{-1}) and tecnazene treated tubers. Untreated tubers had a significantly higher % large yield and a significantly lower % medium yield compared to all other treatments. Dimethylnaphthalene (100 and 300 mg kg^{-1}) treated tubers had significantly lower % large yield and a significantly higher % medium yield compared to untreated tubers. Dimethylnaphthalene (100 and 300 mg kg^{-1}) treated tubers had a significantly higher % large yield and a significantly lower % medium yield compared to tecnazene treated tubers. Treatment time should also be considered when comparing the results of airing time effects. Shorter treatment - longer airing time combinations significantly increased total yield and yield of large sized tubers. The longest treatment - shortest airing time combination reduced large, medium, small and total yield compared to the shortest treatment - longest airing time combination.

The following are the most important points. There were no significant differences in total yield of untreated, tecnazene and dimethylnaphthalene (100 mg kg^{-1}) treated tubers. Dimethylnaphthalene (300 mg kg^{-1}) treatment significantly reduced total yield. Shorter treatment - longer airing time combinations significantly increased yield. Tecnazene treatment significantly increased % medium yield without significantly reducing total yield. Although dimethylnaphthalene (100 mg kg^{-1}) treatment significantly increased % medium compared to untreated tubers, the increase was significantly less than the increase in % medium caused by tecnazene treatment.

In Tables 3.11, 3.12, 3.13 and 3.14 the yield of every treatment - airing time combination are compared for each cultivar. Specific comparisons between the various treatment - airing time combinations are

best made by referring to these tables. However, the following generalizations can be made. Total yield of cv. Maris Peer was affected to a much lesser extent than cv. Red Craigs Royal, by the various treatment - airing time combinations. There was only one significant difference between total yield of cv. Maris Peer treatment - airing time combinations, i. e. the total yield of dimethylnaphthalene (300 mg kg^{-1}) treated tubers, aired for 1 week was significantly less than the yield of tecnazene treated tubers, aired for 7 weeks. All airing times of untreated and seven weeks airing time of dimethylnaphthalene (100 mg kg^{-1}) treated tubers of cv. Maris Peer had significantly higher yields of large sized tubers and significantly lower yields of medium and small sized tubers. These treatment - airing time combinations also had higher % large, lower % medium and lower % small yields. Significantly low yields of large sized tubers and significantly high yields of medium and small sized tubers were caused by tecnazene treatments with longer treatment - shorter airing times. Dimethylnaphthalene (100 mg kg^{-1}) treatments with longer treatment - shorter airing times had similar effects on the yield of cv. Maris Peer tubers as tecnazene treatments with shorter treatment - longer airing times. Dimethylnaphthalene (300 mg kg^{-1}) treatments with shorter treatment - longer airing times had similar effects on the yield of cv. Maris Peer as tecnazene treatments with longer treatments - shorter airing times. The various treatment - airing time combinations had a more severe effect on the total yield of cv. Red Craigs Royal. Untreated tubers with a 1 week airing period had a significatnly lower total yield of cv. Red Craigs Royal. Dimethylnaphthalene (300 mg kg^{-1}) treated tubers of cv. Red Craigs Royal, aired for 4 and 1 week periods had significantly lower total yields. There were no significant differences in large, medium, small and total yield between tubers of cv. Red Craigs Royal treated with all treatments, aired for 7 weeks. Generally, all dimethylnaphthalene (100 mg kg^{-1}) treatment - airing time combinations did not significantly reduce large, medium, small and total yield of cv. Red Craigs Royal.

3.4.2 SECOND DEVELOPMENT EXPERIMENT

Results of sprout length after treatment and after desprouting and airing are presented in Table 3.15.

The results show that the minimum application rate of dimethylnaphthalene isomer mixture is 100 mg kg^{-1}. As a result of later analysis (Chapter A2) the main component of the isomer mixture was found to be 1, 6-dimethylnaphthalene. These sprout growth results, therefore, confirmed the earlier assessment experiment results (2.3) in which the minimum application rate of 1, 6-dimethylnaphthalene was 100 mg kg^{-1}. Sprout control at 175 mg kg^{-1} was as good as application at 300 mg kg^{-1}. At application rates of 175 mg kg^{-1} and above, sprout control was at the level necessary for tubers intended for long-term storage (3.4.4).

None of the application rates significantly retarded sprout growth after 5 weeks airing. Sprout length after airing was significantly longer for most dimethylnaphthalene treatments compared to tecnazene treatment. It is noteworthy that many treatments had significantly longer sprouts, after airing, than untreated controls.

3.4.3 THIRD DEVELOPMENT EXPERIMENT

A visual inspection of the tubers after treatment, before grading, showed that most untreated control tubers had sprouts 25 - 35 mm long. Both dimethylnaphthalene and tecnazene (135 mg kg^{-1}) treated tubers had sprouts 1 - 2 mm long. Many of the untreated tuber sprouts were removed during grading.

Emergence and yield results are presented in Tables 3.16 and 3.17.

There were no significant differences in % total emergence between all tuber treatments. Tecnazene (135 mg kg^{-1}) treated tubers emerged significantly slower than all the other treatments. T50 for untreated tubers was significantly slower than tecnazene (68 mg kg^{-1})

treated tubers. There were no other significant differences in emergence time between untreated, tecnazene (68 mg kg^{-1}) and dimethylnaphthalene treated tubers.

There were no significant differences in total yield between all tuber treatments. Dimethylnaphthalene treatment significantly reduced yield of large tubers and significantly increased yield of medium and small tubers compared to untreated tubers. There were no significant differences between large, medium and small yield of dimethylnaphthalene treated tubers compared to tecnazene (135 mg kg^{-1}) treated tubers. Dimethylnaphthalene treatment significantly reduced yield of large tubers compared to tecnazene (68 mg kg^{-1}) treated tubers. There were no significant differences in large, medium and small yield of tecnazene (68 mg kg^{-1}) treated tubers compared to untreated tubers. Dimethylnaphthalene treatment significantly decreased % large and significantly increased % medium yield, compared to untreated and tecnazene (68 mg kg^{-1}) treated tubers. There were no significant differences in % large and % medium yield between dimethylnaphthalene and tecnazene (135 mg kg^{-1}) treatments. Tecnazene (135 mg kg^{-1}) treatment significantly decreased % large and significantly increased % medium yield compared to untreated tubers. There were no significant differences in % large and % medium yield between untreated and tecnazene (68 mg kg^{-1}) treated tubers.

The following are the most important points. There were no significant differences between total yield of all treatments. Dimethylnaphthalene treatment increased the yield of medium sized tubers to the same extent as tecnazene (135 mg kg^{-1}) treatment and to a significantly greater extent than treatment with tecnazene (68 mg kg^{-1}).

3.4.4 FOURTH DEVELOPMENT EXPERIMENT

The application rates of dimethylnaphthalene were based on the results of the second development experiment. 100 mg kg^{-1} had been shown to be the minimum recommended application rate. 150 mg kg^{-1}

and 200 mg kg^{-1} application rates were intended to cope with the longer treatment period.

Results are presented in Table 3.18. All dimethylnaphthalene treatments significantly reduced sprout length compared to untreated controls. Sprout control was better with increasing dimethylnaphthalene application rates. However, the level of sprout control obtained by applying 200 mg kg^{-1} dimethylnaphthalene was totally inadequate for tubers intended for long-term storage. Accidental treatment of untreated controls with chlorpropham serves to show the level of sprout control which is necessary for tubers under long-term storage.

3.4.5 RESIDUE LEVELS

Residue levels of 1, 4-dimethylnaphthalene in treated tubers were studied. Unpeeled tubers were analysed by methods detailed in Chapter A2. The results (Table 3.19) show that levels of 3 - 4 mg kg^{-1} were found in unpeeled tubers treated with 100 mg kg^{-1} 1, 4-dimethylnaphthalene. Airing tubers for one week did not reduce residue levels. Airing tubers for 7 weeks caused a 30% drop in residue levels. Tubers treated with 300 mg kg^{-1}, 1, 4-dimethylnaphthalene had residue levels of 11 mg kg^{-1}.

3.4.6 HEADSPACE CONCENTRATIONS

Headspace concentrations of 1, 4-dimethylnaphthalene in 10 kg boxes containing treated tubers were studied. They were determined by the methods discussed in Chapter A1. 5.1. Three application rates of dimethylnaphthalene are considered, based on sprout length results from the first and second development experiments (Tables 3.01, 3.02, and 3.15).

(a) 50 mg kg^{-1}. At this application rate, successful sprout suppression was not achieved.

(b) 100 mg kg^{-1}. At this application rate, sprout suppression as good as tecnazene (135 mg kg^{-1}) was achieved.

(c) 300 mg kg^{-1}. At this application rate, sprout suppression was significantly better than tecnazene (135 mg kg^{-1}). Sprout suppression at this application rate was at the level necessary for tubers intended for long-term storage.

The headspace results (Table 3.20) suggest that the minimum effective headspace concentration of 1,4-dimethylnaphthalene is between 3 and 6 mg m^{-3}. Headspace concentrations of 50 mg kg^{-1} treatments had initial levels below 3 mg m^{-3}. Headspace concentrations of 300 mg kg^{-1} treatments did not fall below 3 mg m^{-3}. Headspace concentrations of 100 mg kg^{-1} treatments had initial levels of 6.8 mg m^{-3}, which fell below 3 mg m^{-3} between 27 and 61 days after treatment.

3.4.7 TOXICOLOGY AND COST

The toxicity of dimethylnaphthalene is practically uninvestigated. An LD_{50} of 5 g kg^{-1} in the rat for the 1,6-isomer (Anon, 1976b) was the only oral data identified in a comprehensive search of the literature by the British Industrial Biological Research Association in May 1978. As use of dimethylnaphthalene could lead to a maximum residue level of 3 mg kg^{-1}, an average consumer of tubers (55 oz/week; MAFF 1973 figures) would have a maximum daily intake of 0.67 mg dimethylnaphthalene. To justify such dietary intakes, the authorities would require reassuring results from long-term toxicological studies.

In 1977, a dimethylnaphthalene isomer mixture containing diphenyl and ethylnaphthalene as major impurities was available in commercial quantities. The cost was £0.87 kg^{-1}.

3.5 CONCLUSIONS

Dimethylnaphthalene is an effective sprout suppressant. Under laboratory experimental conditions, dimethylnaphthalene isomer mixture applied at 100 mg kg^{-1} controlled sprout growth as well as tecnazene applied at 135 mg kg^{-1}. Under the conditions of a commercial seed potato store, dimethylnaphthalene (100 mg kg^{-1}) also proved to be as

effective as tecnazene (135 mg kg^{-1}).

Dimethylnaphthalene is suitable for use on seed tubers. Treated tubers are best aired for a period of 4 to 7 weeks before planting. Under these conditions dimethylnaphthalene (100 mg kg^{-1}) did not adversely affect emergence or total yield of treated tubers. Tubers given a high application level of dimethylnaphthalene (300 mg kg^{-1}) will emerge more slowly and could have lower yields. However, airing periods of 7 weeks can significantly reduce the effect of high application rates of dimethylnaphthalene. Treatment with dimethylnaphthalene will increase yield of medium sized tubers. The results suggest that the increase in medium yield caused by dimethylnaphthalene (100 mg kg^{-1}) is not as great as the increase caused by tecnazene (135 mg kg^{-1}), but is greater than the increase caused by tecnazene (68 mg kg^{-1}).

One initial application of 200 mg kg^{-1} dimethylnaphthalene is not sufficient to maintain adequate sprout control for long-term storage. This is particularly the case in the higher temperature, ventilated stores of tubers intended for processing. Under these conditions dimethylnaphthalene must be re-applied. One possible method of re-applying dimethylnaphthalene is as a vapour through ventilation ducts. Studies have shown that the minimum effective headspace concentration of dimethylnaphthalene is between 3 and 6 mg m^{-3}. Successful application of dimethylnaphthalene as a vapour must maintain these minimum headspace concentrations. Applying controlled amounts of dimethylnaphthalene vapour will have an additional advantage of minimizing the high residue levels caused by large initial application rates.

Finally, dimethylnaphthalene is available in commercial quantities at an economic cost.

CHAPTER 4

ASSESSMENT AND DEVELOPMENT EXPERIMENT METHODOLOGY

4.1 INTRODUCTION

The aim of this chapter is to consider the methods used in the previously described assessment (Chapter 2) and development (Chapter 3) experiments. An important aspect of the project was the development of suitable small scale laboratory methods. These methods were used to assess the sprout suppressant properties of a range of chemicals and hopefully accurately predict their performance under commercial conditions.

Volatile sprout suppressant chemicals have been assessed by several laboratory methods. They have been applied as vapours introduced directly into air surrounding tubers and as volatile solids or liquids distributed among the tubers.

It was considered that the most important distinction between these methods was whether or not the experimental conditions would maintain a constant headspace concentration of the test chemicals throughout the assessment period. It has been shown with several volatile chemicals that there is a minimum effective headspace concentration, below which sprout suppressant activity will progressively diminish (Meigh, 1969; Burton, 1958a). Without constantly maintained headspace concentration, inevitable dissipation of the volatile chemical will occur with eventual loss in sprout suppressant activity. Nonanol (Burton, 1958b) and tecnazene (Brown and Reavill, 1954; Beveridge et al., 1976) treatments clearly showed this effect. When headspace concentrations of these chemicals are lowered by airing, sprout suppression ceases.

The concept of a minimum effective headspace concentration is not intended to imply that the mode of action is directly dependent on the chemical being present as a vapour. It is more probable that sprout

suppressant activity will depend directly on a certain minimum chemical concentration being maintained at the point of action in the cell. In simplest terms, sprout suppressant activity will depend directly on the chemical residue concentration within the tuber. The effective minimum headspace concentration is the headspace concentration at which the minimum residue level within the tuber will be reached and maintained.

In considering laboratory assessment methods they were divided into two broad categories, (a) methods in which constant headspace concentrations are maintained, and (b) methods which use one initial application which will maintain minimum effective residue and/or headspace concentrations despite loss through volatilization to the surrounding air.

Some examples of these categories are briefly considered:

(a) Constant headspace laboratory methods

The simplest example of this method is that of storing tubers in a closed box along with the test chemical. Using this method, α-pinene has been shown to be an effective sprout growth inhibitor when applied in an alumina solid carrier to 10 kg tubers, stored in a sealed metal container (Dalziel, 1975). Another example of this method was used to show the successful sprout suppressant activity of dipropargyl ether (Hessel, 1961). Tubers were placed in a closed box (except for a 3.2 mm wide vent) with a dish containing 50 cm^3 dipropargyl ether. Thus the tubers were stored under a constant headspace concentration which was largely determined by the vapour pressure of dipropargyl ether at the particular storage temperature. Perhaps the best constant headspace methods are those in which a known amount of vapour is added to a stream of ventilating air. The stream of air is then passed over a sample of tubers (Meigh, 1969). The chemicals can be applied at constant rates, by diffusion through silicone rubber tubes placed in the air stream (Meigh, 1967). Accurate headspace concentrations are calculated by measuring the ventilation rate and loss in weight of the test chemical.

Using these methods, several chemicals have been shown to be effective sprout suppressants at known headspace concentrations (Meigh, 1969; Meigh et al., 1973). These constant headspace methods measure sprout suppressant activity in terms of the minimum headspace concentration under which sprout control will be maintained.

(b) One initial application laboratory methods

In these methods the tubers are treated with one initial application of the test chemical and then stored for a period of time under conditions which will not maintain constant headspace levels. Dissipation of the volatile chemicals under these storage conditions will lead to an eventual loss of activity. The initial applications can be as vapours introduced directly into air surrounding the tubers (Sawyer and Dallyn, 195), or as volatile solids or liquids distributed among the tubers, e. g. impregnated on paper (Denny et al., 1942), mixed with an inert solid carrier (Brown and Reavill, 1954; Rhodes et al., 1950; Ellison, 1952) or coated on the tuber surface in a suitable solvent, wax or wax emulsion (Findlen, 1955). After application the tuber samples can be stored by a variety of methods, e. g. boxes with lids (not sealed) (Brown and Reavill, 1954), paper bags (Findlen, 1955; Ellison, 1952) or earthenware jars covered with paper (Rhodes, 1950; Denny et al., 1942).

These methods measure sprout suppressant activity in terms of an initial application rate which is necessary to maintain sprout control over a period of time, under the prescribed experimental conditions.

For the assessment and development experiments (Chapters 2 and 3) it was decided that one initial application of the test chemicals would be used. The reason for this decision was that the laboratory method was intended to predict performance under commercial conditions. It was considered that one initial application was the most common method of applying sprout suppressant chemicals in commercial stores. Tecnazene, the most commonly used sprout suppressant in Britain (Anon, 1978), is almost exclusively applied as one initial dusting

at the start of storage. The laboratory method was, therefore, designed to find initial application levels of test chemicals which would successfully maintain sprout suppression over a prescribed treatment period. The test chemicals were compared to untreated and tecnazene treatments under similar conditions.

Constant headspace methods were not used because they measure sprout suppressant activity in terms of a minimum effective headspace concentration below which re-application is necessary. It is difficult to relate this headspace concentration to a required initial application rate. However, constant headspace concentration laboratory methods can be of use when, (a) facilities for re-application are available in the commercial stores, and (b) accurate measurement of headspace concentrations in the stores is possible.

The assessment and development experiments were part of a series of annual experiments conducted by the Agricultural Chemistry section, in which the effects of chemical sprout suppressant treatments on seed potato tubers were studied. Much of the design, management and analysis was based on the accumulated experience of the earlier experiments which were part of the research programme conducted by Dr. John Dalziel. I wish to acknowledge the continual assistance and encouragement given by Dr. Dalziel during all stages of the assessment and development experiments.

In the assessment experiments, the initial applications were applied to tubers stored in 10 kg capacity boxes with loosely fitting lids. Treatment periods of 12 to 14 weeks at 10^{o}C were used. By including a tecnazene control, the test chemicals' performance could be related to a chemical known to work under commercial conditions. The test chemicals were considered successful if sprout growth was similar or less than the tecnazene control. Perhaps the only justification for these somewhat arbitrary conditions was that they appeared to work. The method accurately predicted the application rates of dimethylnaphthalene

which would be necessary under the conditions of a commercial seed potato store. The small scale field experiments also accurately assessed the effects of dimethylnaphthalene treatments on subsequent emergence and yield of treated tubers under commercial conditions.

One feature of the field experiments worthy of mention, was the development of the experimental design. In the assessment experiment (2. 2. 4), the ends of each treatment plot were separated by a 2 m drill containing no tubers. This blank space allowed adequate separation of the plots as the potato harvester passed down the length of the field harvesting one complete drill at a time. This design was considerably improved in the following season's development experiment field work (3. 2. 1. 2). Instead of separating plots by blank spaces, the plots were arranged in such a way that each plot was surrounded by plots containing tubers of the other cultivar. Cultivars were chosen which had similar maturity characteristics yet possessed distinctly different tuber colours. When harvested the plots were easily distinguished by tuber colour. This design offered several advantages. The area occupied by the experiment was considerably reduced. Thus the more compact design made it possible to apply chemical pesticides using a knapsack hand-spray. In this way, herbicide treatments could be discriminantly applied, particularly during the important period when plant emergence was being studied. Later on in the season, fungicide treatments could be applied without tractor wheels damaging the plant foliage. Weed control was only necessary until the potato plants covered the drills. During the previous season, weeds in blank spaces demanded continuous attention throughout. During harvesting, neighbouring plots could be easily distinguished. Planting cultivars with different tuber colours proved a more successful means of separating plots than blank spaces.

Many questions were raised by the assessment and development experiments. The questions were principally concerned with,

(a) the compatibility between results of the assessment experiments and results of other studies using constant headspace concentration methods,

(b) explaining the box effects noted in the assessment and development experiments, e. g. anomalous sprouting,

(c) explaining why one initial application of dimethylnaphthalene (200 mg kg^{-1}) was not successful during long-term storage, and

(d) investigating the feasibility of applying dimethylnaphthalene as a vapour introduced directly to the air surrounding tubers on a commercial scale.

Three headspace concentration experiments were carried out in the hope that some of these questions would be answered.

4.1.1 Headspace studies

First headspace experiment

The aim of this experiment was to explain some of the results of the assessment experiments. Dimethylnaphthalene, benzothiazole, carvone, pulegone, citral, α-pinene and methyl salicylate had been shown to be successful sprout suppressants using constant headspace laboratory methods (Dalziel, 1975; Meigh, 1969; Meigh et al., 1973). Only dimethylnaphthalene and benzothiazole were successful when applied at 100 mg kg^{-1} in the assessment experiments. Of the remainder, only pulegone, carvone and methyl salicylate were successful at 500 mg kg^{-1}. Determining headspace concentrations of tubers in 10 kg boxes would provide a means by which the results of the two different laboratory methods could be compared. In this way an explanation of the assessment experiment results could be found. Headspace concentrations of carvone, pulegone, citral and 1, 4-dimethylnaphthalene were studied. They were determined for duplicate 5 kg tuber samples held in 10 kg boxes at 9°C. Tecnazene (135 mg kg^{-1} and chlorpropham (10 mg kg^{-1}) treated tubers were also included in the experiment. Headspace concentrations were measured on several occasions during a 14 week treatment period.

Second headspace experiment

The aim of this experiment was to explain sprout length after treatment results from the second development experiment (Table 4.01). There were two main results which required further investigation:

(a) The mean sprout length of some application rates of dimethylnaphthalene were longer than the mean sprout length of lower application rates.

(b) There was a sudden drop in mean sprout length between treatments of 150 mg kg^{-1} and 175 mg kg^{-1}. Sprout control at 150 mg kg^{-1} was not any better than at 100 mg kg^{-1}. Sprout control at 175 mg kg^{-1} was as good as sprout control at 300 mg kg^{-1}.

It was also hoped that this experiment could help explain the anomalous sprouting effects noted in the first and second development experiments.

The headspace concentrations of 5 application rates of 1,4-dimethylnaphthalene were studied. The rates were based on the results of the second development experiment; 50 mg kg^{-1}, at which rate sprout control was inadequate; 100 mg kg^{-1} sprout control was as good as tecnazene (135 mg kg^{-1}); 150 mg kg^{-1}, sprout control was not better than 100 mg kg^{-1}; 175 mg kg^{-1}, sprout control was as good as 300 mg kg^{-1}; 300 mg kg^{-1}, sprout control was significantly better than tecnazene (135 mg kg^{-1}). The headspace concentrations were determined for duplicate 5 kg potato samples held in 10 kg boxes at 9°C. The headspace concentrations were determined on five occasions during a 14 week treatment period.

Third headspace experiment

The aim of this experiment was to study the headspace concentrations of tecnazene and chlorpropham in a commercial 4,000 tonne bulk store. Headspace concentrations of tecnazene were determined 6 hours, 24 days and 38 days after treatment. The headspace concentration

of chlorpropham was determined 3 days after treatment. Chlorpropham headspace concentrations were compared to headspace concentrations previously determined in a 3,000 tonne, 1 tonne box store. Tecnazene headspace concentrations in the 4,000 tonne bulk store were compared to the headspace concentration of 5 kg samples in 10 kg boxes, treated in the laboratory.

4.2 MATERIALS AND METHODS

The materials and methods used in these headspace experiments are described in detail in Chapter A1.5.

4.3. RESULTS

Table 4.01. Second development experiment. Mean sprout length of tubers after treatment and after airing (desprouted before airing). Treatments = untreated, dimethylnaphthalene (DMN) and tecnazene (Tec), treatment time = 14 weeks, airing time = 5 weeks, temperature = 10°C. Repeat of Table 3.15.

Cultivar	Treatment	Sprout length after treatment (mm)		Sprout length after airing (mm)	
		mean	S. D.	mean	S. D.
Redskin	Untreated	154.4	81.1	13.1	7.0
	25 mg kg^{-1} DMN	65.2^{ab}	40.1	17.6^{ab}	6.9
	50 mg kg^{-1} DMN	36.3^{ab}	45.2	13.7^{b}	6.6
	75 mg kg^{-1} DMN	42.4^{ab}	32.4	16.9^{ab}	11.0
	100 mg kg^{-1} DMN	11.0^{ab}	23.4	14.0^{b}	8.1
	125 mg kg^{-1} DMN	12.9^{ab}	21.8	16.2^{ab}	7.5
	150 mg kg^{-1} DMN	14.5^{a}	15.8	18.8^{ab}	7.7
	175 mg kg^{-1} DMN	3.2^{ab}	6.6	10.8^{a}	5.4
	200 mg kg^{-1} DMN	6.9^{ab}	10.9	13.5^{b}	6.6
	300 mg kg^{-1} DMN	2.6^{ab}	5.9	11.6	4.9
	135 mg kg^{-1} Tec	20.6	23.1	10.2	5.0
Record	Untreated	114.6	73.3	18.6	7.0
	25 mg kg^{-1} DMN	81.9^{ab}	50.0	22.9^{ab}	9.3
	50 mg kg^{-1} DMN	35.6^{ab}	25.3	27.5^{ab}	11.6
	75 mg kg^{-1} DMN	61.5^{ab}	33.0	25.3^{ab}	8.7
	100 mg kg^{-1} DMN	18.7^{a}	17.8	21.7^{ab}	5.9
	125 mg kg^{-1} DMN	32.0^{ab}	25.5	21.5^{ab}	7.9
	150 mg kg^{-1} DMN	36.8^{ab}	24.3	26.6^{ab}	10.4
	175 mg kg^{-1} DMN	5.5^{ab}	11.7	19.6	7.7
	200 mg kg^{-1} DMN	9.1^{ab}	21.9	22.2^{ab}	7.9
	300 mg kg^{-1} DMN	4.0^{ab}	6.9	20.3^{b}	7.1
	135 mg kg^{-1} Tec	16.3	20.0	17.1	7.7

a Significantly different from corresponding untreated control mean ($p < 0.05$).
b Significantly different from corresponding tecnazene mean ($p < 0.05$).

Table 4.02. Headspace concentrations of carvone, pulegone and citral in 10 kg boxes. Tuber sample size 5 kg, cv. Record, temperature 9°C.

Chemical	Treatment/ box number	Headspace concentration[a] ($mg\ m^{-3}$)				Sprout length (mm)	
		10 - 11[b]	26 - 27	60	97 - 98	mean	S. D.
carvone	100 mg kg^{-1}/1	3.7	1.0	0.5	0.2	177.2	42.1
	100 mg kg^{-1}/2	2.5	0.9	0.4	0.1	178.0	45.6
	500 mg kg^{-1}/1	20.8	8.1	2.6	1.3	5.1	11.9
	500 mg kg^{-1}/2	12.8	3.9	2.1	0.7	21.8	32.1
pulegone	100 mg kg^{-1}/1	5.1	2.1	0.5	0.1	201.4	46.3
	100 mg kg^{-1}/2	6.4	3.7	1.0	0.7	179.8	40.1
	500 mg kg^{-1}/1	38.3	11.7	2.8	1.5	39.1	36.4
	500 mg kg^{-1}/2	38.8	20.2	8.0	5.2	5.0	5.0
citral	100 mg kg^{-1}/1	0.2	0.4	-[c]	-	211.3	62.7
	100 mg kg^{-1}/2	0.2	0.1	-	-	203.6	48.3
	500 mg kg^{-1}/1	3.0	1.0	-	-	188.8	72.0
	500 mg kg^{-1}/2	3.9	1.2	-	-	177.2	71.6

a Mean headspace concentration compiled from Tables A1. 29, A1. 30 and A1. 31.

b Number of days after treatment. Analyses proceeded over a period of days, e. g. 10 to 11 days after treatment.

c No analysis carried out

Table 4.03. Headspace concentrations of 1,4-dimethylnaphthalene, tecnazene and chlorpropham in 10 kg boxes. Tuber sample size 5 kg, cv. Maris Peer, temperature 9°C.

Chemical	Treatment/ box number	Headspace concentration[a] (mg m^{-3})					Sprout length (mm)	
		3[b]	13 - 16	27	61	98 - 99	mean	S.D.
1,4-dimethyl-naphthalene	50 mg kg^{-1}/1	2.5	1.5	1.1	0.6	0.2	74.9	36.7
	50 mg kg^{-1}/2	2.7	1.5	1.0	0.5	0.3	55.2	39.0
	100 mg kg^{-1}/1	6.3	3.7	3.4	1.7	1.2	1.0	0.0
	100 mg kg^{-1}/2	7.3	4.1	3.3	2.3	1.6	1.0	0.0
	150 mg kg^{-1}/1	6.3	6.1	4.5	3.1	1.9	1.0	0.0
	150 mg kg^{-1}/2	7.8	6.1	4.6	2.9	2.0	1.0	0.0
	175 mg kg^{-1}/1	7.1	5.7	3.9	2.8	1.6	1.0	0.0
	175 mg kg^{-1}/2	7.8	5.7	4.3	2.7	2.2	1.0	0.0
	300 mg kg^{-1}/1	9.7	9.5	6.8	6.8	3.4	1.0	0.0
	300 mg kg^{-1}/2	12.0	11.0	6.4	6.0	4.5	1.0	0.0
tecnazene	135 mg kg^{-1}/1	-[c]	0.6	-	0.4	0.5	6.2	9.6
	135 mg kg^{-1}/2	-	0.5	-	0.4	0.5	10.2	18.3
chlorpropham	10 mg kg^{-1}/1	-	n.d.[d]	-	-	-	3.7	3.0
	10 mg kg^{-1}/2	-	n.d.	-	-	-	5.1	5.9

[a] Mean headspace concentration compiled from Tables A1.28 and A1.33.

[b] Number of days after treatment. Analyses proceeded over a period of days, e.g. 13 to 16 days after treatment.

[c] No analysis carried out.

[d] Not detected

Table 4.04. Headspace concentration of tecnazene and chlorpropham in a 4,000 tonne, long-term bulk store, cv. Pentland Dell and Record.

Chemical	Rate	Formulation	Headspace concentration[a] (mg m^{-3})			
			6 hours	3 days	24 days	38 days
tecnazene	37.5 mg kg^{-1}	granular[b]	0.22	-[d]	0.17	0.12
chlorpropham	10 - 20 mg kg^{-1}	atomized solution[c]	-	0.055[e]	-	-

[a] Mean headspace concentration 6 hours, 3 days, 24 days and 38 days after treatment. Store temperature 6 hours after treatment was 13°C. On all other sampling dates, store temperature was 9°C. Compiled from Tables A1.37 and A1.38.

[b] Applied as store was filled.

[c] Applied 35 days after store filling had been completed.

[d] No analysis carried out.

[e] Headspace concentrations of chlorpropham above 3 one tonne boxes held in a 3,000 tonne store were 0.062, 0.033 and 0.021 mg m^{-3} (Table A1.38). The samples were taken in April 1978. Chlorpropham had been applied (10 - 20 mg kg^{-1}; atomized solution) on several occasions previously.

Table 4.05. Headspace concentration of tecnazene in 10 kg boxes 1, 16, 61 and 98 days after treatment. Sample size 5 kg, cv. Maris Peer, temperature 9°C.

Storage season	Formulation	Rate/ box number	Headspace concentration[a] ($mg\ m^{-3}$)			
			1 day	16 days	61 days	98 days
1977-78	Fusarex dust	135 mg kg^{-1}/1	-[b]	0.63	0.41	0.47
		135 mg kg^{-1}/2	-	0.50	0.41	0.45
1978-79	Fusarex dust	135 mg kg^{-1}/1	0.29	0.32	-	-
		135 mg kg^{-1}/2	0.23	0.33	-	-
1978-79	Hortag granules	37.5 mg kg^{-1}/1	0.28	0.02	-	-
		37.5 mg kg^{-1}/2	0.27	0.07	-	-

[a] Mean headspace concentration compiled from Tables A1.33 and A1.34.

[b] No analysis carried out.

Table 4.06. Log headspace concentration versus time plots. Correlation coefficients of plots in Figures 4.01, 4.02, 4.03 and 4.04.

Figure	Chemical	Treatment/box number	Correlation coefficient[a]
4.01	1,4-dimethyl-naphthalene	50 mg kg^{-1}/1 and 2	-0.966
		100 mg kg^{-1}/1 and 2	-0.942
		150 mg kg^{-1}/1 and 2	-0.985
		175 mg kg^{-1}/1 and 2	-0.961
		300 mg kg^{-1}/1 and 2	-0.907
4.02	1,4-dimethyl-naphthalene	50 mg kg^{-1}/1	-0.974
		50 mg kg^{-1}/2	-0.957
		100 mg kg^{-1}/1	-0.968
		100 mg kg^{-1}/2	-0.938
		150 mg kg^{-1}/1	-0.991
		150 mg kg^{-1}/2	-0.982
		175 mg kg^{-1}/1	-0.980
		175 mg kg^{-1}/2	-0.950
		300 mg kg^{-1}/1	-0.936
		300 mg kg^{-1}/2	-0.900
4.03	carvone	100 mg kg^{-1}/1	-0.962
		100 mg kg^{-1}/2	-0.976
		500 mg kg^{-1}/1	-0.973
		500 mg kg^{-1}/2	-0.968
4.04	pulegone	100 mg kg^{-1}/1	-0.992
		100 mg kg^{-1}/2	-0.962
		500 mg kg^{-1}/1	-0.960
		500 mg kg^{-1}/2	-0.971

[a] Corresponding significance of $p < 0.01$ for all values.

FIGURE 4.01 Headspace Concentration (mg m^{-3}) of 1,4-Dimethylnaphthalene in 10kg Boxes Containing Treated Tubers, cv, Maris Peer, Sample Size 5kg Temperature 9°C. Combined Data of Duplicate Treatment Boxes

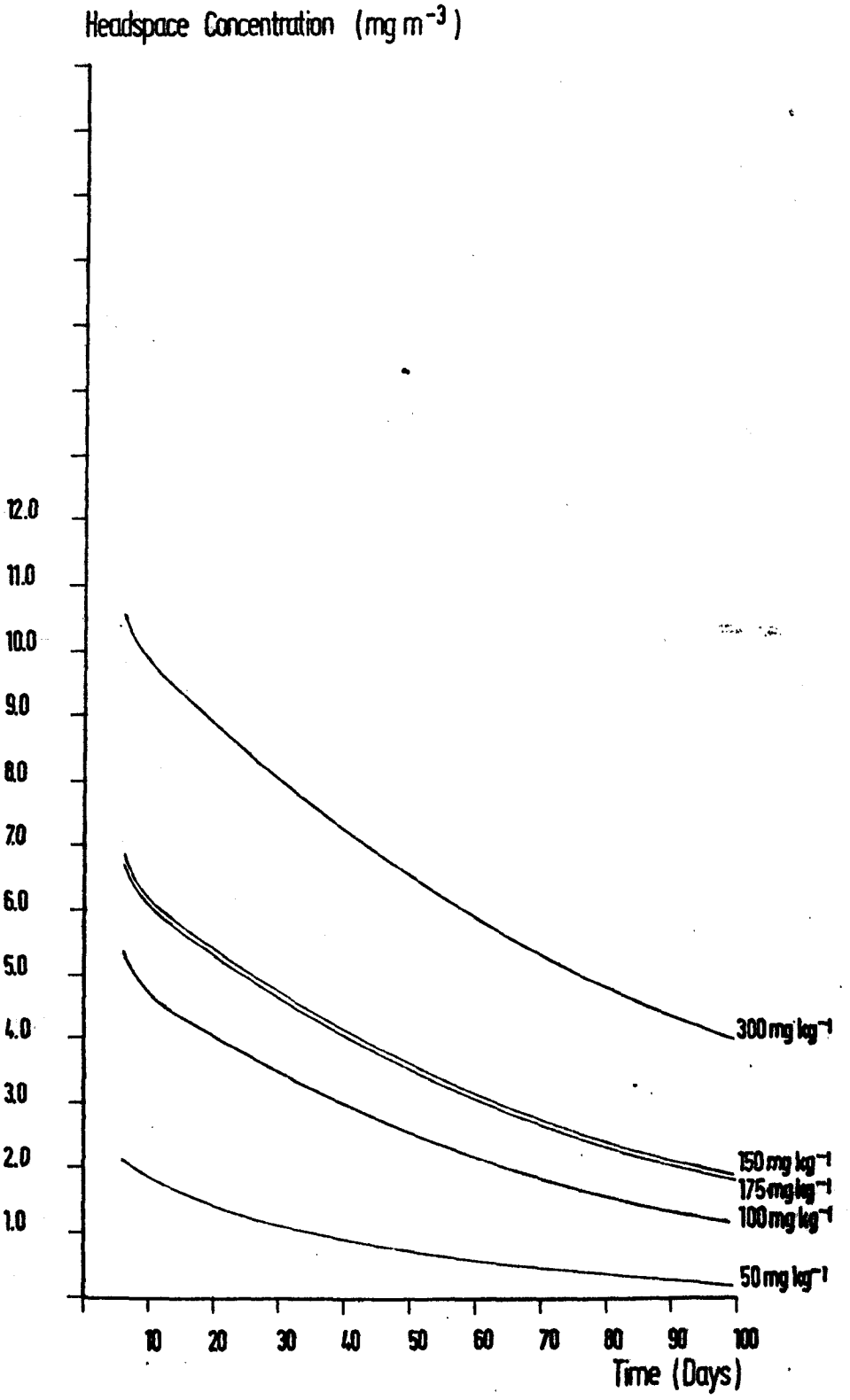


FIGURE 4.02 Log Headspace Concentration ($mg\ m^{-3}$) of 1,4-Dimethylnaphthalene in 10kg Boxes Containing Treated Tubers, cv, Maris Peer, Sample Size 5kg, Temperature 9°C

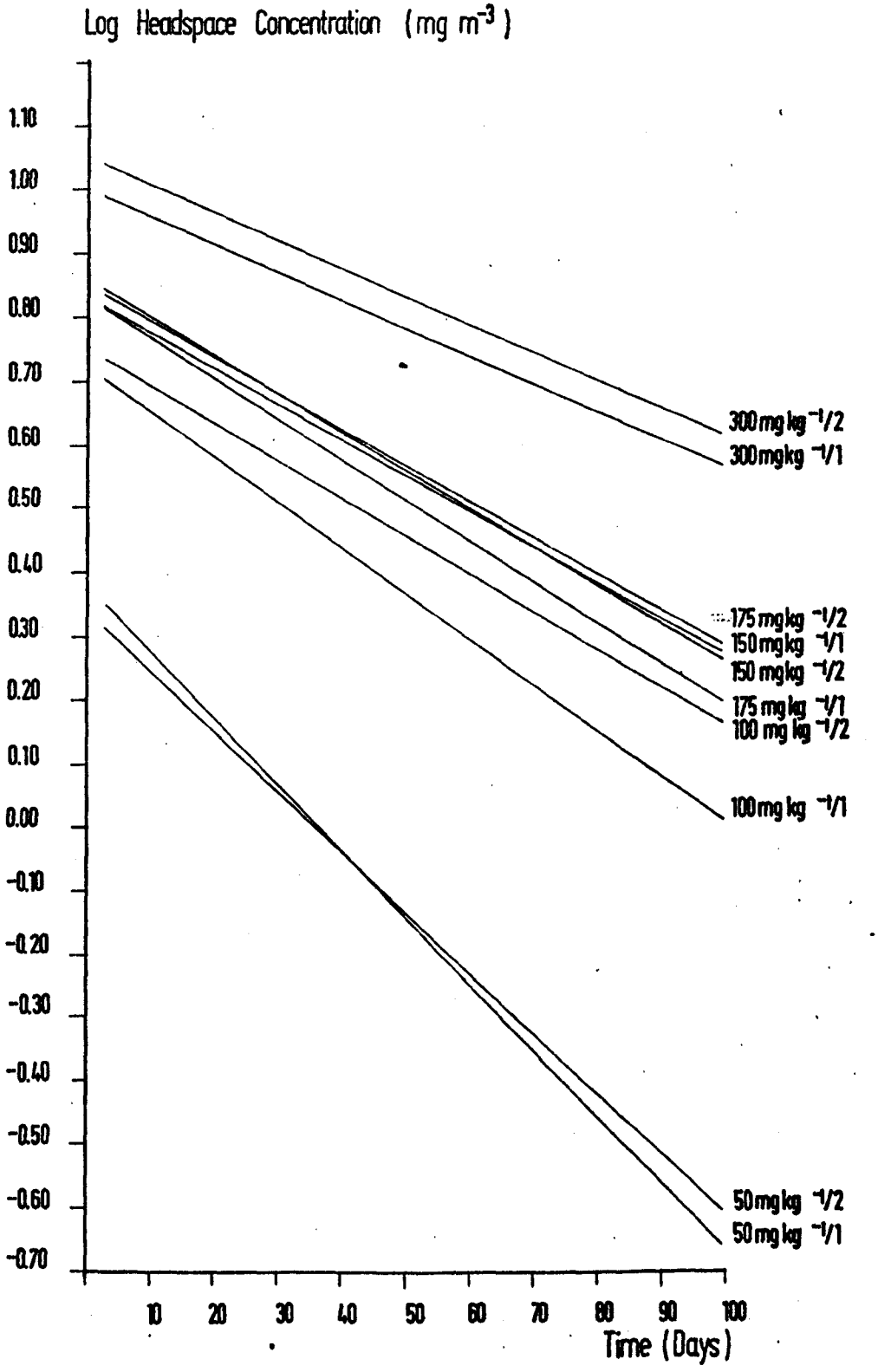


FIGURE 4.03 Log Headspace Concentration (mg m^{-3}) of Carvone in 10kg Boxes Containing Treated Tubers, cv. Record, Sample Size 5kg, Temperature 9°C

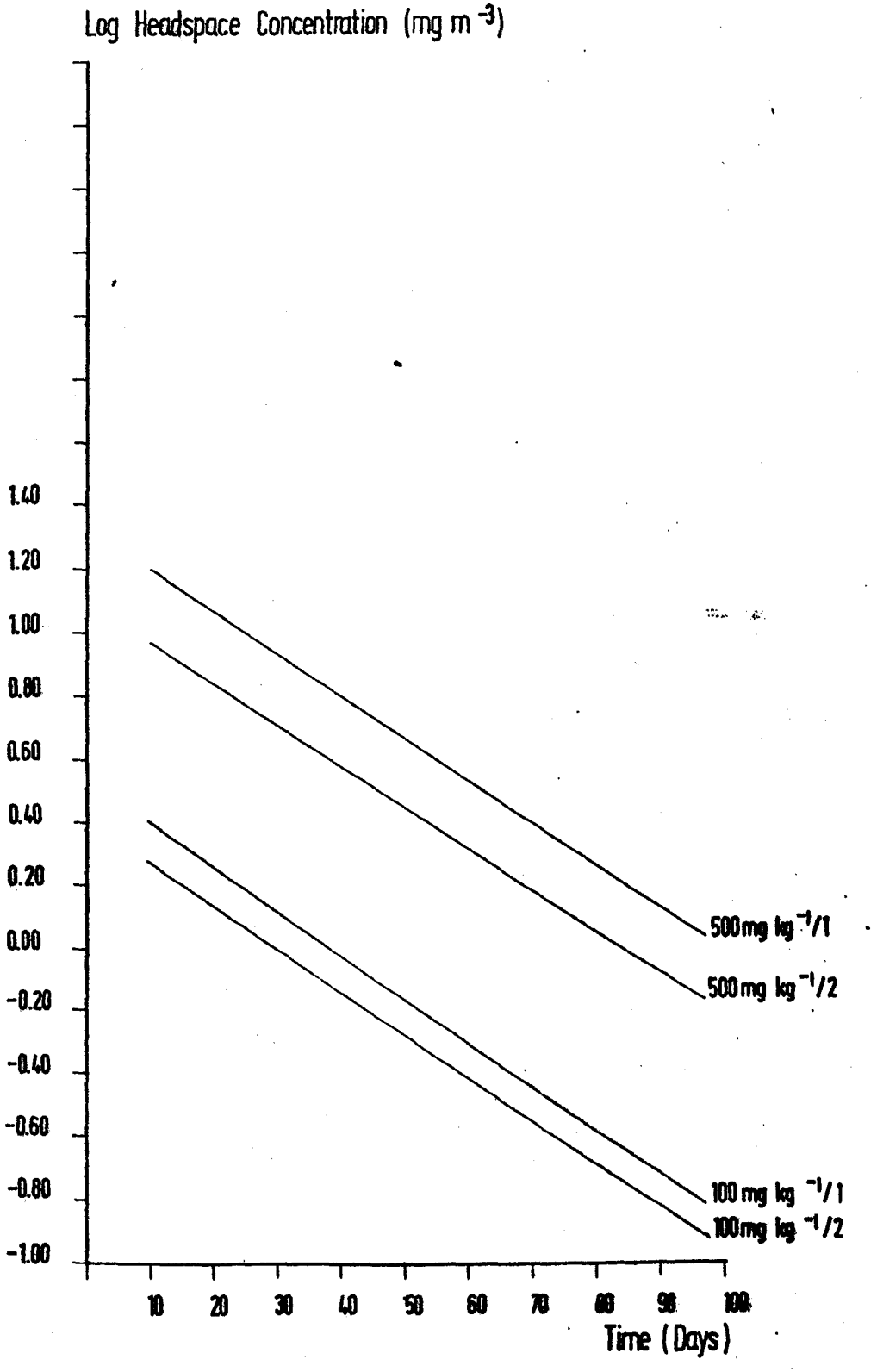
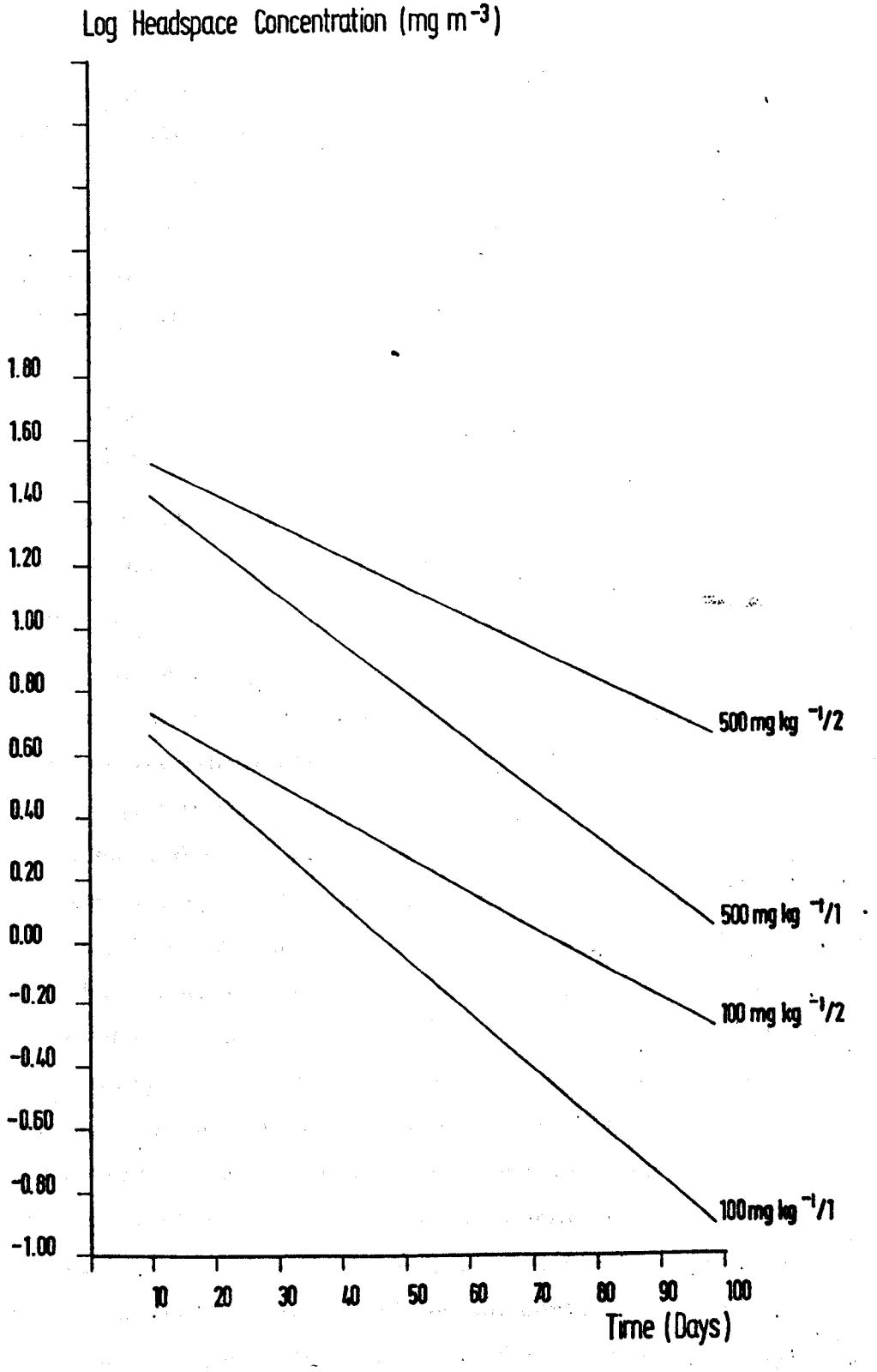


FIGURE 4.04 Log Headspace Concentration (mg m^{-3}) of Pulegone in 10kg Boxes Containing Treated Tubers, cv Record, Sample Size 5kg, Temperature 9°C



4.4. DISCUSSION

In the following discussion the results from the three headspace experiments are considered collectively. Many of the results are presented in graphical form. All graphs were drawn from best fitting straight lines determined by linear regression analysis of the analytical data (Parker, 1973; Bailey, 1959). Best fitting straight lines were determined for headspace concentration v. time data points and log headspace concentration v. time data points. In every case, better fitting straight lines were obtained using log concentration values. As a consequence, all graphs (Figures 4.01, 4.02, 4.03 and 4.04) are derived from the best fitting straight line of log concentration v. time. The correlation coefficients for all the lines in Figures 4.01, 4.02, 4.03 and 4.04 are given in Table 4.06. All correlation coefficients were ≤ -0.900 with a corresponding significance of $p < 0.01$.

The results of the experiments taken collectively (Tables 4.02, 4.03, 4.04 and 4.05) can be summarized as follows.

Headspace concentrations increased with initial application rate. Therefore, at these application rates under the experimental conditions the chemicals were not behaving ideally. They did not appear to achieve their saturation vapour pressures (Al. 4). Each chemical was present as a solid or liquid in the enclosed confines of a 10 kg box. Had the chemicals behaved ideally then the vapour pressure (hence headspace concentration) of the chemicals would depend only on the nature of the chemicals and the temperature. The amount of each chemical present would not have affected the headspace concentration. With these results one can only speculate why the chemicals do not reach their saturation vapour pressures and why headspace concentration increases with application rate. These effects could probably be due to sorption by the tubers, solid carrier, and cardboard box walls. Each observed headspace concentration is the result of an equilibrium between sorbed chemical and its vapour. As more chemical is applied the strongest sorption sites become filled leaving more, weakly sorbed and/or non-sorbed chemical. As the proportion of weakly sorbed and/or non-sorbed chemical increases, so the

equilibrium headspace concentration increases towards the saturated headspace concentration. Such sorption effects can only provide some of the reasons for the observed headspace concentrations, a complete understanding of which must also include the effects of humidity (Currah and Meigh, 1968; Mackay and Wolkoff, 1973; Mackay and Leinonen, 1975; Acree et al., 1963; Queen, 1953; Caseley, 1968). The results provide the simplest explanation for pulegone, carvone and citral being unsuccessful sprout suppressants when applied at 100 mg kg^{-1}. At these application rates their headspace concentrations were not as high as the minimum headspace concentrations found in previous studies (Meigh, 1969). This was also the reason for citral applied at 500 mg kg^{-1} and α-pinene applied at 100 mg kg^{-1}, being ineffective. All 1, 4-dimethylnaphthalene headspace concentrations were within the previously determined minimum effective headspace concentration range of 0 - 14 mg m^{-3} (Meigh et al., 1973).

Headspace concentrations decreased during the 14 week treatment period. This effect is most probably due to the gradual dissipation of the chemical from the box to the outside air. The results illustrate the concept of initial headspace levels falling below the minimum effective headspace concentration as treatment periods progress. This could be the principal reason for dimethylnaphthalene treatment producing much better sprout control when applied at 300 mg kg^{-1} compared to 100 mg kg^{-1}. The headspace results of 1, 4-dimethylnaphthalene are depicted graphically in Figure 4.01. Headspace concentrations determined for each application rate are plotted against each treatment time. The results could be interpreted in the following manner referring also to Table 4.01. Sprout control at 50 mg kg^{-1} was inadequate as the minimum effective headspace concentration was not reached. Sprout control at 300 mg kg^{-1} was complete because headspace concentrations did not fall below the minimum effective headspace concentration. Sprout control at 100 mg kg^{-1} was not as good as 300 mg kg^{-1}, as during the treatment period, headspace levels fell below the minimum effective headspace concentration.

Correspondingly sprout growth occurred. Using this explanation of the results, one could predict that at 9 - 10°C, the minimum effective headspace concentration of dimethylnaphthalene lies between 3 and 6 mg m^{-3}.

The rate at which headspace concentrations fell with treatment time varied between chemicals, e. g. the decrease in headspace concentrations of pulegone was much faster than 1, 4-dimethylnaphthalene, which in turn was faster than tecnazene. These results show the importance of the relative volatility (vapour pressure) of the chemicals. Some chemicals may be too volatile, their headspace concentrations falling below the minimum effective headspace concentration in too short a time to be of use commercially. It is probably for this reason that α-pinene was not effective when applied at 500 mg kg^{-1} under non-constant headspace conditions. The vapour pressure of α-pinene at 10°C is higher than all of the other chemicals studied. Thus the headspace concentration of α-pinene could be expected to drop more rapidly than the other chemicals. The vapour pressure of each chemical will be an important criterion of its success as a volatile sprout suppressant. Some chemicals may not be volatile enough, others may be too volatile for use over prolonged storage periods in commercial stores.

One feature of the 1, 4-dimethylnaphthalene results was the comparatively small difference in headspace concentration between treatments, e. g. the difference in headspace concentration between initial application rates of 50 mg kg^{-1} (unsuccessful sprout suppression) and 100 mg kg^{-1} (successful sprout suppression) was only c. 4 mg m^{-3}. This result plays an important part in explaining some box effects. Headspace concentrations of each box with 1, 4-dimethylnaphthalene, carvone or pulegone treatments are depicted graphically in Figures 4. 02, 03, 04. The results show that boxes with identical chemical treatments do not necessarily have identical headspace concentrations. Some boxes of 1, 4-dimethylnaphthalene treatments had lower headspace concentrations than treatments with lower application rates and vice versa. As small differences in headspace concentration will affect the level of sprout

control, these results explain why some boxes with higher application rates have longer mean sprout lengths than boxes with lower application rates (Table 4. 01). Small differences in headspace concentration affecting the level of sprout control could also account for anomalous sprouting effects. Most tubers with untypically long sprouts were found in one corner of the boxes (3. 4. 1. 1). It is possible that at these corners there is a disproportionately high level of chemical dissipation compared to the rest of the box. This could be due to the position of the box in the cold room (e. g. near a heat exchanger fan), the construction of the box (e. g. larger than normal air space between the box and its lid) or a combination of these factors. The effect would cause a localized reduction in headspace concentration and corresponding untypical sprout growth.

Mean sprout length of cv. Record treated tubers showed a remarkably accurate correlation with headspace levels (Table 4. 02). This effect was noted particularly with each pair of boxes treated with carvone and pulegone at 500 mg kg^{-1}. For each pair, the box with the highest headspace concentration had the lowest mean sprout length. These results help to illustrate further the extent to which differences in headspace concentrations can affect the resultant mean sprout length. Unfortunately, cv. Maris Peer mean sprout length did not correlate as well with headspace concentration (Table 4. 03). Large sprouts were removed from these tubers before the experiment started. It is noteworthy that of all the chemical treatments using cv. Maris Peer (i. e. 1, 4-dimethylnaphthalene, tecnazene and chlorpropham), only 1, 4-dimethylnaphthalene at application rates of over 100 mg kg^{-1} completely prevented any new sprout growth.

Headspace concentrations of tecnazene were studied in a 4, 000 tonne bulk store similar to the one used in the dimethylnaphthalene long-term storage experiment (3. 1. 4). Tecnazene was applied in a granular formulation as the store was being filled. The granules were applied at the manufacturers recommended rate, equivalent to 37. 5 mg kg^{-1} tecnazene. Headspace concentrations of tecnazene determined 6 hours, 24 days and 38 days after treatment are presented in Table 4. 04. The tecnazene treat-

ment ceased to be effective between 24 and 35 days after application. At this time sprout growth could be noted visibly. On the 35th day after tecnazene treatment, chlorpropham was applied as an atomized solution at an application rate of 10 - 20 mg kg^{-1}. The headspace concentration of chlorpropham was determined 3 days later (Table 4. 04). During the tecnazene treatment period the store ventilation programme had included many hours external ventilation intended to reduce the store temperature. It was considered that this external ventilation caused the fall in tecnazene headspace concentration. (The higher initial temperatures would also play a part in this effect. At higher temperatures the vapour pressure of tecnazene would be higher causing greater dissipation and also higher headspace concentrations (Al. 4)). The fall in tecnazene headspace concentrations was more rapid than had occurred in 10 kg boxes (Table 4. 05). These results helped explain why dimethylnaphthalene had not been effective in the long-term storage experiment. The ventilation programmes adopted in the store would have resulted in a more rapid dissipation of dimethylnaphthalene compared to treatments held in 10 kg boxes. It was also noted that tecnazene headspace concentrations in the store were lower than in 10 kg boxes (Table 4. 05). It is probable that this is due to the lower application rates of tecnazene in the bulk store. 37. 5 mg kg^{-1} tecnazene treatments in 10 kg boxes showed a rapid loss in headspace concentration over 16 days. This could possibly be explained by movement of tecnazene from weaker sorption sites (granules) to stronger sorption sites (cardboard walls, and tubers) between the first and sixteenth day after treatment.

It was noted that of all the chemicals studied, chlorpropham had much lower headspace concentrations.

4. 5 CONCLUSIONS

The results of the headspace concentration experiment help confirm that there is a minimum headspace concentration below which chemical sprout suppression is ineffective. This concept has important

implications when considering the suitability of sprout suppressant chemicals for use in commercial stores. Methods of maintaining the minimum effective headspace concentration can be by one high initial application or by re-applying several times during the storage period. Generally, the best method will be determined, firstly by the level of the minimum effective headspace concentration and secondly, on the volatility of the sprout suppressant chemical. Clearly, chemicals with low minimum effective headspace concentrations and low volatility are best. In this respect, chlorpropham is undoubtedly the best chemical presently available. However, if re-application is necessary, which may be inevitable in long-term stores with external ventilation programmes, the more volatile chemicals may be favoured. Unless their minimum effective headspace concentration is low (e. g. at the same level as chlorpropham) the chemicals will require frequent applications of higher effective headspace concentrations. More volatile chemicals will be favoured as they will be more easily and more uniformly distributed through the treated tubers.

Accurate headspace analyses could predict break in sprout suppression before visible symptoms develop.

The results indicate that dimethylnaphthalene could be successfully introduced directly as a vapour in air distributed through store ventilation ducts. Methods of introduction could include warming dimethylnaphthalene in a ventilating air stream, the procedure adopted with nonanol (Burton, 1958b), or by passing ventilating air over paper cartridges impregnated with dimethylnaphthalene, a method which has been proposed for chlorpropham (vanVliet and Sparenberg, 1970).

Finally, the results show that chemical volatility is an important criterion which should be included in laboratory assessment methods. Constant headspace methods can provide an accurate measurement of the minimum effective headspace concentration. However, they cannot assess the rate of chemical dissipation which must inevitably occur in

commercial stores. This disadvantage can be overcome to some extent as the relative volatility of chemicals can be determined from published vapour pressures, provided reliable data are available. However, it is considered that the best laboratory assessment method will include conditions under which chemical dissipation will occur. The laboratory conditions should be chosen in order that the rate of dissipation is similar to that under the commercial storage conditions being considered. With the development of new analytical methods (Chapter A1), the minimum effective headspace concentration can be accurately determined under those laboratory conditions.

ANALYTICAL SECTION

INTRODUCTION

This analytical section (Chapters A1 and A2) considers the methodology and results of, (1) The analysis of air surrounding potato tubers, and (2) Residue analysis of tubers treated with dimethylnaphthalene.

Chapter A1 describes trace organic vapour analysis of air surrounding potato tubers. One of the original aims of the research project was to collect and identify the volatile compounds produced by stored potato tubers (Burton and Meigh, 1971). These would then be assessed for sprout suppressant activity. Methods suitable for this work were studied. Collection methods were assessed experimentally and some preliminary experiments using gas chromatographic analysis were completed. At this stage in the project, as a result of the assessment experiments (Chapter 2), several chemicals had been shown to possess sprout suppressant properties. It was considered more important that the main research effort was devoted to studying these new sprout suppressant chemicals. Trace organic vapour analysis methods, originally intended for potato volatile analysis were adapted for quantitative headspace analysis of sprout suppressant chemicals. Consequently a technique for quantitative headspace analysis of 10 kg potato boxes was devised. This technique was then further developed for analysing the air in bulk potato stores.

Chapter A1 is divided into five parts. Part A1.1 discusses the methods available for trace organic vapour analysis. Part A1.2 presents the preliminary potato volatile, collection and analysis experiments. Part A1.3 presents the preliminary sprout suppressant headspace experiments, including the development of the necessary analytical apparatus. Part A1.4 describes the development of the procedure finally used to analyse the headspace of potatoes treated with volatile sprout suppressant chemicals. Part A1.5 describes the analytical

procedures adopted for determining vapour concentrations of, dimethylnaphthalene, α-pinene, citral, carvone, pulegone, chlorpropham and tecnazene in 10 kg potato boxes. The methods used to determine vapour concentrations of chlorpropham and tecnazene in bulk potato stores are also included.

Of the analytical methods available for trace organic vapour analysis, porous polymer adsorbent methods were used most. The use of porous polymer adsorbents was a relatively new technique when this project started. Detailed published information only became available as development work in the project proceeded. Parts A1.2, A1.3, A1.4 and A1.5 describe the work chronologically. Parts A1.2 and A1.3 deal with early preliminary development experiments, parts A1.4 and A1.5 present results of later work. The methods discussed in part A1.1 include all recent published information on the porous polymer adsorbent technique. Chapter A1 therefore contains an up-to-date account of a particular application of the porous polymer trace vapour analysis technique, based on results from this project and from other research workers.

Chapter A2 describes dimethylnaphthalene residue analysis methods and results. It provides an account of the sampling method, sample clean-up using alumina columns, and sample analysis by gas chromatography.

This analytical section is primarily concerned with the methods used to concentrate and separate trace organic components present in air, headspace gases or potato tubers. Gas chromatographic, U.V. spectrophotometric and olfactory methods were used to detect and quantify these compounds.

CHAPTER AI

ANALYSIS OF TRACE ORGANIC VAPOURS USING GAS CHROMATOGRAPHY

Potato volatile analysis and headspace analysis of potatoes treated with sprout suppressant chemicals both involve trace organic vapour determinations from a highly dilute sample. However, they are two distinctly different types of analytical problem.

The study of potato volatiles involves the quantitative collection and analysis of a large number of chemicals varying from permanent gases at ambient temperatures (e.g. ethylene) to high molecular weight vapours (e. g. dimethylnaphthalene). Collection methods must accurately reflect an unknown sample composition and subsequent gas chromatographic analysis must be capable of resolving a highly complex mixture.

Headspace analysis of potatoes treated with sprout suppressant chemicals, presents an easier analytical problem, as, normally, only one known chemical is considered on each sampling occasion. However, quantitative analysis requires that the analytical method is first of all shown to be accurate and precise. Analysis of a 10 kg potato box headspace presents an additional problem. Sample volume must be as small as possible in order that dilution effects are avoided. The analysis method must therefore have a high sensitivity. The method must also be rapid and capable of studying a wide range of compounds with differing physical and chemical properties.

PART A1.1

METHODS

The trace organic vapour analysis methods used in this project are based on those found in medical, food, and environmental research. The principal aims of these methods are, qualitative and quantitative concentration of samples, effective removal of water from large sample volumes, provision of a convenient means of sample transfer and storage, and qualitative and quantitative analysis of samples.

Gas chromatography has permitted major advances in the field of volatile analysis. However, the limited sensitivity of currently available detectors usually necessitates concentration of volatiles from a highly dilute sample. Direct injections (using a gas-tight syringe) of a very dilute vapour sample (air or headspace gases), produce a response only for those major components that possess relatively high vapour pressures and are in sufficient amounts to activate the detector. Although a larger sample would contain greater amounts of the materials to be detected, a large injection is not consistent with narrow solute bands, sharp peaks and high resolution. Consequently dilute vapour samples usually require some type of concentration procedure.

Large headspace or ambient air samples contain relatively large amounts of water vapour, e. g. at a relative humidity of 50% a cubic meter of air at 25°C contains 11. 3 g of water. Large amounts of water affect the concentrating procedure and subsequent analysis (Schultz et al., 1971; Bertsch et al., 1974; Pellizzari et al., 1975a). The best concentrating method should also include the ability to remove water.

Sample location and the ability to store samples before analysis will affect the choice of concentrating procedure adopted. A sample location in excess of a few yards from a gas chromatograph will clearly not favour collection by gas-tight syringe. In addition, adsorption

losses can occur with higher-boiling components when transferring samples by means of a syringe (Cropper and Kaminsky, 1963). Glass sampling bulbs (Cropper and Kaminsky, 1963; Fienland et al., 1961), and plastic sampling bags (Altshuller, 1963; McEwen, 1966) have been used to transfer samples from the location of collection to the analytical instrument. Sampling bags have been used to transfer relatively concentrated samples such as volatile organic material of plant origin, automobile exhaust, and smog (Bertsch et al., 1974). However, lossess due to adsorption and diffusion of components (McEwen, 1966; Cropper and Kaminsky, 1963; Altshuller and Clemons, 1962), and desorption of contaminants from the bag surface (Altschuller, 1963), can occur during storage.

A1.1.1 CONCENTRATING AND RECOVERY TECHNIQUES

In general the concentrating techniques have used the following trapping methods:-

1. Cryogenic.
   (Altschuller, 1963; Teranishi et al., 1972; Nursten and Williams, 1969; Morgan and Day, 1965).
2. Liquid phase, using ambient or sub-ambient temperatures.
   (Meigh, 1956; Altshuller, 1963; Cropper and Kaminsky, 1963; Colson, 1963; Novak et al., 1965; Dravnieks and Krotoszynski, 1966; Aue and Pankaj, 1971; Kaiser, 1973; Pellizzari et al., 1975a; Russell, 1975; Jennings and Filsoof, 1977).
3. Solid adsorbent using ambient or sub-ambient temperatures.
   (Turk et al., 1962; Altschuller, 1963; Grob and Grob, 1971; Schultz et al., 1971; Kaizer,1973; Raymond and Guiochon, 1974; Bertuccioli and Montedoro, 1974; Clark and Cronin, 1975; Pellizzari et al., 1975a; Russell, 1975; Becka and Feltl, 1977; Holzer et al., 1977; Charalambous, 1978).

Recovery of trapped vapours has been accomplished by the following methods:-

1. Thermal.
   (Teranishi et al., 1972; Kaiser, 1973; Raymond and Guiochon, 1974; Holzer et al., 1977).

2. Vacuum.
   (Turk et al., 1962).
3. Steam Desorption.
   (Saunders, 1965; Chiantella et al., 1966).
4. Solvent Extraction.
   (Grob and Grob, 1971; Aue and Pankaj, 1971).

Thermal and vacuum methods allow introduction of the total sample into the gas chromatograph. However, these methods can be subject to artifactual processes such as decomposition, polymerization, isomerization (Turk et al., 1962; Kaiser, 1973; Russell, 1975), or incomplete recovery (Pellizzari et al., 1975b; Clark and Cronin, 1975). Steam desorption and solvent extraction alleviate these problems. However, quantitative concentration of dilute solutions is difficult and gas chromatographic analysis is limited to small aliquots of liquid samples. Therefore, only a fraction of the sample can be examined. As a result the sensitivity of the overall method is reduced. On occasions only trace quantities of material may be accumulated. In such cases the entire sample must be analysed. Thermal and solvent extraction methods of recovery are most often used.

A1.1.1.1 CRYOGENIC METHODS

Cold traps, cooled with liquid Nitrogen (-196°C), liquid Oxygen (-183°C), or dry ice (-78°C) are often used to concentrate trace organic volatiles (Morgan and Day, 1965; Teranishi et al., 1972; Schultz et al., 1971; Nursten and Williams, 1969).

Cryogenic methods are particularly suitable for analysis of low molecular weight organic volatiles (C_1 - C_6). Using empty cold traps cooled in liquid Nitrogen, the limiting concentration below which methane and ethylene will not be collected is 0.5 p.p.m. (Altschuller, 1963).

Cryogenic methods are most effective when combined with sorption

on solid adsorbents and gas chromatographic phases. (Kaiser, 1973; Becka and Feltl, 1977). Using these methods quantitative concentration of low molecular weight compounds can be obtained.

The principal difficulty with freeze-out techniques is the presence of water. With large sample volumes, quantities of water will accumulate, which is a major problem during trapping and subsequent analysis. In addition, erratic results can be produced when micro-fog is formed due to samples being cooled too quickly or to too low a temperature (Kaiser, 1973).

Sample size can be extended using desiccants. Choice of desiccant is important as they can also remove organic volatiles (Farrington et al., 1959; Schultz et al., 1971) although selective removal by chosen desiccants can be used as subtractive steps prior to trapping (Williams, 1965; McEwen, 1966).

Cryogenic concentration is the only technique presently available which reflects a true sample composition of low molecular weight compounds. In addition, oxidation or polymerization of constituents is minimized during their concentration (Bertsch et al., 1974; Pellizzari et al., 1975a).

Provided the trapping temperature can be maintained, storage of samples is satisfactory.

A1.1.1.2 LIQUID PHASE AND SOLID ADSORBENT METHODS

A number of solid materials, liquids coated on supports acting as stationary phases, and chemically bonded stationary phases, have been shown to be suitable for concentrating trace organic vapours.

These sorbents have a high affinity for organic compounds at ambient or sub-ambient temperatures. They have little or no affinity for water.

These sorbents provide a convenient means of sampling, sample storage and analysis. They are packed in small volume tubes through which the sample passes, normally by means of a small vacuum pump. The sorbents concentrate the trace organic volatiles while rejecting water. When sampling has been completed the packed tubes can be stored with no loss of sample, and provide an effective, convenient means of sample transfer to the analytical instrument.

These methods are sensitive, particularly when the total sample is directly desorbed into the analytical instrument. Qualitative and quantitative sorption - desorption is possible for extremely dilute samples ($\mu g\ m^{-3}$).

Liquid phases

Support coated liquid stationary phases (Dravnicks and Krotoszynski, 1966; Novak et al., 1965; Colson, 1963; Cropper and Kaminsky, 1963; Pellizzari et al., 1975a; Russell, 1975), and chemically bonded stationary phases (Aue and Pankaj, 1971; Pellizzari et al., 1975a), have been used for trace organic vapour analysis. Application of these phases has the advantage that selectivity can be incorporated by choosing the appropriate phase (Pellizzari et al., 1975a; Bertsch et al., 1974). In addition, chemically bonded stationary phases are essentially non-extractable (by definition), and exhibit lower background contamination during thermal and solvent desorption, than support coated liquid phases (Aue and Pankaj, 1971; Pellizzari et al., 1975a).

Carbonaceous materials

Carbonaceous materials have been shown to be suitable adsorbents. Activated charcoal is an adsorbent of high affinity for organic compounds. Vacuum desorption (Turk et al., 1962) and steam desorption

(Chiantella et al., 1966; Saunders, 1965) have been applied to recover organic vapours adsorbed on charcoal. Solvent extraction of charcoal was found to be most effective using carbon disulphide (Jennings and Nursten, 1967). Qualitative and quantitative desorption using successive extractions of charcoal with carbon disulphide has been shown (Grob and Grob, 1971). Small (2 mg) activated charcoal traps with thermal desorption methods have been used for headspace vapour analysis (Clark and Cronin, 1975).

Qualitative and quantitative analyses have been made using graphitized carbon black, followed by heat desorption (Raymond and Guiochon, 1973, 1974).

However, the application of carbonaceous materials is controversial, due to problems of irreversible adsorption and artifactual processes (Holzer et al., 1977; Russell, 1975; Kaiser, 1973; Turk et al., 1962; Pellizzari et al., 1975b; Clark and Cronin, 1975).

Organic porous polymer adsorbents

The use of these adsorbents has recently become widespread for the qualitative and quantitative concentration of trace organics from dilute media (air and water) as well as for headspace analysis in general (Schultz et al., 1971; Zlatkis et al., 1973; Bertsch et al., 1974; Bertuccioli and Montedoro, 1974; Pellizzari et al., 1975a; Holzer et al., 1977). Thermal desorption techniques are most often applied, although solvent extraction has been used (Filmer and Land, 1978).

A number of commercially available adsorbents have been studied, assessing their suitabilities for concentration from very dilute media (Gearhart and Burke, 1973; Butler and Burke, 1976). No single adsorbent is best for every sampling application. The adsorbent must be chosen to fit a particular problem (Butler and Burke, 1976).

Concentration using porous polymers can be affected by incomplete or substance-specific adsorption of low molecular weight and polar compounds. Generation of artifacts during thermal desorption can also occur (Bertuccioli and Montedoro, 1974; Schultz et al., 1971). Incomplete or substance-specific adsorption is an inherent limitation of the method which depends on the chosen adsorbent-adsorbate combination. Generation of artifacts during thermal elution can be largely eliminated by proper solvent extraction clean-up, and thermal conditioning of the porous polymer adsorbent (Holzer et al., 1977; Pellizzari et al., 1975b).

A1.1.2 POROUS POLYMER ADSORBENTS

In this project, porous polymer adsorbent methods were used for most trace organic volatile analyses. They were considered to be an effective and convenient method for:-

(a) Concentrating trace organic volatiles.

(b) Drying samples before gas chromatographic analysis.

(c) Transferring from sampling location to analytical instrument.

(Schultz et al., 1971; Bertucioli and Montedoro, 1974; Pellizzari et al., 1975a, 1976a; Bertsch et al., 1974; Holzer et al., 1977).

Thermal desorption analysis methods were adopted. This method provides greater sensitivity and is also more convenient than solvent extraction (Zlatkis et al., 1973; Raymond and Guiochon, 1974; Pellizzari et al., 1975b).

A1.1.2.1 POROUS POLYMER PRECOLUMNS

The adsorbents are normally packed into short, glass tubes, c. 100 mm x 5 - 10 mm i.d. Glass wool plugs or scintered discs hold the adsorbent in place. This packed tube or precolumn constitutes the organic volatile trap. When thermal recovery is adopted, the precolumn dimensions are such that it will fit into the modified injection port of a gas chromatograph.

A1.1.2.2 CHOICE OF POROUS POLYMER ADSORBENT

Several porous polymer adsorbents are available commercially. As no single adsorbent is best for every sampling application, the adsorbent chosen must be the best for a particular sampling problem. Evaluation of these adsorbents for a particular trace volatile sampling task will involve the following criteria:-

Sampling capacity

Air to be sampled is drawn through a precolumn at ambient temperature. Under these conditions the trace organic volatiles are retained and concentrated on the precolumn. The precolumn quantitatively traps components until the least retained component begins to be eluted. Sampling capacity (sample volume, dm^3. weight of adsorbent, g^{-1}) is determined by the retention volumes and efficiencies (number of theoretical plates) of the precolumn for the least retained components (Butler and Burke, 1976; Pellizzari *et al.*, 1976a; Raymond and Guiochon, 1974). The sampling capacity ($dm^3 g^{-1}$) for a particular porous polymer adsorbent-trace organic volatile-temperature combination thus indicates the conditions under which quantitative adsorption will occur. In general, sampling capacity of lower molecular weight compounds will be less than that of higher molecular weight compounds. Sampling capacity will increase with decreasing temperature.

Thermal stability

Thermal desorption is normally the best means to recover trapped volatiles. The ideal adsorbent would be one which has a large sampling capacity while at the same time providing for rapid desorption of the sample. The speed of desorption depends primarily on the desorption temperature. For adsorbents with poor thermal stabilities, maximum permitted precolumn temperatures may be too

low to provide rapid desorption of the highest boiling sample components (Butler and Burke, 1976).

Low background contribution

When porous polymers are operating within their maximum recommended temperature limit, background bleed must be low, e.g. the presence of compounds such as benzaldehyde and methyl styrene has been attributed to bleed from a styrene, divinylbenzene porour polymer adsorbent (Schultz et al., 1971). Prior treatment by solvent extraction and/or thermal conditioning will effectively reduce bleed for most porous polymer adsorbents. For some, however, prior treatment does not reduce bleed to acceptable levels (Pellizzari et al., 1975b; Bertucioli and Montedoro, 1974).

Low affinity for water

Most porous polymers have little or no affinity for water. However, some may trap up to ten times as much as others, which could be enough to complicate gas chromatographic analysis (Pellizzari et al., 1976a; Russell, 1975).

A1.1.2.3 QUALITATIVE/QUANTITATIVE ADSORPTION BY POROUS POLYMERS

Sampling capacity (A1.1.2.2) is the most important factor affecting qualitative/quantitative adsorption by porous polymers. It is conceivable that sampling capacity could be decreased by displacement chromatography if large quantities of compounds of secondary interest are present and/or collected (Pellizzari et al., 1976a). High levels of humidity also may affect sampling capacity (Pellizzari et al., 1976a; Russell, 1975). Loss in qualitative/quantitative adsorption can be caused by excessively fast sampling rates (Bertsch et al., 1974), due to insufficient time of contact between organic molecules and

adsorbent (Russell, 1975).

It is important therefore, that for each analytical problem, a particular adsorbent-precolumn design combination is assessed experimentally.

Qualitative and quantitative adsorption is most easily determined by connecting two precolumns in series. After sampling has been completed, the second precolumn of the series is analysed for any components eluted from the first (Grob and Grob, 1971; Aue and Pankaj, 1971; Raymond and Guiochon, 1974; Bertsch et al., 1974; Russell, 1975; Pellizzari et al., 1976a).

A1.1.3 TENAX GC POROUS POLYMER ADSORBENT

For headspace analysis of potato sprout suppressant chemicals, Tenax GC, 60/80 mesh (Enka N.V., The Netherlands), was considered the best commercially available adsorbent. Tenax GC has become widely accepted in air and water analyses (Holzer et al., 1977).

Tenax GC is a porous polymer of 2, 6-diphenyl-p-phenylene oxide which has good thermal stability. Up to 300 - 360°C little background bleeding is observed (Zlatkis et al., 1973; Holzer et al., 1977; Daemen et al., 1975). It has no affinity for water.

Its sampling capacity has been extensively studied and compared with other adsorbents. Quantitative adsorption-desorption of many test compounds has been shown. An example of some retention volumes at 25°C are:-

Benzene 26 $dm^3 g^{-1}$; Toluene 128 $dm^3 g^{-1}$; n-Propylbenzene 1560 $dm^3 g^{-1}$; 1-Pentene 3 $dm^3 g^{-1}$; 1-Hexene 17.4 $dm^3 g^{-1}$; 1-Heptene 116 $dm^3 g^{-1}$; 1-Nonene 2300 $dm^3 g^{-1}$.

It is therefore best suited for quantitative adsorption of higher molecular weight volatile compounds (above C_7). Its high thermal

stability makes it ideally suited for the higher desorption temperatures necessary for rapid analysis of higher molecular weight compounds (Pellizzari et al., 1975a, 1976a; Russell, 1975; Butler and Burke, 1976; Holzer et al., 1977).

Its sampling capacity for several test compounds has been shown to be unaffected by humidity, or the presence of large concentrations of compounds of secondary interest (Pellizzari et al., 1976a; Janak et al., 1974).

No indication has been found that repeated use of Tenax GC precolumns results in any decrease in trapping efficiency (after recycling fifteen times) (Pellizzari et al., 1976a).

The effects of transportation and storage on samples trapped on Tenax GC precolumns have been studied (Pellizzari et al., 1976a). Recoveries of test compounds were quantitative after storing or transporting for one week, with losses over longer periods. The amounts lost, correlated with the volatility of each test compound. Recoveries were acceptable if analysis was carried out within three weeks regardless of whether the precolumns had been transported or stored. (Pellizzari et al., 1976a). However, on other occasions storage of precolumns for up to four months has shown no loss in trapped volatiles (Bertsch et al., 1974).

Solvent extraction with acetone, methanol, benzene, ethyl acetate or pentane and/or thermal conditioning for 18 - 24 hours at 275 - 360°C can effectively eliminate background bleed to an acceptable level (Pellizzari et al., 1975b; Russell, 1975; Holzer et al., 1977).

PART A1.2

POTATO VOLATILE COLLECTION AND ANALYSIS, PRELIMINARY EXPERIMENTS

Two headspace samples containing potato volatiles were studied. The first was of a sealed 54 dm^3 glass tank containing 25 kg potatoes, through which was passed a current of purified air (System 1). Volatiles from this system could only be those produced by the potatoes or organisms associated with the potatoes. The second headspace was taken from the centre of a 750 kg potato clamp (System II). The larger sample of potatoes provided greater amounts of volatile material, necessary for assessing analytical methods. However, several of the trapped compounds would have been present in the surrounding air.

Some 20 - 30 compounds have been previously found to be evolved by potatoes. The rate of volatile production is low. It has been estimated to be in the order of 1ng $kg^{-1}h^{-1}$ (Meigh et al., 1973; Burton and Meigh, 1971). A good Gas Chromatographic-Mass Spectrum requires about 50 ng of each compound (Schultz et al., 1971). Large headspace volumes are therefore necessary.

A1.2.1 POTATO VOLATILE COLLECTION

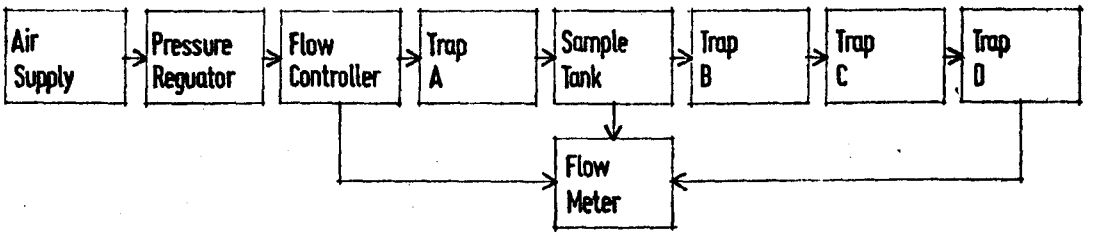
Cryogenic methods were used. Empty cold traps of similar design to those used in flavour research (Nursten and Williams, 1969) were considered to be an effective means of trapping potato volatiles. Liquid nitrogen, solid carbon dioxide-acetone and ice were used as coolants.

A1.2.1.1 EXPERIMENTAL APPARATUS AND OPERATING CONDITIONS

System I With which volatiles from 25 kg tubers were collected. The

collection system is outlined in Fig. A1. 01.

Fig. A1. 01. Flow diagram of potato volatile collection System I.



1. Air supply (BOC, Glasgow).
2. Pressure regulator., 15MPa - 200 kPa. (C.S. Milne and Co. Ltd.).
3. Flow controller. Micro-metering valve (Whitey, -21RS2, Techmation, Middlesex).
4. Cold trap A.
5. 54 dm^3 glass sample tank.
6. Cold trap B.
7. Cold trap C.
8. Cold trap D.
9. Flow meter. 20 cm^3 bubble meter.

The system was designed in order that the potato volatiles could only be in contact with glass surfaces. The only exception to this was a short, flexible, polypropylene tube linking the sample tank and trap B.

Potato sample

25 kg of washed potatoes were held in the sample tank. cv. Record, Desiree, P. Hawk, P. Crown, M. Piper and M. Peer were studied.

Sample tank

54 dm^3 glass container (530 mm x 225 mm x 550 mm, external dimensions). Its lid was sealed using silicone grease. 2, glass, "T" shaped tubes (500 mm x 430 mm x 6 mm o.d. x 4 mm i. d.; 50 mm x 430 mm x 6 mm o. d. x 4 mm i. d.) extended within the tank. The ends of the 430 mm "arm" were sealed. This "arm" was perforated along its length. The shorter "T" shaped tube was fixed on the lid of the sample tank, the longer "T" tube extended to the bottom of the tank. Air from trap A entered the tank via the shorter "T" tube, passed downwards, through the potato sample, and left via the longer "T" tube. The longer "T" tube was connected to trap B by means of a short length of polypropylene tubing.

Cold traps

The trap dimensions are described in Fig. A1. 02. The cold traps were made of glass with Teflon stop-cocks. A Teflon liner was used for the B34 joint. Traps B, C and D were arranged in such a way that their entrance-exit arms could be coupled directly using spring clips. The coolants were held in Dewar flasks. Liquid nitrogen or solid carbon dioxide-acetone was used to cool traps A, C and D. Trap B was cooled by ice. A siphon device to remove water was attached to the Dewar flask containing ice. The cold trap arrangement was held on a mobile table (Plate A1. 01). After sampling, the traps were sealed and stored in solid carbon dioxide-acetone.

Operating conditions

Volatile collection periods proceeded for 1 to 6 weeks. Flow rates remained constant throughout the sampling period. Flow rates between 6 and 20 $cm^3\ min^{-1}$ were adopted. The experiment was conducted at temperatures between 10 and 15°C.

Fig. Al. 02. Cold trap dimensions

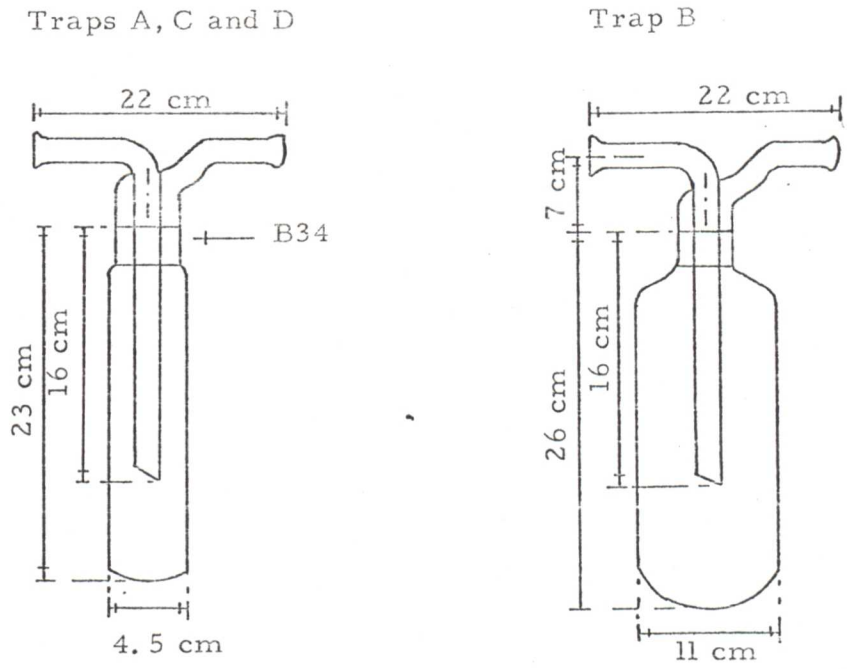
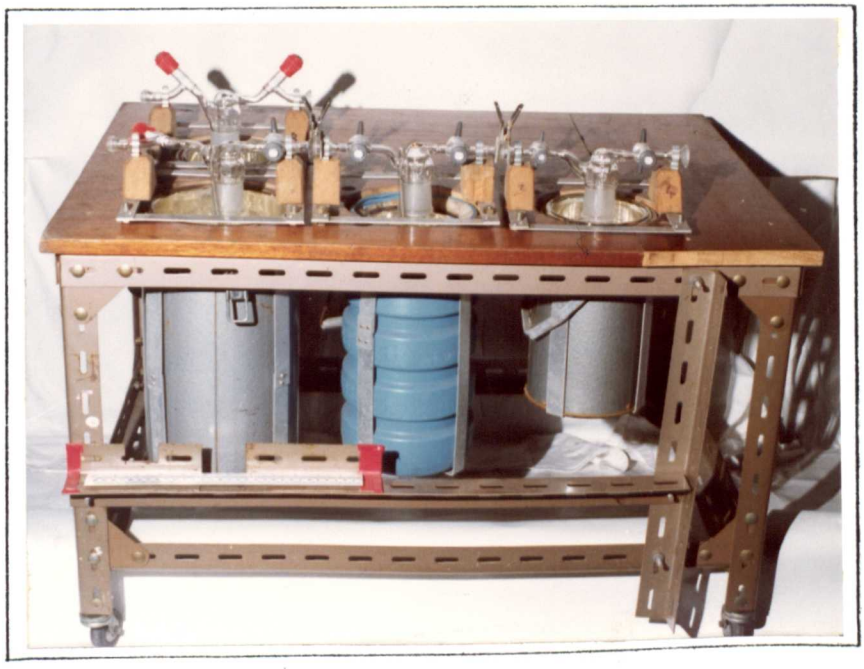


Plate Al. 01. Mobile cold trap arrangement.



System II With which volatiles from 750 kg tubers were collected, using the same cold traps as System I.

Fig. A1. 03. Flow diagram of potato volatile collection System II.

750 kg potatoes, cv. Maris Peer, were stored in a solid wall box.

Air samples were removed from the centre of the box by a small diaphragm pump (Dymax Mk II, Charles Austen Pumps Ltd., Surrey). Narrow bore glass and Teflon tubing (3. 6 mm o. d. x 1. 6 mm i. d.) linked the box and cold trap A. The sampling rate (measured by 20 cm^3 bubble meter) was 10 cm^3 min^{-1}. Sampling periods of 5 and 10 weeks were adopted. Traps A, B, C and D were cooled by solid carbon dioxide-acetone.

The experimental apparatus was contained in a glass house, continuously ventilated by a fan. A thermostat controlled heater prevented temperatures falling below 4. 5°C. Temperatures were continuously monitored. During the 5 week sampling period (December to January), temperatures did not exceed 9°C. During the 10 week period (January to April), average daily temperatures were higher 4. 5 - 12°C. On five days during the 10 week period the temperature reached 20°C.

After sampling, the traps were sealed and stored in solid carbon dioxide-acetone.

A1. 2. 1. 2 RESULTS

System I

Tuber health

Provided healthy tubers were used, tuber health remained good

during the sampling periods. Moisture tended to accumulate on the lid of the sample tank. When the sample tank was opened after sampling was completed, a distinct "musty potato" odour was detected. From a brief visual inspection, no marked degree of sprout suppression was observed.

Cold Trap Performance

The first experiments were conducted using liquid nitrogen in traps A and D, solid carbon dioxide-acetone in trap C and ice in trap B. Liquid nitrogen cold traps were unsatisfactory. Large amounts of air were condensed in traps A and D. Liquid nitrogen had to be added every four hours. The traps could not be left overnight. No potato volatiles were collected by this method.

In following experiments solid carbon dioxide-acetone was used to cool traps A, C and D, with B cooled by ice. This arrangement proved satisfactory. Several grams of material were collected in sampling periods exceeding one week. Solid carbon dioxide need only be added every 24 hours. Most condensed material was present in trap C, with a little in trap D. However, by sniffing the effluent from trap D, a distinct odour was detected. This odour differed slightly from that detected by sniffing the effluent from the sample tank.

System II

Tuber health remained good during the storage period (October to April). By late March, sprouting had occurred throughout the stack.

Several grams of material were collected using solid carbon dioxide-acetone to cool traps A, B, C and D. Occasionally ice had to be removed from the entrance arm of trap A. Trap A contained most material, trap D least.

A1. 2. 1. 3 DISCUSSION

The aim of the experiments was to collect the vapours evolved by healthy conventionally stored potatoes. At the same time it was important that any vapours collected should be attributable only to evolution by potatoes.

System I was designed to meet both these requirements. Purified air and an all-glass system would minimise contamination from external sources and reduce adsorption effects. Comparing this system with that previously adopted (Burton and Meigh, 1971), it was thought that a constant flow of air, through a larger sample of tubers, would provide greater amounts of trapped material. If potato volatiles are allowed to accumulate (Burton and Meigh, 1971), further production could be inhibited (provided an equilibrium relationship between the headspace concentration of potato volatiles, and potato volatile production does exist). However, moisture accumulations in the sample tank (despite increasing the flow rate from 6 cm^3 min^{-1} to 20 cm^3 min^{-1}, at the expense of trapping efficiency), and "musty potato" odours detected when the tank was opened, suggested that the conditions of System I were not those of normal potato storage.

System II was designed to allow sampling from a stack of what could be regarded as conventionally stored tubers. The larger sample would also provide more material, necessary for development of analytical methods. However, the volatiles collected would almost certainly have been contaminated by compounds present in urban ambient air (Raymond and Guiochon, 1974; Pellizzari et al., 1976b; Bertsch et al., 1974; Holzer et al., 1977; Grob and Grob, 1971; Nursten and Sheen, 1974; Meigh et al., 1973). It was intended to trap an air sample after the tubers had been removed to determine which trapped components could have been contaminants from external sources.

The use of liquid nitrogen as a coolant was abandoned due to

the large amounts of air trapped and the frequency with which the traps needed replenished. Sniffing the exit port of the last trap (System I) clearly showed, as one could expect (Altshuller, 1963), that solid carbon dioxide-acetone will not qualitatively trap potato volatiles. However, it was considered sufficient, if in these preliminary experiments, some condensate was obtained, in order that the correct analytical method could be devised.

A1.2.1.4 CONCLUSIONS

The large potato sample provided greater amounts of trapped material, and is therefore the best means of obtaining volatiles for analytical technique assessment. In order that the identified compounds can be attributed solely to potatoes a sealed system is necessary. The storage conditions of the sealed system used in this experiment require adjustment as they cannot be considered typical of normal storage.

Cryogenic methods are considered best for trapping potato volatiles. These methods more accurately assess the true sample composition, including the lower molecular weight compounds. As large sample volumes are necessary, limited porous polymer adsorbent sampling capacity at ambient temperatures would result in a loss of some of the lower molecular weight compounds (Holzer et al., 1977).

The cold trap arrangement used in these preliminary experiments would be considerably improved by including a final porous polymer trap, cooled by solid carbon dioxide. The trap would be capable of retaining low molecular weight compounds (Beckla et al., 1977).

The best solution may be to adopt an all adsorbent system. Adsorbent traps at ambient and sub-ambient temperatures would provide a means of fractionation prior to analysis.

A1. 2. 2 POTATO VOLATILE ANALYSIS

In some experiments the contents of the cold traps (A1. 2. 1. 1) were analysed by warming the trap and passing the vapours into a 0. 5 or 1. 0 cm^3 sample loop of a gas sampling valve. The contents of the sample loop were then injected onto a conventionally packed analytical column.

In other experiments trapped vapours were firstly transferred to a 1 dm^3 glass sample vessel. The function of the sample vessel was to provide a means of (a) concentrating the contents of several cold traps and (b) thermally fractionating the cold trap contents, under reduced pressure if desired. The cold traps could be connected to the vessel and the contents transferred by warming the trap and cooling the vessel, under reduced pressure if necessary. A magnetic stirrer in the vessel helped to provide a uniform mix. By flushing the vessel with inert gas, the volatiles could be transferred to the sample loop of the gas sampling valve. Samples could also be withdrawn from the vessel by gas syringe, from a sampling port situated on top of the vessel. This method of transferring volatiles was assessed using a limonene, α-pinene test mixture.

A1. 2. 2. 1 EXPERIMENTAL APPARATUS AND OPERATING CONDITIONS

The chromatographic conditions were

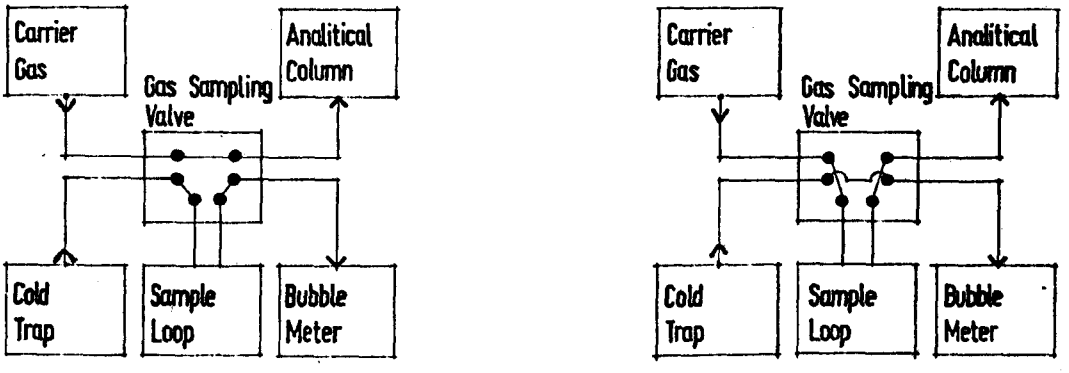
5% OV17 on GC Q, 100/120, 1. 8 m x 3. 5 mm i. d. glass column. Nitrogen carrier gas, cleaned by passing through molecular sieve (Molecular sieve 5A, Phase Separations Ltd., Queensferry, Great Britain).

The samples were transferred to the analytical column via a six-port, 2 position gas sampling valve (Pye Unicam Ltd., Cambridge, England). The valve was mounted on the gas chromatograph in the

manner recommended by the manufacturers, and was connected to the analytical column by the 160 mm x 1.6 mm o.d. x 0.7 mm i.d. stainless steel tubing provided with the gas sampling valve kit (Pye Unicam Ltd., Cambridge, England).

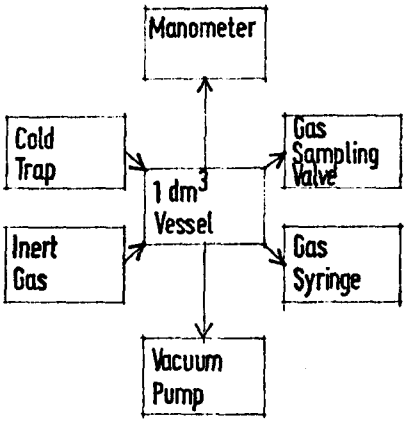
In some experiments a cold trap containing potato volatiles (-78°C) was connected directly to the sample loop (0.5 or 1.0 cm^3) of the sample valve, (Fig. Al. 04). The volatiles were transferred by warming the cold trap to room temperature (20°C). After several cm^3 had passed through the sample loop (measured by bubble meter), the gas chromatograph carrier gas was re-routed through the sample loop, flushing the sample onto the analytical column. All connections to and from the sample valve were of 1.6 mm o.d. x 0.7 mm i.d., stainless steel tubing.

Fig. Al. 04. Flow diagram of gas sampling valve operation.



In other experiments, cold trap samples could be transferred firstly to a 1 dm^3 glass sample vessel (Fig. Al. 05).

Fig. A1. 05. Flow diagram of glass sample vessel operation.



Connections between the vessel and cold trap, inert gas supply, vacuum pump, manometer and sampling valve, were sealed by Teflon stop-cocks. The gas syringe sampling port was sealed by a silicone rubber septum.

The vessel and gas sampling valve were connected by 20 mm x 1. 6 mm o. d. x 0. 7 mm i. d., stainless steeel tubing.

Nitrogen was used as inert gas, its flow rate regulated by a fine flow controller (Brooks, Emerson Electric Company, Pennsylvania).

0. 1 cm^3 α-pinene (Laboratory reagent grade, Hopkin and Williams, Essex, England) and limonene (Laboratory reagent grade, B. D. H., Poole, England), were added to the vessel.

A1. 2. 2. 2 RESULTS

Direct transfer of cold trap contents into the sample loop, with subsequent analysis was unsatisfactory. The chromatograms obtained, showed several poorly resolved compounds.

Analysis of the limonene, α-pinene test mixture, flushed from the sample vessel and injected via the gas sampling valve was also unsatisfactory. Sensitivity was low, with the compounds producing chromatograms with broad tailing peaks.

A1. 2. 2. 3 DISCUSSION

Resolution of potato volatiles by the conventionally packed analytical column was unsatisfactory.

The poor chromatograms obtained by injecting via the gas sampling valve were considered to be also due to there being insufficient material present in the sample loop. Tailing peaks obtained by injecting a limonene, α-pinene test mixture suggested that adsorption was occurring along the sample loop, and tubing connecting the sampling valve to the analytical column. The sample loop and connecting tubing were not heated. The connecting tubing was also unnecessarily long.

Poor performance by the gas sampling valve and analytical column did not allow satisfactory assessment of the sample vessel transfer technique.

A1. 2. 2. 4 CONCLUSIONS

It was considered that the best method of analysing the contents of the cold traps would be to concentrate and dry the contents with porous polymer adsorbents, rather than using the sample vessel.

High resolution capillary columns would be used to analyse the complex mixture of potato volatiles, desorbed from porous polymer adsorbents.

For introduction of desorbed vapours onto high resolution capillary columns, the vapours would be concentrated in a small carrier gas volume to prevent excessive band spreading and decreased column efficiency. This would be achieved by desorbing for 5 - 10 minutes, retrapping the vapours in a low volume liquid nitrogen cooled cold trap. After the desorption period, the analytical column carrier gas

would be routed through the low volume trap, and the trap rapidly heated. (Schultz et al., 1971; Bertsch et al., 1974; Pellizzari et al., 1975b).

A desorption-injection unit was constructed (A1. 3. 2. 3). The gas sampling valve was used as a switching valve, directing the analytical column carrier gas through the liquid nitrogen cooled cold trap. It was considered that the performance of the valve would be improved by heating it and shortening the connecting tubing.

PART A1.3

SPROUT SUPPRESSANT HEADSPACE ANALYSIS, PRELIMINARY EXPERIMENTS

A technique was used for analysing the headspace of potatoes treated with, dimethylnaphthalene, α-pinene, pulegone, citral, carvone, tecnazene and chlorpropham (A1. 5). This part describes the development of the analytical apparatus and preliminary headspace analysis experiments.

A1. 3. 1 COLLECTION AND ANALYSIS METHODS

Collection

Porous polymer adsorbent methods were considered best (A1. 1. 2). The volatile sprout suppressants were concentrated on adsorbent filled precolumns. Of the commercially available adsorbents, Tenax GC was considered best for the headspace analysis of these compounds (A1. 1. 3).

Analysis

Analysis of the sprout suppressant vapours was performed using conventionally packed analytical columns.

These higher molecular weight volatile compounds can be analysed by connecting the precolumn directly onto the analytical column. The compounds were heat desorbed and retrapped on an analytical column held at ambient temperatures. The analytical column was then rapidly heated, allowing the compounds to be eluted and quantified. Temperatures were chosen in order that periods of 5 - 10 minutes would complete the desorption process. The analytical column temperature programme varied for each compound - sampling situation studied. Chromatographic conditions were adjusted in order that the sprout suppressant was sufficiently well resolved from other compounds of secondary interest.

In general, the best analytical column temperature during desorption is the highest temperature at which the compound of interest will remain trapped by the analytical column. In this way, the maximum number of compounds which are trapped only at lower temperatures are eluted and separated from the compound of interest.

A low volume, liquid nitrogen cooled, cold trap was used for more rapid analyses (Al. 5). The contents of each precolumn were firstly heat desorbed and re-trapped in the low volume cold trap. After completing the desorption period, the analytical column carrier gas was routed through the cold trap. The contents were then injected onto an isothermal analytical column by rapidly heating the cold trap. After injection was complete, the carrier gas was re-routed and no longer flowed through the cold trap. By these means a more rapid isothermal sample analysis could be adopted, whilst desorption of the next sample proceeded.

A desorption-injection unit was used for these rapid headspace analyses. Its design included a precolumn heater, liquid nitrogen cold trap and carrier gas switching valve.

Al. 3. 2 ANALYTICAL APPARATUS DEVELOPMENT

Porous polymer precolumns and desorption-injection methods were designed and assessed experimentally. The best operating conditions for these methods of analysis were determined. The best operating conditions are those under which (a) background contribution from analytical apparatus is minimised and, (b) quantitative adsorption - desorption-injection is obtained. The following text considers the factors affecting background contribution from analytical apparatus. Quantitative analytical conditions are dealt with in the other relevant headspace analysis parts (Al. 3. 3, Al. 4., Al. 5).

The term background contribution describes all factors affecting gas chromatograph baseline stability, including introduction of foreign compounds. The best operating conditions are those under which base-

line stability remains unaffected by the complete adsorption-desorption-injection process. The analysis of a porous polymer precolumn which does not contain a trapped sample should ideally result in the baseline remaining unaltered.

Background contribution by the apparatus is one of the major factors affecting the sensitivity of this analytical technique. In the development experiments the levels of background contribution were classified into three levels. At an attenuation of 50×10^{-12} A f. s. d., these levels were described as:-

(a) No background level: baseline remained unaltered.

(b) Acceptable background level: baseline stability is affected, but accurate sample peak identification and area measurement is possible.

(c) Unacceptable background level: accurate sample peak identification and area measurement is impossible.

A1. 3. 2. 1 POROUS POLYMER PRECOLUMNS

Precolumns were made from 6. 35 mm o. d. x 3. 2 mm i. d., precision ground glass tubing.

Several porous polymer adsorbents were used:-

Chromosorb 101, Chromosorb 102, 100/120 mesh (Johns-Manville, Denver, Colorado).

Porapak Q, 100/120 mesh (Waters Associates Inc., Framington, Massachusetts).

Tenax GC, 60/80 mesh (Enka N. V., The Netherlands).

Tenax GC was favoured most, principally due to its higher thermal stability.

The trapped samples were thermally desorbed. They were injected into the gas chromatograph either by direct desorption onto the analytical column (A1. 3. 2. 2.) or via a desorption-injection unit (A1. 3. 2. 3).

The precolumns were connected for desorption by special low volume 6.35 mm i.d. Wade couplings (Perkin Elmer, Beakonsfield, England). These couplings used neoprene sealing rings to effect gas tight seals.

Preliminary experiments

76 mm long precolumns, completely filled with adsorbent were used. A desorption heater (A1. 3. 2. 2) was designed to cover and heat the complete precolumn and precolumn couplings. Temperatures between 140 and 240°C were used.

Using these precolumns, unacceptable background levels occurred.

At first these levels were thought to be due to artifacts arising from poorly conditioned porous polymer adsorbents. However, results of further experiments showed that the coupling sealing rings were the cause. At the elevated desorption temperatures, compounds were eluted from the sealing rings. High background levels were caused because the compounds were concentrated by the ambient analytical column (A1. 3. 2. 2) or the desorption-injection unit cold trap (A1. 3. 2. 3). Background levels from neoprene, graphite and silicone rubber sealing rings were all unacceptable.

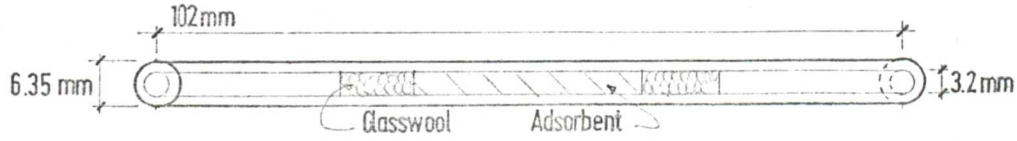
It was found that at temperatures below 70°C, silicone rubber sealing rings did not affect background levels. The precolumn couplings could be kept below 70°C by increasing the length of the precolumn to 102 mm, and heating only the centre portion of the precolumn. With 102 mm precolumns and silicone rubber sealing rings, no background level was obtained.

It was found that samples were more rapidly analysed when the precolumn was desorbed in the opposite direction to sampling.

Precolumn design and method of preparation

The precolumn design used for all headspace analyses is depicted to scale in Fig. Al. 06.

Fig. Al. 06. Scale diagram of porous polymer precolumn.

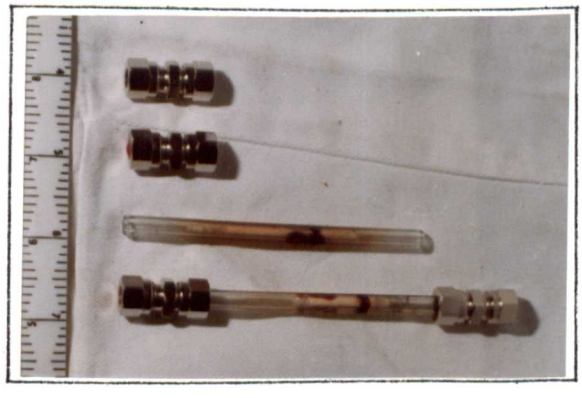


102 mm lengths of glass tubing were cut, the broken ends annealed by heating. The tubes were then acid cleaned (concentrated nitric acid), washed (water, acetone, toluene) and silanated (Hexamethyldisilazane: Toluene, 1 : 10).

Tenax GC was prepared by filling a 914 mm x 6. 35 mm o. d. x 3. 2 mm i. d., glass column and thermally conditioning at 300°C for 24 hours with inert gas flow. 50 mg Tenax GC were then added to a glass tube and held in place by two plugs of silanated glass wool. The adsorbent filled precolumn was then further conditioned at 240°C for 30 minutes with helium which had passed through a liquid nitrogen cooled cold trap. With this conditioning procedure no background levels were detected.

The precolumn was sealed by attaching two 6. 35 mm i. d. couplings (Wade, Perkin Elmer), one end of which contained a rubber septum (Plate Al. 02).

Plate Al. 02. Porous polymer precolumn design.



A1. 3. 2. 2 POROUS POLYMER PRECOLUMN ANALYSIS BY DIRECT DESORPTION

The porous polymer precolumn was connected to a conventionally packed 6. 35 mm o. d. x 3. 2 mm i. d., glass, analytical column by a 6. 35 mm i. d., coupling (Wade, Perkin Elmer).

The sample was desorbed by positioning the desorption heater (A1. 3. 2. 3) round the centre portion of the precolumn, and immediately connecting the gas chromatograph carrier gas supply to the precolumn. Desorption temperatures of 140 - 240°C for periods of 5 - 10 minutes were used.

Provided the precolumn couplings were not warmed above 70°C (A1. 3. 2. 1), no background levels were detected.

The chromatographic conditions varied, depending on the compounds being analysed (A1. 4 and A1. 5). In general, analytical column temperatures during desorption ranged between 20° and 125°C. Flow rates between 30 and 60 cm^3 min^{-1} were used.

Standard solutions were analysed by injecting into a heated, empty, glass precolumn, connected to the analytical column. A Hamilton, series 7001, 1 mm^3, microlitre syringe (Hamilton, Bonaduz, Switzerland) was used to inject the solutions.

Identical precolumn temperature and chromatographic conditions were adopted for samples and standard solutions.

A1. 3. 2. 3 POROUS POLYMER PRECOLUMN THERMAL DESORPTION-INJECTION UNIT

Although the unit was originally intended as a means of desorbing and injecting potato volatiles (A1. 2. 2. 4), it was finally used for rapid sprout suppressant headspace analyses (A1. 5).

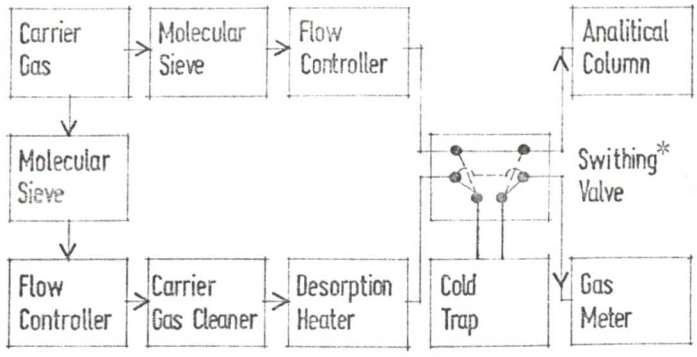
The unit was built around a Pye gas sampling valve (A1. 2. 2. 1) with modifications to existing pieces of equipment. It was constructed and mounted on the gas chromatograph as depicted in Plate A1. 03. The unit consisted of several components, the design and operation of which were experimentally determined. They are represented schematically in Fig. A1. 07.

Switching valve

Six port, 2 position, low volume, gas sampling valve (Pye Unicam Ltd., Cambridge, England). Constructed of stainless steel with a Teflon slider. Thermal limit 100°C. The valve was mounted as close as possible to the analytical column (cf. manufacturers recommendations A1. 2. 2. 1). 87 mm x 1. 6 mm o. d. x 0. 7 mm i. d., stainless steel tubing connected the valve and gas chromatograph injection port.

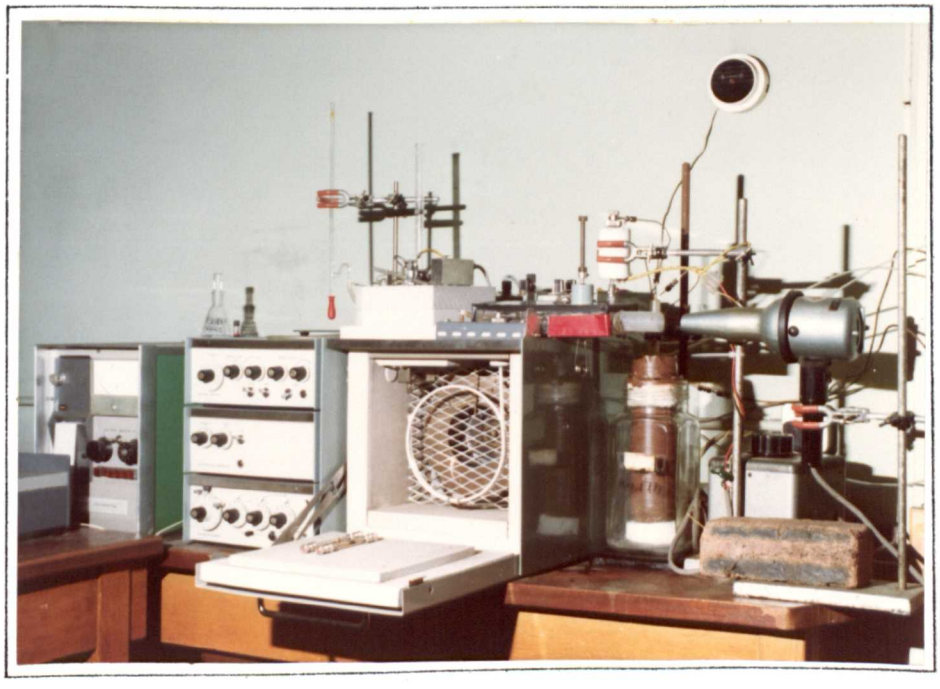
In preliminary experiments the performance of this switching valve was compared to an 8 port, 2 position valve (Model 2608200, Becker, Berkshire) which had a higher thermal limit of 200°C. When operated at 145°C, the 8 port valve produced unacceptable background levels. This was principally due to compounds eluted from silicone rubber sealing rings used in its construction. The valve's performance was also limited by its larger internal volume.

Fig. Al. 07. Flow diagram of thermal desorption-injection unit.



Sample trap (solid lines). Sample inject (broken lines).

Plate Al. 03. Thermal desorption-injection unit



* Switching valve
Analytical column

Low volume cold trap

305 mm x 1. 6 mm o. d. x 0. 7 mm i. d., 17. 5 mm diameter coil of stainless steel tubing. The coil was attached to the switching valve by low volume couplings (Pye Unicam Ltd., Cambridge, England). The cold trap was cooled by liquid nitrogen.

Oil Bath

Silicone oil or liquid paraffin were used to rapidly heat the cold trap. Temperatures up to 160°C were used.

Desorption heater

67 mm x 40 mm diameter, aluminium block with a 7 mm diameter hole extending through the length of the 67 mm axis. The block contained a 300 W, 250 V heating cartridge, controlled by a variable transformer. The temperature of the block was determined by a mercury in glass thermometer placed in a small 7 mm diameter hole in the block.

Carrier gas inlet-injection ports

The unit design included two injection ports (Pye Unicam Ltd., Cambridge, England). These allowed introduction of standard solutions either directly to the analytical column, or via the cold trap.

Flow controller

Fine flow controllers (Brooks, Emerson Electric Company, Pennsylvania).

Connecting tubing

Carrier gas supply, molecular sieve, and flow controllers were connected by 3. 2 mm o. d. x 1. 2 mm i. d., copper tubing. All other connecting tubing was 1. 6 mm o. d. x 0. 7 mm i. d., stainless steel.

Hot air bath

The switching valve and its connecting tubing to the desorption heater, cold trap, flow controller and analytical column were contained in a hot air bath, temperature 90°C. The bath was constructed from Perspex and heated by an electric fan.

In preliminary experiments a hot water jacket was constructed around the valve and connecting tubing. This system was considered safer than using an electric fan as hydrogen leaks from the gas chromatograph can occur. Noise levels were also considerably reduced. However, the system only remained water tight for a few days.

Heating tape was also used, however, hot air was the simplest system to construct and operate.

Gas meter

20 cm^3 bubble meter.

Carrier gas

Helium (BOC Special Gases, BOC, Glasgow) was used for all analyses. Flow rates of up to 15 cm^3 min^{-1} through the cold trap were adopted.

In preliminary experiments nitrogen (BOC, Glasgow) was used. With this gas, material (nitrogen ?) accumulated in the coldtrap in sufficient amounts that when vaporized by heating the cold trap, the flame ionization detector was extinguished!

Carrier gas cleaner

In preliminary experiments molecular sieve 5A cleaners were used. Despite these, trace contaminants were trapped by the cold trap, producing unacceptable background levels. An additional carrier gas cleaner was included. The cleaner consisted of 610 mm x1. 6 mm

o. d. x 0. 7 mm i. d., 17. 5 mm diameter coil of stainless steel tubing cooled in liquid nitrogen. Using this additional cleaner, background levels due to carrier gas contaminants were eliminated.

Desorption-injection unit operation

The unit was best operated in the following order:-

1. Switch valve to sample trap position.
2. Connect the precolumn to the switching valve (desorbing in opposite direction to sampling).
3. Slide the desorption heater into position, heating the central portion of the precolumn.
4. Rapidly connect the precolumn to the carrier gas supply.
5. Immediately cool the cold trap with liquid nitrogen.
6. After completing the necessary desorption period, remove the liquid nitrogen.
7. Immediately operate the switching valve to sample inject position.
8. Immediately heat the cold trap with hot oil.
9. Warm the trap for 30 seconds.
10. Return the switching valve to sample fill position.
11. Remove the hot oil.
12. Remove desorbed precolumn.

Analysis of standard solutions

Standard solutions were analysed by injecting either directly onto the analytical column or into a heated, empty, glass precolumn, connected to the desorption-injection unit.

A Hamilton, series 7001, 1 mm^3, microliter syringe (Hamilton, Bonaduz, Switzerland), was used to inject the solutions.

Identical precolumn temperatures and chromatographic conditions were adopted for samples and standard solutions.

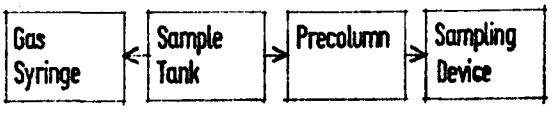
A1. 3. 3 HEADSPACE ANALYSIS, PRELIMINARY EXPERIMENTS

The aim of these experiments was to investigate quantitative headspace analysis by porous polymer precolumns. A standard headspace was prepared by adding small amounts of α-pinene and dimethylnaphthalene to a 54 dm^3 sealed glass tank. Headspace samples from the tank, trapped on porous polymer precolumns were compared to headspace samples taken by gas syringe.

A1. 3. 3.1 METHODS

Headspace analysis apparatus is depicted schematically in Fig. A1.08.

Fig. A1.08. Flow diagram of headspace analysis apparatus.



Sample tank

54 dm^3 glass tank. A hole in the lid provided a sampling point. The hole was sealed by a silicone rubber septum, through which gas syringe samples were taken. The septum was removed when porous polymer precolumns were used. A mercury in glass thermometer was fitted inside the tank.

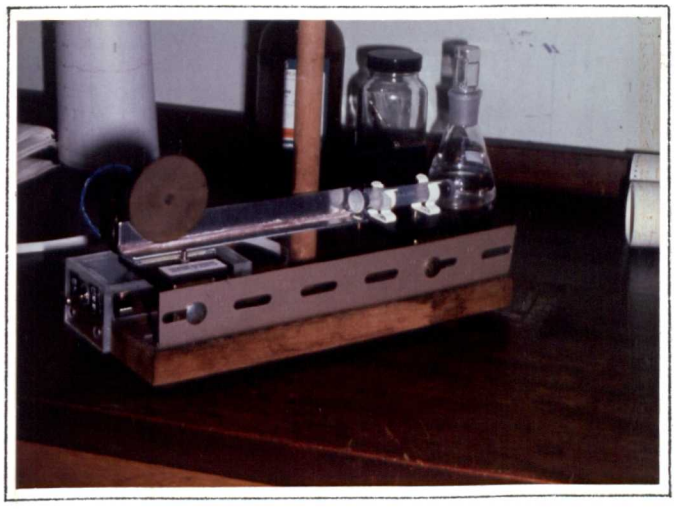
Standard Compounds

0.1 cm^3, α-pinene (Laboratory reagent grade, Hopkins and Williams, Essex, England) and 0.1 cm^3, 1, 4-dimethylnaphthalene (puris, Koch-Light, Bucks, England) were added to the tank.

Precolumn

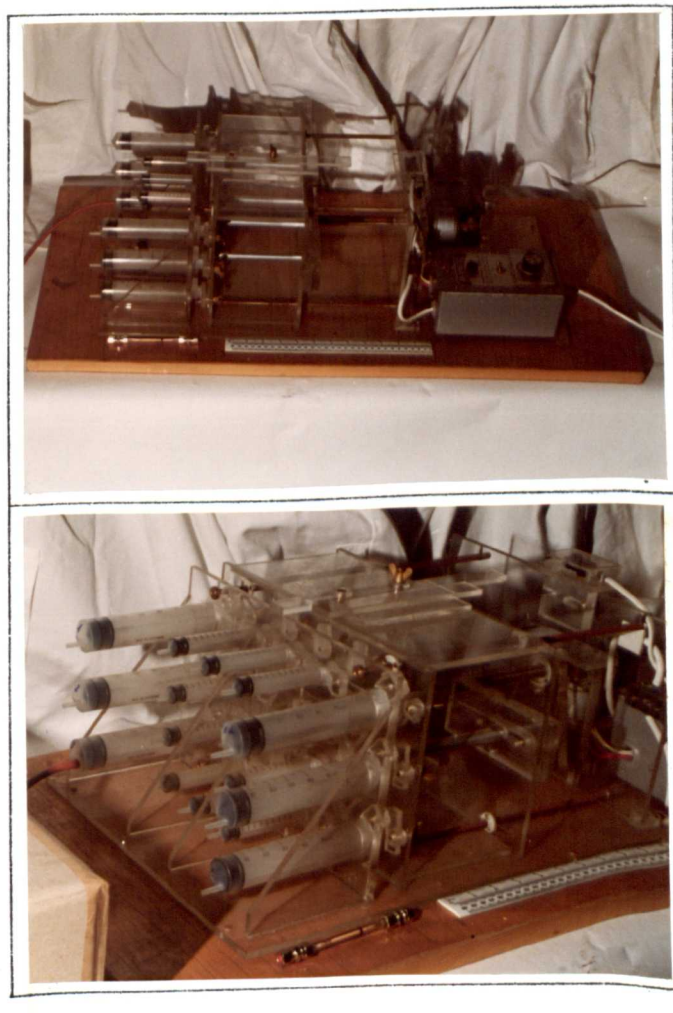
Tenax GC, 102 mm porous polymer precolumns were used (A1. 3. 2. 1).

Plate A1. 04. Syringe sampling device. Two designs were used.



First design

Used only in preliminary headspace studies (A1. 3). Single 5 cm^3 syringe. Fixed sampling rate of 3.2 cm^3 min^{-1}.



Second design

Used in all headspace studies (A1. 3, A1. 4 and A1. 5). Six, 50 cm^3 and ten, 10 cm^3 syringes. Variable sampling rates between 0. 25 and 11 cm^3 min^{-1}. Sample volume controlled automatically by a micro-switch.

Sampling device

Two sampling devices were used to control sampling rate (construction details in Plate A1. 04. They both consisted of mechanically operated syringes, connected to the precolumn by 6. 5 mm o. d. x 3. 2 mm i. d. rubber tubing.

Gas syringes

Several gas syringes were used;

1000 mm^3, gas-tight with Chaney adaptor, Hamilton Series 1001, (Hamilton, Bonaduz, Switzerland).

500 mm^3, gas-tight with Chaney adaptor, Hamilton Series 1750, (Hamilton, Bonaduz, Switzerland).

10 cm^3, gas-tight, Hamilton series 1010, (Hamilton, Bonaduz, Switzerland).

1 cm^3, glass (Rocket of London).

1 cm^3, plastic disposable (B-D plastipak, Becton and Dickinson Co. Ltd., Republic of Ireland).

Gas syringe samples were taken by filling the syringe three times, the last fill accurately measured and injected onto the analytical column.

Sampling position

Both precolumn and gas syringe samples were taken from a position 64 mm from the top of the tank.

Analysis

Precolumn samples were analysed by direct desorption onto the analytical column (A1. 3. 2. 2), gas syringe samples by direct injection onto the analytical column.

Precolumn sample desorption conditions:- Temperature 230°C, time 7 - 10 minutes, flow rate 6 cm^3 min^{-1}.

Precolumn sample chromatographic conditions:- 50°C (7 - 10 minutes), increasing to 200°C (7 minutes), at 30°C min^{-1}. 5% OV17, on GC Q 100/120, Helium, 30 cm^3 min^{-1}, Detector 200°C.

Gas syringe sample chromatographic conditions:- 200°C isothermal. Detector 200°C, Injector 250°C.

Standard solution addition to a porous polymer precolumn

Preparation:- An empty glass precolumn and two adsorbent packed precolumns were connected in series by two 6.35 mm i.d. Wade Couplings, fitted with silicone rubber sealing rings. The empty glass precolumn was heated to 230°C, the packed precolumns remaining at room temperature. A carrier gas-injection port (A1. 3. 2. 3) was connected to the empty glass precolumn. Air or Helium which had previously passed through a liquid nitrogen cold trap was used as carrier gas. Flow rate was 6 cm^3 min^{-1}. A 1 mm^3 aliquot of 0.1%, 1,4-dimethylnaphthalene, acetone solution was injected into the empty glass precolumn by a Hamilton series 7001, 1 mm^3, microlitre syringe.

Analysis:- Direct desorption onto analytical column (A1. 3. 2. 2). 230°C, 7 - 10 minutes, 6 cm^3 min^{-1}.

Chromatographic conditions:- 50°C (7 - 10 minutes), increasing to 200°C (7 minutes) at 30°C min^{-1}. 5% OV17 on GC Q 100/120, Helium, 30 cm^3 min^{-1}, Detector 200°C.

Headspace concentration calculated from published values

The vapour pressures of dimethylnaphthalenes were extrapolated from published values (Osborn and Douslin, 1975).

Plots of log p v. $\frac{1}{T}$ were drawn for the solid compounds at temperatures between 55 and 110°C. Vapour pressure at 15 and 20°C was extrapolated from these plots.

The vapour pressures of α-pinene at 15 and 20°C were calculated from the published vapour pressure-temperature equation (Hawkins and Armstrong, 1954).

Headspace concentration was calculated from vapour pressure using Equation A1. 02 (A1. 4. 2. 2).

Equation A1. 02

$$\frac{g}{V_s} = \frac{P_s M}{RT} \quad g\ m^{-3}$$

where:-

P_s	=	vapour pressure of compound (Pa).
M	=	molecular weight of compound.
R	=	8. 314 Pa m^{-3} K^{-1}.
T	=	headspace temperature (K).
g	=	weight of compound evaporated (g).
V_s	=	headspace volume (m^3).

A1. 3. 3. 2 RESULTS

Table A1.01. Results of preliminary headspace experiments conducted on three different days, using a 54 dm^3 tank.

Day 1, 15 - 17°C

Sample Method	Sample Volume	Sample Number	Mean conc. α-P. mg m^{-3}	S. D.	Mean conc. DMN. mg m^{-3}	S. D.
1001 syringe	1000 mm^3	11	96	10.9	31	4.0
1 cm^3 plastic syringe	1 cm^3	4	38	1.3	10	1.0
1 cm^3 glass syringe	1 cm^3	3	75	3.0	14	2.0
Precolumn	25 or 30 cm^3	5	*91	9.2	12	1.6

Day 2, 18 - 20°C

Sample Method	Sample Volume	Sample Number	Relative mean conc. α-P, %	Mean conc. DMN. mg m^{-3}	S. D.
1001 syringe	1000 mm^3	7	100	26	2.5
1001 syringe	500 mm^3	4	120	51	3.0
1750 syringe	500 mm^3	7	105	26	6.4
1750 syringe	250 mm^3	7	129	53	1.9
Precolumn	25 cm^3	4	61	9	1.8

Day 3, 20°C

Sample Method	Sample Volume	Sample Number	Relative mean conc. α-P, %	Mean conc. DMN. mg m^{-3}	S. D.
1001 syringe	1000 mm^3	10	100	17	0.7
1750 syringe	500 mm^3	8	130	13	3.4
1010 syringe	2.5 cm^3	7	145	21	2.7

* mean of two samples

Table Al. 02. Adsorption and recovery of standard solutions from the first of two porous polymer precolumns connected in series.

Sample	Number of Samples	Mean peak area (mm^2)	S. D.	$\frac{\text{Precolumn sample area}}{\text{Direct injection area}}$ %
Precolumn 1 mm^3, 0.1% 1, 4 DMN	6	354.9	12.32	90.5
*Direct injection 1 mm^3, 0.1% 1, 4 DMN	3	392.3	6.66	

* Direct injection onto an isothermal analytical column (200° C). In later experiments (Al. 4 and Al. 5), the standard solutions were injected via a heated empty glass precolumn (Al. 3. 2. 2). Under these conditions, standard peak area and precolumn sample peak area were more similar.

Table Al. 03. Calculated vapour pressure and headspace concentration of α-pinene and dimethylnaphthalene (DMN) at 15 and 20°C.

Compound	Vapour pressure (Pa)		Headspace concentration (mg m^{-3})	
	20°C	15°C	20°C	15°C
1, 8 - DMN	0.453	0.253	29	16
2, 3 - DMN	0.240	0.133	15	9
2, 6 - DMN	0.227	0.120	15	8
2, 7 - DMN	0.320	0.173	20	11
α-Pinene	432.2	313.5	24117	17795

A1. 3. 3. 3 DISCUSSION

The results of Table A1. 01 are typical both qualitatively and quantitatively of many similar experiments conducted during the development of this analytical technique.

The headspace values determined by gas syringe and porous polymer precolumns bear little resemblance to each other. Precolumn values were frequently as little as 15% of the value determined by gas syringe. Gas syringe design, and sample volume also influenced the headspace value obtained. Headspace values determined by the same method, tended to vary daily although this was later thought to be due mainly to temperature gradients within the tank (A1. 4).

In these preliminary experiments the standard headspace of the 54 dm^3 tank was intended to be used as a means of assessing desorption-injection techniques (A1. 3. 2). Porous polymer precolumns, charged with a known headspace volume from the tank, would assess desorption either directly onto the analytical column or via the desorption-injection unit. The desorption technique would be considered successful if porous polymer precolumn determined headspace concentrations were equal to those obtained by gas syringe.

At first, anomalies between gas syringe and porous polymer determinations were attributed to the desorption methods which were therefore exhaustively adapted and refined (A1. 3. 2).

The desorption-injection techniques were then re-examined. A different method was used to prepare precolumns containing known amounts of standard compounds. An aliquot of standard solution was vaporized in carrier gas and passed through two precolumns, connected in series, at ambient temperature. Air or Helium was used as carrier gas (A1. 3. 3. 1, A1. 4, A1. 5) (Russell, 1975).

The standard compounds were quantitatively recovered from the first precolumn in series, with no elution of compounds to the

second precolumn (Table Al. 02).

The analytical techniques were thus shown to be correct, the validity of results such as those in Table Al. 01 were confirmed.

Published vapour pressure data were consulted (Hawkins and Armstrong, 1954; Osborn and Douslin, 1975). Headspace concentrations calculated from these data (Table Al. 03) were compared to the experimental values in an attempt to determine which analysis method was accurate. Unfortunately the results were inconclusive. Vapour pressure data of 1, 4-dimethylnaphthalene was not available. Comparison with values of other isomers proved useful. The vapour pressure values of dimethylnaphthalenes were extrapolated from values at higher temperatures and were not reliable (Osborn and Douslin, 1975). However, they showed that the experimentally determined headspace values were of the correct magnitude. They were unable to confirm which headspace analysis method was correct. α-pinene calculated headspace concentrations were much higher than the observed values, and thus only served to cast more doubt on both analysis methods. However, it was possible that (a) the tank headspace was not saturated and/or (b) the published vapour pressure values were inaccurate. The accuracy of many published values has been questioned (Sinke, 1974; Westrum and McCulloch, 1963).

Al. 3. 3. 4 CONCLUSIONS

Quantitative adsorption-desorption by Tenax GC precolumns had been shown both in this work and by others (Pellizzari et al., 1975a, 1976a; Russell, 1975; Butler and Burke, 1976; Holzer et al., 1977). There was no apparent reason why this should not apply when sampling a 54 dm^3 tank (or 10 kg potato boxes). Quantitative adsorption had been shown under similar field conditions of humidity, and in the presence of compounds of secondary interest (Pellizzari et al., 1976a). However, it was considered important that these preliminary results shown be explained, as they cast some doubt on the analysis method.

PART A1.4

POROUS POLYMER ADSORBENT AND GAS SYRINGE HEADSPACE ANALYSIS. A COMPARATIVE STUDY USING NAPHTHALENE AS A REFERENCE SUBSTANCE

INTRODUCTION

The aim of this work was to establish a headspace containing a known concentration of a chosen reference substance. Conditions were arranged in order that the concentration could be calculated from published vapour pressure/temperature data. The headspace of known composition was then used to assess the accuracy of the porous polymer adsorbent and gas syringe analysis techniques.

Naphthalene was chosen as the reference substance. Naphthalene has similar physical/chemical properties as dimethylnaphthalene and has reliable vapour pressure/temperature data which have been determined for the temperature range under consideration (Ambrose et al., 1975). Naphthalene is recommended as a reference substance for inter-comparisons of investigations in the low vapour pressure region. Under these conditions it is considered to behave ideally (Sinke, 1974).

The principles involved in this study are similar to those on which the gas-saturation method of low vapour pressure determination is based (Thomson, 1959). In the gas-saturation method a current of inert gas is passed through the substance whose vapour pressure is to be determined, at a slow enough rate to ensure equilibrium saturation. The vapour pressure is then computed on the assumption that the ratio of the vapour pressure to the total pressure is the same as the ratio of the volume of vapour to the total volume of vapour and inert gas (Dalton's Law). The volume of vapour must be computed by the gas laws, from the weight of material vaporized. The method is thus limited by the condition that there must be no association in the vapour.

The volume of inert gas is measured usually by a standardized gas meter, after the evaporated material has been removed. The evaporated material can be removed by methods such as cold traps or suitable liquid or solid sorbents from which by subsequent analysis the weight of vaporized material can be determined.

Headspace sampling using porous polymer adsorbents is directly analogous to the step in vapour pressure determination by gas-saturation in which the evaporated material is trapped and quantified. In the work described here, a procedure similar to that used in the gas-saturation method was adopted. By maintaining conditions previously shown to achieve complete saturation by naphthalene vapour (Sinke, 1974), a headspace of known naphthalene content was established.

Two types of naphthalene containing headspaces were studied:-

1. The dynamic headspace of a gas stream which had previously passed through a saturation cell containing naphthalene crystals.
2. The static headspace of a 54 dm^3 glass tank on the bottom of which had been placed naphthalene crystals.

The dynamic headspace, once complete saturation is established, will contain a concentration of naphthalene equal to that calculated from published vapour pressure/temperature data. The static headspace of a 54 dm^3 glass tank represents sampling conditions more typical of those found when analysing the headspace of 10 kg potato boxes. The naphthalene content of this static headspace can be related to the calculated concentration. The large volume of the glass tank helps minimize any dilution effects caused by removing headspace samples.

A1. 4. 1 MATERIALS AND METHODS

A1. 4. 1. 1 POROUS POLYMER PRECOLUMN

Porous polymer precolumn design was the same as described previously (A1. 3. 2. 1), i. e. glass tube 102 mm long, 3. 2 mm internal

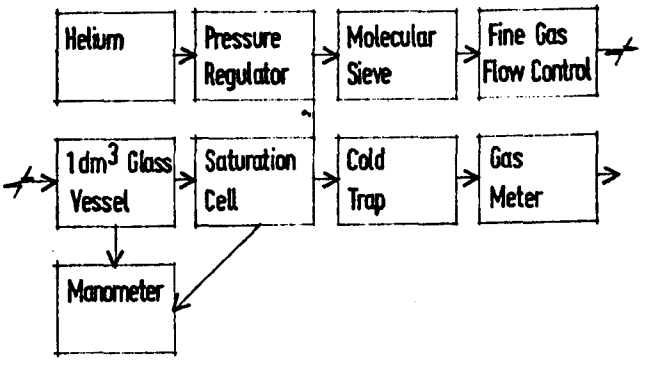
diameter, and 6.35 mm outer diameter. The adsorbent used was Tenax GC.

A1.4.1.2 DYNAMIC HEADSPACE

Headspace apparatus

A flow diagram of the apparatus is outlined in Fig. A1.09.

Fig. A1.09. Flow diagram of dynamic headspace apparatus.



The apparatus consisted of:-

1. Cylinder of Helium (BOC Special Gases, BOC, Glasgow).
2. Pressure regulator. 15 MPa - 200 kPa. (C. S. Milne and Co. Ltd.).
3. Molecular sieve type 5A (Phase separations Ltd., Queensferry, Great Britain).
4. Fine gas flow controller (Brooks model 8744A, Instrument Division, Emerson Electric Co.)
5. I dm^3 glass cylindrical vessel.
6. Mercury manometer.
7. Saturation Cell containing naphthalene crystals (BDH Purity for molecular weight determination).
8. Cold trap (solid CO_2 and acetone).
9. Gas meter (20 cm^3 bubble meter).

The 1 dm^3 glass vessel and saturation cell were held in a thermostated water bath. Passage through the vessel allowed sufficient time for the inert gas temperature to equilibrate to the saturation cell

temperature.

Saturation cell pressure was measured by a mercury manometer from (a) a sampling port on the 1 dm^3 glass vessel and (b) the sampling port of the sampling cell.

Atmospheric pressure was measured by a mercury barometer. Temperatures were measured by a mercury in glass thermometer to an accuracy of $\pm$ 0.02°C. The thermometer was checked by comparing with a mercury in glass thermometer certified by the National Physical Laboratory (Teddington, London).

Saturation cell

Saturation cell design varied with successive modifications intended to guarantee complete saturation and provide suitable sampling points for analysis by porous polymer precolumn or gas syringe. Three saturation cell designs were used (Systems 1, 2 and 3). They were constructed from glass tubing. The saturation cells' dimensions were:-

System 1	914 mm x 3.5 mm i.d., volume 9 cm^3.
System 2	1524 mm x 3.5 mm i.d., volume 15 cm^3.
System 3	230 mm x 9.5 mm i.d., volume 16 cm^3.

A sampling cell was connected to the end of each of these saturation cell designs. The sampling cell consisted of a 25 cm^3 empty glass vessel through which passed the saturated inert gas. The sampling cell was fitted with a sampling port by means of which porous polymer precolumn or gas syringe samples of the saturated gas could be taken. The sampling port consisted of a 6.35 mm i.d. coupling suitable for inserting precolumns. The coupling was sealed with a silicone rubber septum when using the gas syringe. Both porous polymer precolumn and gas syringe samples were taken from the centre of the sampling cell.

Operating conditions

Flow rates:- Normal flow rates through Systems 1, 2 and 3 were set in the range 10 - 15 cm^3 min^{-1}. These flow rates did not vary over the period of the experiment which on occasions lasted several days. When studying the effect of flow rate on the degree of saturation, flow rates between 2.5 and 400 cm^3 min^{-1} were used.

Pressure:- Atmospheric pressure was measured daily. Pressure within the headspace system was studied using System 1.

With flow rate	=	10 cm^3 min^{-1}
Pressure in 1 dm^3 glass vessel	=	16 mm Hg higher than atmospheric pressure.
Pressure in sampling cell	=	4 mm Hg higher than atmospheric pressure.

Temperature:- Room temperature varied between 18 and 20°C. Temperatures of the saturation cell systems were in the range 20 - 25°C. Water bath temperature on most occasions was maintained between ± 0.02°C and ± 0.1°C over a period of several hours.

A1.4.1.3 STATIC HEADSPACE

The apparatus consisted of:-

(a) 54 dm^3 glass tank (530 mm x 225 mm x 550 mm, external dimensions.

(b) 10 g naphthalene crystals (BDH, purity for molecular weight determinations).

(c) 2 sampling ports, one with a 450 mm x 6.35 mm o.d. glass sampling tube extending within the tank.

(d) 300 mm x 3 mm i.d. stainless steel air leak.

(e) Mercury in glass thermometer $\pm$ 0.02°C.

(f) Hair hygrometer (Fischer type 3, Drebach, DDR).

The tank was wrapped in polystyrene and cardboard in order to prevent excessive temperature variation.

The sampling ports were the same as those used in the sampling cell of the dynamic headspace.

Most porous polymer and all gas syringe samples were taken from a position 64 mm from the top of the tank. The thermometer was placed at this sampling position.

The sampling tube was used for porous polymer analysis of the centre of the tank.

Operating conditions

Temperatures studied were in the range 17 - 19°C. Temperature control over a period of hours varied between $\pm$ 0.02°C and $\pm$1.0°C. Overnight temperature was not controlled.

Humidity varied between 45 - 60% R.H.

A1.4.1.4 SAMPLING CONDITIONS

Porous polymer sampling

One end of the porous polymer precolumn was placed in the headspace, the 6.35 mm i.d. sampling port providing a gas-tight seal. The other end was attached to a 20 cm^3 bubble meter. The bubble meter was either connected to the syringe sampling device (Plate A1.04) or vented to atmosphere. Volumes of 1.0 to 10.0 cm^3 were studied. The headspace was either pulled or pushed through the porous polymer precolumn. Sampling rates were measured accurately by a stopwatch. The syringe sampling device pulled the inert gas through at rates

between 0.25 and 11 cm^3 min^{-1}. By sealing the exit point of the sampling cell the gas flow from the saturation cell could be pushed through the porous polymer precolumn. The method was used at sampling rates between 7 and 13 cm^3 min^{-1}. When two precolumns were connected in series a 6.35 mm i.d. coupling was used. The first precolumn was placed in the headspace, the unconnected end of the second precolumn attached to the bubble meter.

Gas syringe sampling

A new Hamilton series 1001, 1000 mm^3 gas-tight syringe, fitted with a Chaney adaptor, was used.

Volumes varied between 250 and 750 mm^3.

Sampling rates between 0.25 and 2.0 cm^3 min^{-1} were studied. These were accurately determined using a stopwatch.

To clean the syringe between samples, a fine wire was passed through the needle.

A1.4.1.5 ANALYSIS

Gas chromatographic analysis

A Pye series 104 gas chromatograph with a flame ionisation detector was used. The chromatographic conditions were:-

Helium 60 cm^3 min^{-1}; 5% OV 17 (50% Phenylmethyl silicone) on 100 - 120 mesh GC Q support (Applied Science Laboratories, Inc.); oven temperature 140°C isothermal or temperature programme 20 - 140°C at 49°C min^{-1}, (5 minutes isothermal 20°C, 8 minutes isothermal 140°C), detector temperature 250°C and injection temperature 240°C.

Preparation of porous polymer precolumns to assess analytical technique

Known quantities of naphthalene (0.5 µg) were added to porous

polymer filled precolumns (Al. 3. 3. 1). Standard solutions were injected into heated empty glass precolumns and swept by carrier gas into a connecting cold porous polymer filled precolumn. The empty glass precolumn temperature was 230°C, the porous polymer filled precolumn temperature 20°C. Helium, purified by molecular sieve 5A and a $N_{2(l)}$ cold trap, was used as carrier gas.

Analysis of porous polymer samples

The porous polymer precolumn was connected directly to the analytical column by a 6. 35 mm i. d. coupling, fitted with silicone rubber seals. 0. 75 μg of 1-methylnaphthalene were added to the precolumn as a recovery standard. The precolumn was heated at 230°C for 5 minutes and the analytical column held at 20°C. After the 5 minute desorption period, the analytical column temperature was increased to 140°C at 49°C min^{-1}. The temperature was then held at 140°C for 8 minutes.

The area of the peaks corresponding to naphthalene and 1-methylnaphthalene were calculated by peak height x width at $\frac{1}{2}$ height. The areas were compared with those of standard solutions of naphthalene and 1-methylnaphthalene. The standard solutions were analysed under the same chromatographic conditions. The solutions were added to the analytical column by injection into a connecting empty precolumn at 230°C.

Analysis of gas syringe samples

Gas syringe samples were analysed by direct injection onto the analytical column, isothermal at 140°C. The samples were compared to standard solutions injected under the same conditions.

Al. 4. 2. CALCULATION OF THE THEORETICAL HEADSPACE CONCENTRATION

In the following calculations, Dalton's Law and the ideal gas laws are assumed to be valid.

A1. 4. 2. 1 SAMPLING USING A POROUS POLYMER PRECOLUMN

The calculation is based on that presented for use in the gas-saturation method of vapour pressure determination (Thompson, 1959). The calculation assumes that no water is added to the inert gas at any stage in the procedure.

Let:- T_s = temperature of headspace system (K).

T_m = temperature of gas meter (K).

P_s = total pressure in the headspace sampling cell (Pa).

P_m = total pressure in gas meter (Pa).

p_s = vapour pressure of naphthalene (Pa), at T_s.

g = weight of naphthalene evaporated (g).

M = molecular weight of naphthalene.

V_m = measured volume of inert gas (m^3).

V_a = volume of inert gas passing through the porous polymer precolumn (m^3), measured at T_s, P_s.

$$V_a = V_m \left(\frac{T_s}{T_m}\right) \left(\frac{P_m}{P_s}\right)$$

In the headspace sampling cell the volume of vaporized naphthalene at T_s, P_s, may be calculated from the ideal gas laws to be:-

$$\frac{gRT_s}{MP_s} \qquad \text{where } R = 8.314 \text{ Pa m}^3 \text{ K}^{-1}$$

From Dalton's Law, at the headspace sampling cell:-

$$\frac{p_s}{\frac{gRT_s}{MP_s}} = \frac{P_s - p_s}{V_a}$$

$$p_s = \frac{gRT_m (P_s - p_s)}{MV_m P_m}$$

$$\frac{g}{V_m} = \frac{p_s MP_m}{RT_m (P_s - p_s)} \text{ g m}^{-3} \qquad \text{Equation A1. 01}$$

All samples taken by porous polymer precolumns were compared to this calculated value of g/V_m. (As V_m is the volume of inert gas, this is not the concentration of naphthalene in the headspace sampling cell).

Experimental conditions were chosen in order that:-

1. It was reasonable to make the approximation that P_m equalled atmospheric pressure, i. e. slow sampling rates.

2. The difference between P_s and P_m was minimized, i. e. slow flow rates through the sampling cell.

Under these conditions, the influence of pressure change would be minimal with respect to any corresponding change in the value of g/V_m.

Temperature change, however, with corresponding change in vapour pressure would most influence the value g/V_m.

Temperature of the sampling cell, therefore, was measured for each sample. The difference between P_s and P_m need only be measured once. Atmospheric pressure was measured daily.

A1. 4. 2. 2 SAMPLING USING A GAS SYRINGE

Let:- T = temperature of the gas syringe (K).

V_s = measured volume containing inert gas and naphthalene vapour at temperature T (m^3).

p_s = vapour pressure of naphthalene at sampling cell temperature (Pa).

M = molecular weight of naphthalene.

$$\frac{g}{V_s} = \frac{p_s M}{RT} \quad g\ m^{-3} \qquad \text{Equation A1. 02}$$

All samples taken by gas syringe were compared to this calculated value of g/V_s. When T is equal to the headspace sampling cell temperature, g/V_s is the concentration of naphthalene in the sampling

cell. On most occasions T was equal to the temperature of the headspace sampling cell. Equation A1. 02 assumes that if T was less than the temperature of the headspace sampling cell, the headspace sample is supersaturated or that if naphthalene is lost from the gas phase by the decrease in temperature, the increase in temperature caused by the injection port of the gas chromatograph is sufficient to vaporize all naphthalene present.

A1. 4. 2. 3 VAPOUR PRESSURE VALUES OF NAPHTHALENE

The vapour pressure of naphthalene (Pa) is related to temperature (K) by Equation A1. 03 (Ambrose et al., 1975).

Equation A1. 03———— $$T \log_{10} p = \frac{1}{2} a_o + \sum_{s=1}^{3} a_s E_s(x)$$

In this equation $E_s(x)$ is the Chebyshev polynomial in x of degree s, x being defined by:-

$$x = \frac{(2T - (T_{max} + T_{min}))}{T_{max} - T_{min}}$$

Where T_{max} and T_{min} are two temperatures outside the range of the experimental measurements used to derive this relationship (Ambrose et al., 1970).

The vapour pressure of naphthalene for each temperature studied was calculated from Equation A1. 03 in the form:-

$$T \log p = \frac{a_o}{2} + a_1 E_1(x) + a_2 E_2(x) + a_3 E_3(x)$$

where: $E_1(x) = x$, $E_2(x) = 2x^2 - 1$, $E_3(x) = 4x^3 - 3x$.

$T_{max} = 344$ K, $T_{min} = 230$ K.

$a_o = 301.6247$, $a_1 = 791.4937$, $a_2 = -8.2536$, $a_3 = 0.4043$.

A1. 4. 3. RESULTS

In the following results the naphthalene concentration determined experimentally by the porous polymer or gas syringe methods is expressed as a percentage of the calculated value, i. e. as "% g/V_m" for porous polymer determined values, or as "% g/V_s" for gas syringe determined values. When a number of samples are considered over a range of temperatures, the value "mean % g/V_m" or "mean % g/V_s" is the mean of the sample values of "% g/V_m" or "% g/V_s", calculated at each sample temperature.

Table A1. 04. Assessment of gas chromatographic analytical technique used in naphthalene headspace concentration studies.

1. Recovery of 1-methylnaphthalene internal standard

   Themean recovery rate from 56 samples was 98. 0% standard deviation, 2. 38%.

2. Recovery from porous polymer precolumns containing known Quantities of naphthalene.

Sample Number	% Recovery
1	101. 8
1	99. 1

3. Reproducibility of analytical technique. Mean peak area of standard solutions injected via a heated empty precolumn (230°C), connected to the analytical column (20°C) with subsequent temperature programmed analysis.

Sample	Sample Number	Mean peak area (mm^2)	S. D.
0. 5 µg naphthalene	6	283. 5	2. 80
0. 75 µg 1-methylnaphthalene	6	398. 3	4. 00

Table A1.05. Effect of dynamic headspace saturator cell design on % g/V_m determined by porous polymer precolumn.

Headspace system	Sample Number	Volume (cm^3)	Sampling rate ($cm^3 min^{-1}$)	Mean temperature (°C)	Mean % g/V_m	S. D.
1	20	5.1	1.1	22.0 ± 4.63	97.7	3.96
2	11	5.0	1.0	22.0 ± 0.10	98.0	2.26
3	1	5.0	1.0	21.95 ± 0.02	99.2	

Table A1.06. Effect of dynamic headspace saturator cell design on % g/V_s determined by gas syringe. Syringe clean preceeding each sample.

Headspace system	Sample Number	Volume (cm^3)	Sampling rate ($cm^3 min^{-1}$)	Mean temperature (°C)	Mean % g/V_s	S. D.
1	9	250	0.25	22.0 ± 05	77.8	5.04
2	11	250	0.25	22.0 ± 05	76.8	5.95

Table A1.07. Effect of inert gas flow rate through dynamic headspace saturator cell on % g/V_m, determined by porous polymer precolumn. Dynamic headspace System 2. Sample volume, 5.0 cm^3; sampling rate, 1.0 cm^3 min^{-1}; mean temperature, 22.0 $\pm$ 0.10°C.

Sample Number	Flow rate cm^3 min^{-1}	Mean % g/V_m	S.D.
1	2.5	100.9	
3	5.5	96.5	1.84
2	8.3	98.4	3.54
3	16.2	97.1	2.16
2	400	99.5	0.00

Table A1.08. Effect of dynamic headspace saturator cell temperature on % g/V_m, determined by porous polymer precolumn. Dynamic headspace System I.

Sample Number	Volume (cm^3)	Sampling rate ($cm^3 min^{-1}$)	Mean temperature (°C)	Mean % g/V_m	S.D.
9	5.1	1.1	24.2 $\pm$ 0.12	96.1	3.24
11	5.0	1.1	21.9 $\pm$ 0.07	99.0	4.18

Table A1.09. Performance of static headspace system.

Sampling method	Sample number	Volume	Sampling rate (cm^3 min^{-1})	Temperature (^oC)	Mean % g/V	S.D.
*Syringe	6	250 mm^3	0.25	18.15 ± 0.02	64.8	2.85
*Porous polymer	19	5.1 cm^3	1.0 - 13.2	18.0 ± 0.12	85.3	2.40
‡Porous polymer	5	9.5 cm^3	1.1	18.1 ± 0.05	89.3	1.79

* Samples taken on same day

‡ Samples taken 24 hours later

Table A1.10. Performance of gas syringe. Effect of sample volume and sampling method. The syringe not being cleaned before or during the experiment.

Headspace system	*Sampling method	Sample number	Temperature (°C)	Volume (mm^3)	Sampling rate ($cm^3 min^{-1}$)	Mean conc. ($g\ m^{-3}$)	S. D.	Mean % g/V_s
Static	1	3	17.8 ± 0.15	500	2	0.877	0.081	304.3
"	1	3	18.1 ± 0.15	250	2	1.615	0.222	545.1
Dynamic	2	5	21.95 ± 0.02	250	2	0.530	0.017	121.8
"	2	7	"	500	2	0.453	0.040	104.1
"	2	5	"	750	2	0.420	0.051	96.5
"	3	5	"	500	2.0	0.448	0.011	103.0
"	4	6	"	500	2.0	0.781	0.066	179.5

* Sampling method.

1 = Syringe filled twice to volume + 100 mm^3, expelling 100 mm^3 before injecting into gas chromatograph.

2 = Syringe filled once to volume + 20 mm^3, expelling 20 mm^3 before injecting into gas chromatograph.

3 = Syringe filled once to volume before injecting (accurately timed).

4 = Syringe filled twice to volume before injecting (accurately timed).

Table A1.11. Performance of gas syringe. Effect of cleaning syringe after each sample. Dynamic headspace System 1; temperature, 21.95 ± 0.02°C; sampling method 3 (Table A1.10).

Sample volume (mm^3)	Sampling rate ($cm^3\ min^{-1}$)	Conc. ($g\ m^{-3}$)	% g/V_s	*Result of syringe clean
250	2.0	0.304	70.4	White
250	2.0	0.670	155.1	Red
250	2.0	0.309	71.1	White
250	2.0	0.304	70.4	White
250	2.0	0.302	69.9	-ve
250	2.0	0.358	82.9	-ve
500	2.0	0.260	60.2	-ve
500	2.0	0.273	63.2	-ve
500	2.0	0.575	133.1	Red
500	2.0	0.264	61.1	-ve
500	2.0	0.258	59.7	-ve
500	2.0	0.261	60.4	-ve

* Result of syringe clean -
-ve, nothing removed.
red, piece of red silicone rubber from sampling cell port removed.
white, piece of white silicone rubber from gas chromatograph injection port removed.

Table A1.12. Performance of gas syringe. Effect of sampling rate. Syringe clean preceeding each sample; dynamic headspace System I; temperature, 21.95 ± 0.02°C; sampling method 3 (Table A1.10).

Sample number	Volume (mm^3)	Sampling rate ($cm^3\ min^{-1}$)	Mean conc. ($g\ m^{-3}$)	S. D.	Mean % g/V_s
5	250	2.00	0.315	0.024	72.4
6	250	0.50	0.343	0.022	78.9
6	250	0.25	0.341	0.027	78.4
5	500	2.00	0.263	0.006	60.5
5	500	1.00	0.288	0.006	66.2
8	500	0.50	0.319	0.013	73.8
6	500	0.25	0.314	0.020	72.2
6	750	2.00	0.206	0.026	47.4
7	750	0.50	0.298	0.009	68.5
2	750	0.25	0.290	0.004	66.7

Table A1.13. Performance of gas syringe. Effect of sample volume. Syringe clean preceeding each sample; dynamic headspace System I; temperature, 21.95 ± 0.02°C; sampling method 3 (Table A1.10).

Sample number	Volume $(mm)^3$	Rate $(cm^3\ min^{-1})$	Mean conc. $(g\ m^{-3})$	S.D.	Mean % g/V_s
5	250	2.00	0.315	0.024	72.4
5	500	2.00	0.263	0.006	60.5
6	750	2.00	0.206	0.026	47.4
6	250	0.25	0.341	0.027	78.4
6	500	0.25	0.314	0.020	72.2
2	750	0.25	0.290	0.004	66.7

Table A1.14. Performance of gas syringe. Effect of sampling method. Dynamic headspace System I; syringe clean preceeding each sample; temperature, 21.95 ± 0.02°C; sample volume 500 mm^3.

Method	Sample number	Sampling rate $(cm^3 min^{-1})$	Mean conc. $(g\ m^{-3})$	S.D.	Mean %g/V_s
Filled once before injecting	8	0.50	0.319	0.013	73.8
Filled four times before injecting	2	0.50	0.418	0.038	96.1
Filled seven times before injecting	5	0.50	0.493	0.016	113.3

Table A1.15. Performance of gas syringe. Effect of placing a silicone rubber plug in the gas syringe needle. Dynamic headspace System I; temperature, 21.95 ± 0.02°C; sample volume, 500 mm^3.

Method	Sample number	Sampling rate ($cm^3 min^{-1}$)	Mean conc. ($g\ m^{-3}$)	S.D.	Mean % g/V_s
Filled once before injecting	8	0.50	0.319	0.013	73.8
Filled once before injecting plus rubber plug	3	0.50	0.448	0.099	103.0

Table A1.16. Performance of porous polymer precolumn. Concentration of static headspace. Effect of sampling rate and sample volume. Conducted over 3 days.

Sample number	Volume (cm^3)	Sampling rate ($cm^3 min^{-1}$)	Mean temp. (°C)	Mean conc. ($g\ m^{-3}$)	S.D.	Mean % g/V_m
Day 1						
2	5.1	12.8	17.1 ± 0.57	0.224	0.002	84.0
2	5.1	3.9	17.1 ± 0.85	0.231	0.009	86.5
2	5.1	1.6	17.0 ± 1.20	0.224	0.014	84.5
2	5.1	1.0	18.0 ± 0.07	0.245	0.005	83.3
4	5.1	0.5	18.0 ± 0.06	0.255	0.006	86.8
2	5.1	0.2	17.9 ± 0.02	0.299	0.011	103.3
Day 2						
5	5.0	13.2	17.9 ± 0.12	0.250	0.004	85.7
5	5.1	4.0	17.9 ± 0.16	0.245	0.004	84.0
6	5.1	1.6	18.0 ± 0.10	0.251	0.008	85.5
3	5.1	1.0	18.0 ± 0.06	0.253	0.008	86.4
Day 3						
6	2.5	1.0	17.9 ± 0.11	0.260	0.016	88.5
5	9.5	1.1	18.1 ± 0.05	0.264	0.005	89.3
3	5.1	0.5	18.1 ± 0.10	0.268	0.014	91.1
5	5.1	0.3	18.0 ± 0.05	0.290	0.012	98.7

Table A1.17. Performance of porous polymer precolumns. Effect of sample volume on % g/V_m. Dynamic headspace Systems I, 2 and 3; sampling rate 1.0 cm^3 min^{-1}; temperature range, 21.7 - 24.3°C.

Sample number	Volume (cm^3)	Mean % g/V_m	S.D.
5	2.5	96.3	4.72
32	5.0	97.8	3.37
3	9.1	97.1	4.60

Table A1.18. Performance of porous polymer precolumns. Effect of sample volume on % g/V_m. Dynamic headspace Systems I, 2 and 3; sampling rate 1.5 - 2.0 cm^3, min^{-1}; temperature range, 21.7 - 22.1°C.

Sample number	Volume (cm^3)	Mean % g/V_m	S.D.
3	2.5	85.5	3.39
17	5.0	88.6	3.84
4	9.3	85.9	3.36

Table A1.19. Performance of porous polymer precolumns. Effect of sampling rate on % g/V_m. Dynamic headspace Systems I, 2 and 3; temperature range, 21.7 - 24.3°C.

Sample number	Volume (cm^3)	Sampling rate (cm^3 min^{-1})	Mean % g/V_m	S.D.
2	2.5 and 5.0	0.2 - 0.3	169.5	8.13
6	2.4 - 9.6	0.5 - 0.7	110.5	8.95
32	4.9 - 5.1	0.9 - 1.1	97.8	3.37
17	4.9 - 5.2	1.5 - 2.0	88.6	3.84
13	4.9 - 10.0	3.5 -13.3	84.4	12.07

Table A1.20. Performance of porous polymer precolumns. Adsorption of naphthalene by a porous polymer precolumn with one end sealed, the open end placed in a naphthalene headspace.

Headspace	Sample number	Temp. (°C)	Time in headspace (min.)	µg adsorbed	S.D.	Adsorption rate (µg min^{-1})
Dynamic	4	21.8 ± 0.13	5.0	0.576	0.060	0.115
"	3	21.8 ± 0.13	10.0	0.657	0.089	0.129
Static	1	18.25	8.5	0.344		0.041
"	4	18.25 ± 0.25	20.0	0.657	0.082	0.033

Table A1. 21. Performance of porous polymer precolumns. Comparison of adsorption rates.

Headspace	Sample number	Sampling rate (cm^3 min^{-1})	*Expected adsorption rate (μg min^{-1})	Observed adsorption rate (μg min^{-1})
Dynamic	7	0.0	-	0.12
"	1	0.2	0.09	0.15
"	-	0.28	0.12	-
"	1	0.3	0.13	0.21
"	6	0.5	0.24	0.26
"	23	1.0 - 1.1	0.43 - 0.47	0.45
Static	5	0.0	-	0.03
"	-	0.13	0.03	-
"	7	0.25	0.06	0.07
"	7	0.5	0.13	0.13
"	16	1.0 - 1.1	0.25 - 0.28	0.26

* Expected adsorption rate -

Dynamic system, Adsorption rate (μg min^{-1}) = calculated g/V_m (21.8°C) x sampling rate.
Static system, Adsorption rate (μg min^{-1}) = calculated g/V_m (18.25 °C) x sampling rate.

Table Al. 22. Performance of porous polymer precolumn. Sampling with two porous polymer precolumns connected in series. Naphthalene content of the porous polymer precolumn second in series. Dynamic headsapce systems I, 2 and 3.

Sample number	Volume (cm^3)	Sampling rate ($cm^3\ min^{-1}$)	Temp. (°C)	µg Naphthalene detected
1	10.0	9.7	22.1	*ND
1	9.5	4.2	22.1	ND
1	5.0	1.9	21.9	ND
2	9.3	1.6	22.1	ND
1	9.6	0.75	22.15	ND

* ND = no naphthalene detected. Detection limit = 0.005 µg N.

Table Al. 23. Performance of porous polymer precolumn. Naphthalene content of porous polymer precolumn connected second in series to an empty precolumn. Dynamic headspace System 3.

Sample number	Volume (cm^3)	Sampling rate ($cm^3\ min^{-1}$)	Temp. (°C)	Conc. ($g\ m^{-3}$)	$\% \frac{g}{V_m}$
1	5.0	1.0	21.95	0.106	24.5
1	1.1	1.0	22.05	0.076	17.4

Table A1.24. Performance of porous polymer precolumn. Effect of using a 450 mm x 6.35 mm o.d. x 3.2 mm i.d. glass sampling tube connected to a porous polymer precolumn, to take samples from the centre of the static headspace.

Sample number	Volume (cm^3)	Sampling rate (cm^3 min^{-1})	Temp. (°C)	Conc. ($g\ m^{-3}$)	$\% \frac{g}{V_m}$
1	5.2	1.0	20.05	0.180	50.3
1	5.2	1.0	20.05	0.098	27.3
1	5.1	1.0	20.05	0.146	40.6

Table A1.25. Comparison of results of porous polymer precolumn, ($\% g/V_m$) and gas syringe ($\% g/Vs$) methods. Porous polymer sample volume, 5.0 cm^3; gas syringe sample volume, 250 mm^3.

Headspace	Sample number	Volume	Rate (cm^3 min^{-1})	Temp. range (°C)	Mean % g/V	S.D.
Dynamic (1 and 2)	21	250 mm^3	0.25	21.9 - 22.1	77.3	5.47
Dynamic (1, 2 and 3)	32	5.0 cm^3	1.0	21.7 - 24.3	97.8	3.37
*Static	6	250 mm^3	0.25	18.15 ± 0.02	64.8	2.85
*Static	6	5.0 cm^3	1.6	18.0 ± 0.10	85.5	3.10

* Samples taken on same day

A1. 4. 4. DISCUSSION

A1. 4. 4. 1. GAS CHROMATOGRAPHIC ANALYTICAL TECHNIQUE

1-methylnaphthalene recovery standards and porous polymer precolumns containing known amounts of naphthalene were used to assess the analytical technique. The results (Table A1. 04) show complete desorption of adsorbed standards and reproducible chromatographic analysis.

A1. 4. 4. 2. HEADSPACE SYSTEMS

Several methods can be used to establish a headspace of known composition (Altshuller, 1963; Kaiser and Debbrecht, 1977). Many of the methods use the principle of measuring the loss in weight of a volatile compound after passing over or through it a measured volume of inert gas. Additional control over the rate of vaporization can be achieved by adding the volatile compound to an involatile solvent (Fowlis and Scott, 1963) or placing the compound in permeation tubes (O'Keeffe and Ortman, 1966; Meigh, 1967), or capillary tubes (Raymond and Guiochon, 1973; Altshuller and Cohen, 1960). Other methods include the dilution of a known quantity of vapour by a measured volume of inert gas (Pellizzari et al., 1975a; Altshuller and Clemons, 1962), and saturation of an inert gas by the vapour of a volatile compound (Kaiser and Debbrecht, 1977).

The static headspace methods used in this work were intended to represent sampling conditions equal to those of 10 kg potato boxes. The dynamic headspace was used as a means of further verifying the static headspace results.

Dynamic headspace Systems I, 2 and 3

In previous work on the determination of the vapour pressure of naphthalene (Sinke, 1974), saturation was achieved in a saturation cell,

volume approximately 10 cm^3, filled with crushed naphthalene crystals. Oxygen was used as the inert gas with flow rates up to 500 $cm^3\ s^{-1}$. A decrease in naphthalene concentration with increasing flow rate indicated that complete saturation was not being achieved.

The saturation cells in Systems I, 2 and 3 satisfy the necessary volume. Flow rates were on most occasions between 5 and 15 $cm^3 min^{-1}$, the highest rate being 400 $cm^3 min^{-1}$. Helium was used as the inert gas, providing better penetration of the crystalline naphthalene than molecular oxygen. The results (Tables Al. 05, Al. 06, Al. 07, Al. 08) show that; (1) all three systems yielded the same headspace composition, lengthening or otherwise increasing the volume of the saturation cell making no difference to the naphthalene concentration obtained, (2) varying flow rates between 2. 5 and 400 $cm^3\ min^{-1}$, similarly had no effect, and (3) the headspace composition was sensitive to temperature variation. Naphthalene concentration change with temperature equalled that of calculated values.

By maintaining conditions similar to those known to achieve complete saturation, and from the experimental results, it is reasonable to assume that complete saturation was attained.

Static system

Both porous polymer precolumn and gas syringe results (Table Al. 09 and Table Al. 16) show that at the temperatures studied, incomplete saturation was obtained. Also the headspace concentration at the same experimentally determined temperature tended to vary from day to day. Porous polymer analyses show that the headspace concentration at 18°C was 11 - 15% less than the calculated value. This difference is most likely to be caused by; (1) Temperature variation within the tank, and/or (2) Non-ideal behaviour of naphthalene.

A temperature gradient through the height of the tank will contribute to the difference between calculated and experimental concentration values. At 18°C a temperature decrease of 1.1 - 1.5°C would result in a decrease of 11 - 15% in the calculated headspace concentration. The temperature of the tank was measured at the point of sampling, 480 mm above the naphthalene crystals. Although a temperature gradient as large as 1.5°C is unlikely, a temperature gradient of 0.6°C has been noted between the top and bottom of the surrounding cardboard. A varying temperature gradient within the tank would also best explain the daily variation in headspace concentration at the same experimentally determined temperature.

The tank design would have been improved by including a mixing device (Kaiser and Debbrecht, 1977). Such a device would have helped eliminate temperature gradients and provide a more homogeneous headspace.

A1.4.4.3. GAS SYRINGE

Common analytical column pressures at the injection port are approximately 200 kPa. When a gas syringe is inserted into the gas chromatograph, even the smallest leak between barrel and plunger can cause significant sample loss, due to the increased pressure (Kaiser and Debbrecht, 1977). This effect is most probably the reason for the lower headspace concentration values obtained using the 1 cm^3 glass syringe (Table A1.01).

The initial analyses using the static headspace (Table A1.10) yielded results similar to those of the preliminary headspace experiments (Table A1.01), i.e. variability between samples of the same volume and low correlation between samples of different volumes. However, the difference between this work and previous preliminary experiments (Part A1.3) was that the values could be related to a known headspace concentration using the dynamic headspace. The results of

Table Al. 10 show that sampling method and sample volume play an important part in this analytical technique. They also suggested that adsorption of naphthalene by the syringe surfaces could have been occurring.

It was noted that during the course of a series of samples, small pieces of silicone rubber from the sampling cell port and gas chromatograph injection port, became lodged in the syringe needle. The results of Table Al. 11 show the effect of cleaning the syringe after sampling. On every occasion after an untypically high concentration value, a piece of red silicone rubber from the sampling port was found in the syringe needle. Red silicone rubber would have been present in the syringe needle before sampling took place.

Sampling rate (Table Al. 12), sample volume (Table Al. 13), and sampling method (Table Al. 14) were then studied, a syringe clean preceeding each sample. The results of these experiments are best explained by adsorption of naphthalene on the gas syringe surfaces. Naphthalene has been previously found to be adsorbed by glass gas-sampling bulbs (Colson, 1963) and experimental apparatus (Sinke, 1974). Adsorption losses of higher-boiling compounds have been found when transferring samples by means of a syringe (Cropper and Kaminsky, 1963).

The results also suggest that naphthalene adsorbed by surfaces which are heated when the gas syringe is placed in the injection port of the gas chromatograph will be desorbed. Naphthalene adsorbed by surfaces which are not heated will not be desorbed. Assuming that, (a) there is a limit to the amount of naphthalene adsorbed by a given surface area, (b) the amount of naphthalene adsorbed varies inversely with sampling rate, and (c) surfaces nearest the headspace and, therefore, nearest the heated injection port will adsorb first, it follows, as the results suggest, that low sample volumes and slower sampling rates will favour a higher proportion of adsorbed naphthalene on surfaces

from which recovery is possible.

The composition of the gas syringe also influenced the degree of naphthalene adsorption. Stainless steel has been shown to adsorb organic compounds more strongly than glass (Levins and Ottenstein, 1967). Rubber septum caps in glass gas-sampling bulbs have caused adsorption losses of higher boiling compounds such as toluene (Cropper and Kaminsky, 1963). The results (Tables A1. 01 and A1. 15) showed that the composition of the gas syringe affected the amount of naphthalene it adsorbed. The plastic syringe used in the preliminary headspace experiments (Part A1. 3. 3) appeared to strongly adsorb naphthalene. Silicone rubber fragments placed in the syringe needle result in higher concentration values (Table A1. 15). When silicone rubber is present in the syringe needle and the syringe filled once, concentrations close to the calculated value are obtained (Tables A1. 10 and A1. 15). Perhaps a better gas syringe design would incorporate an adsorbent in the needle which would thermally desorb when placed in the heated injection port of a gas chromatograph.

From the results the best method of sampling using a gas syringe, is to take as low a volume as possible with a slow sampling rate. In all following gas syringe analyses the sample volume taken was 250 mm^3 and sampling rate 0. 25 cm^3 min^{-1}. The syringe was cleaned before each sample. The accuracy and precision of this sampling method were studied using 21 samples taken over a period of 10 days. (Table A1. 25). When compared with porous polymer values of "mean % g/V", the gas syringe values are 79% using the dynamic headspace and 76% using the static headspace.

A1. 4. 4. 4. POROUS POLYMER PRECOLUMNS

As there is little doubt that porous polymer precolumns adsorb trace organic volatiles quantitatively (Part A1. 1), the aim of this work was to assess the sampling method and apparatus.

The results using the static headspace (Table A1.16) show the effect of sample volume and sampling rate. There is a good correlation between different sample volumes taken at the same sampling rate. The lowest sample volumes (2.5 cm^3) are less precise, a reflection of low volume measurement by a 20 cm^3 bubble meter. The results of sampling rate show that there is a certain minimum sampling rate below which higher concentration values are obtained. This lower limit lies between 1.0 and 0.2 $cm^3\ min^{-1}$.

The results using the dynamic headspace (Systems 1, 2 and 3) (Tables A1.17 and A1.18) show the effect of sample volume and sampling rate. There is a good correlation between different sample volumes taken at the same sampling rates. Sampling rate affects the concentration of naphthalene measured (Table A1.19).

The results of placing one end of a porous polymer precolumn in a naphthalene containing headspace and sealing the other end (Table A1.20) shows that adsorption occurs with no gas flow through the precolumn.

This ability to adsorb with no flow rate could account for the higher concentrations obtained when using slow sampling rates. The results suggest that within the localised headspace of the porous polymer precolumn, equilibration occurs between headspace from which naphthalene has been adsorbed and the surrounding naphthalene containing headspace. The rate of this equilibration is reflected by the rates of adsorption of naphthalene, (Table A1.20), which are affected by temperature and/or the composition of the inert gas. At slow sampling rates the amount of naphthalene adsorbed by a porous polymer precolumn could depend on this equilibration rate only, being independent of the volume of headspace passed through. From these results it follows that for sampling rates less than (1) 0.28 $cm^3\ min^{-1}$ using the dynamic system at 21.8° C and (2) 0.13 $cm^3\ min^{-1}$ using the static system at

18.25°C, the adsorption rate with no gas flow would exceed the rate of adsorption corresponding to each particular sampling rate. In Table A1.21, the rate of adsorption with no flow is compared to (1) the rate of adsorption one would expect for each sampling rate and (2) the observed adsorption rate. With the dynamic headspace at 21.8°C sampling rates of 0.2 and 0.3 cm^3 min^{-1} should have rates of adsorption equal to or less than the rate of adsorption with no flow. It is noteworthy that the experimental adsorption rate is greater than the rate of adsorption with no flow, for both cases.

Clearly more experimental work is required to explain the factors which cause adsorption with no flow and how sampling rate affects these factors. Nevertheless, whatever the reasons for this effect may be, it is important that the rate of adsorption with no flow is determined for each headspace being studied. Sampling adsorption rates approaching this value should be avoided. Once sampling has been completed the porous polymer precolumn should be removed immediately.

The quantitative recovery of porous polymer filled precolumns under the experimental conditions, was checked by using two connected precolumns, analysing the precolumn second in series (Table A1.22). No naphthalene was found in these precolumns.

The effect of decreasing % g/V_m values with increasing sampling rate (Table A1.19) was therefore not due to incomplete adsorption by the porous polymer precolumn at faster sampling rates. With sampling rates greater than 2 cm^3 min^{-1}, results were variable, due to errors in volume measurement at fast sampling rates. The relationship between % g/V_m values and sampling rates between 0.9 and 2.0 cm^3 min^{-1} was studied, using all 55 experimental values taken at these rates, sample volumes 2.5 - 9.5 cm^3, temperature range 21.7 - 22.1°C. At these sampling rates there was a significant correlation between sampling rate and % g/V_m values. This effect of sample rate was shown only by the

dynamic headspace (with the exception of higher % g/V_m values at low sampling rates). It was therefore a combined effect of headspace system and sampling method. As incomplete saturation in this system was unlikely (Part A1. 4. 4. 2) and quantitative recovery by porous polymer precolumns had been established (Parts A1. 1 and A1. 4. 4. 4), values lower than the calculated g/V_m value were most probably due to errors in volume measurement. Errors in volume measurement could occur as a combined result of the effects of sampling method, apparatus and composition of the dynamic headspace. Errors in volume measurement could also account for values greater than the calculated g/V_m value at slow sampling rates. However, at slow sampling rates it is more probable that these higher values were the result of adsorption rates independent of the volume of headspace sampled.

Results show that by sampling with glass tubes preceeding the porous polymer precolumn (Tables A1. 23 and A1. 24) values less than the calculated g/V_m were obtained. This loss of naphthalene was most probably due to adsorption by the sampling tube surfaces (Colson, 1963; Sinke, 1974; Cropper and Kaminsky, 1963).

A1. 4. 5. CONCLUSIONS

Using the static headspace, porous polymer precolumns are shown to be accurate and precise when sampling rates greater than 1. 0 cm^3 min^{-1} are used. The factors affecting the choice of sampling rate should include consideration of the adsorption rate with no flow. An accurately determined concentration value will remain constant with increasing sampling rate. Sampling tubes should not be used. The porous polymer precolumn should be inserted into the headspace being studied and removed immediately after sampling has finished.

From work with the dynamic headspace the best gas syringe sampling technique was devised. The method should include, (1) A syringe clean before each sample, (2) Low sample volumes and

(3) Low sampling rates. Gas syringe analysis is highly dependent on sampling method. The best sample volume and sampling rate must be determined accurately in order that valid intercomparisons of headspace compositions can be made. The gas syringe method is less accurate and less precise than the porous polymer method.

The best results for each method obtained on the same day using the static headspace are:-

Method	Sample number	Volume	Sampling rate ($cm^3 min^{-1}$)	Conc. ($g m^{-3}$)	S.D.	% g/V
Porous polymer	5	5.1 cm^3	4.0	0.245	0.004	84.0
Gas syringe	6	250 mm^3	0.25	0.192	0.008	64.8

Work with porous polymer precolumns and the dynamic headspace was disappointing in that clearly more experiments are necessary in order to understand the effects of sampling rate and apparatus design. The results show that the dynamic headspace apparatus and sampling method would not be suitable for accurate determinations of vapour pressure. However, it is worth consideration that this method and apparatus can show that concentration differences of 0.04 $g m^{-3}$ are significant (i.e. the difference in concentration values obtained at 21.95°C between sampling rates of 0.9 and 2.0 $cm^3 min^{-1}$).

Before this work with a naphthalene containing headspace, the best method of sampling 10 kg. potato boxes was devised. It was thought best to sample at very low rates overnight. The sampling device would switch off automatically when sampling was complete. It was for this purpose that the syringe sampler (Plate A1.04) was designed. Sampling tubes connected to precolumns would be used to sample from the centre of each box. Clearly such a method would not have worked.

PART A1. 5

HEADSPACE ANALYSIS OF POTATOES TREATED WITH VOLATILE SPROUT SUPPRESSANT CHEMICALS

The headspace of 5 kg samples of potatoes treated with 1, 4 - dimethylnaphthalene, carvone, citral, pulegone, tecnazene and chlorpropham were studied. The potato samples were stored in 10 kg capacity potato boxes.

The headspace concentration of tecnazene and chlorpropham in commercial potato stores was also determined.

A1. 5. 1. HEADSPACE ANALYSIS OF 5 kg POTATO SAMPLES TREATED WITH 1, 4 - DIMETHYLNAPHTHALENE, CARVONE, CITRAL AND PULEGONE

The potato samples were stored in 10 kg potato boxes at 9°C for a period of 14 weeks. 1, 4 - dimethylnaphthalene samples were analysed on five occasions; 3, 13, 27, 61 and 99 days after treatment. Carvone and pulegone samples were analysed on four occasions. Carvone, 10, 26, 60 and 97 days after treatment, and pulegone, 10, 27, 60 and 98 days after treatment. Citral samples were analysed on two occasions, 11 and 27 days after treatment.

A1. 5. 1. 1. METHODS

Treatment of potato sample

1, 4 - Dimethylnaphthalene (Aldrich, Gillingham, England) was applied at five different rates:- 50 mg kg^{-1}, 100 mg kg^{-1}, 150 mg kg^{-1}, 175 mg kg^{-1} and 300 mg kg^{-1}, $\pm$ 2 mg kg^{-1}, cv. Maris Peer was used.

Carvone (Koch-Light, Colnbrook, Bucks., England), citral (Hopkin and Williams, Chadwell Heath, England) and pulegone (R. Emanuel Ltd., Wembley, England) were applied at two different rates:- 100 mg kg^{-1}

and 500 mg kg^{-1} $\pm$ 2 mg kg^{-1}. cv. Record was used.

A 28 g, screw top, glass jar, containing alumina and sprout suppressant chemical was prepared for each 5 kg potato sample. 12.5 g of alumina (Alumina "O" Spence and Son, Airdrie, Scotland) was added to the jar, followed by the necessary amount of sprout suppressant chemical. The jar was sealed and mixed overnight using an end-over-end shaker. The contents of the jar were then evenly dusted over the 5 kg potato sample.

Each treatment was duplicated. The two boxes corresponding to each treatment were stored in pairs, one box on top of the other. Their relative positions did not change throughout the storage period.

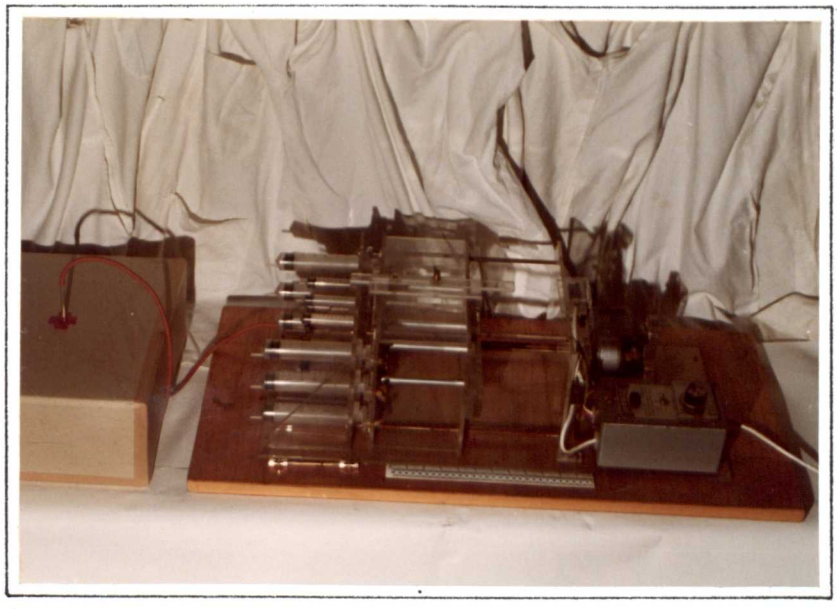
Headspace sampling

Each box was removed from its storage position and carefully placed on a table in the temperature controlled room. A 6.35 mm diameter hole was made in the centre of the lid.

Headspace sampling proceeded by the method described in Parts A1.3 and A1.4 using the syringe sampling device (Plate A1.04). See Plate A1.05. A porous polymer precolumn was inserted 40 mm into the box. Sample volumes of 45 cm^3 were taken. On the first 1,4-dimethylnaphthalene sampling date, sampling rates of 9 cm^3 min^{-1} were adopted. For all subsequent analyses, a sampling rate of 4.5 cm^3 min^{-1} was used. Using the sampling device, four boxes were sampled at one time. Adsorption rate with no flow (A1.4.4.4.) was also determined for each chemical.

After sampling, the holes in the boxes were sealed with PVC tape, and the boxes replaced. The porous polymer precolumns were sealed with Wade couplings (A1.3.2.1.).

Plate A1. 05. Headspace sampling method. 1, 4-Dimethylnaphthalene, carvone, citral and pulegone treatments in 10 kg boxes.



Porous polymer precolumn analysis

All four chemicals could be rapidly analysed using the thermal desorption-injection unit. (A1. 3. 2. 3.). The best analysis conditions for each chemical were determined using porous polymer precolumns to which had been added known amounts of standard solutions (A1. 3. 3. 1.). Standard solutions of each chemical in hexane (1 mg cm^{-3}) were prepared and stored in a refrigerator. 0. 5 mm^3 aliquots of standard solution were injected using a Hamilton series 7001 microlitre syringe. The operating conditions of the thermal desorption-injection device were, air bath 90°C and oil bath 150°C.

1, 4 - Dimethylnaphthalene:- Desorption conditions; 240°C, 5 min, 15 cm^3 min^{-1}. Chromatographic conditions; Helium 60 cm^3 min^{-1}, 5% OV17 on 100 - 120 mesh GCQ in 1 m x 3. 2 mm i. d. x 6. 35 mm o. d. glass column, 195°C isothermal, Detector 250°C, Injector 250°C.

Carvone:- Desorption conditions; 240°C, 5 min, 15 cm^3 min^{-1}. Chromatographic conditions; Helium 60 cm^3 min^{-1}, 5% OV17 on 100 - 120 mesh GCQ in 1 m x 3. 2 mm i. d. x 6. 35 mm o. d. glass column, 150°C isothermal, Detector 250°C, Injector 250°C.

Citral:- Desorption conditions; 150°C, 5 min, 15 cm^3 min^{-1}. Chromatographic conditions; Helium 60 cm^3 min^{-1}, 5% OV17 on 100 - 120 mesh GCQ in 1 m x 3.2 mm i.d. x 6.35 mm o.d. glass column, 150°C isothermal, Detector 250°C, Injector 250°C.

Pulegone:- Desorption conditions; 240°C, 5 min, 15 cm^3 min^{-1}. Chromatographic conditions; Helium 60 cm^3 min^{-1}, 5% OV17 on 100 - 120 mesh GCQ in 1 m x 3.2 mm i.d. x 6.35 mm o.d. glass column, 150°C isothermal, Detector 250°C, Injector 250°C.

A1.5.1.2 RESULTS

Table Al. 26. Recovery of standards from porous polymer precolumns (S_2) compared with standards injected into a heated empty glass precolumn (S_1) using the thermal desorption-injection device.

Standard	Sample number	Sample	Mean Peak area (mm^2)	S. D.	Recovery % S_2/S_1
1, 4 - dimethylnaphthalene	5	S_1	327. 2	3. 94	
1, 4 - dimethylnaphthalene	5	S_2	325. 7	4. 32	99. 5
carvone	6	S_1	163. 0	3. 30	
carvone	6	S_2	159. 2	2. 77	97. 7
citral	3	S_1	110. 8	1. 45	
citral	3	S_2	105. 1	2. 39	94. 9
pulegone	6	S_1	163. 5	2. 28	
pulegone	6	S_2	146. 2	2. 84	89. 4

Table A1.27. Adsorption rate with no flow; porous polymer precolumns with one end placed in the headspace, the other end sealed.

Sample number	Headspace sample	Adsorption time (min)	Adsorption rate ($\mu g\ min^{-1}$)
1	1,4 - DMN/300 mg kg^{-1}	5	0.002
1	1,4 - DMN/300 mg kg^{-1}	10	0.003
1	carvone/500 mg kg^{-1}	5	0.003
1	carvone/500 mg kg^{-1}	10	0.003
1	citral/500 mg kg^{-1}	10	0.002
1	pulegone/500 mg kg^{-1}	5	0.004
1	pulegone/500 mg kg^{-1}	10	0.003

Table A1.28. 1, 4-Dimethylnaphthalene headspace concentrations (mg m^{-3}) of potatoes in 10 kg boxes, 3, 13, 27, 61 and 99 days after treatment.

Sample	3 days		13 days		27 days		61 days		99 days	
	Mean conc.	S. D.	Mean conc.	S. D.	Mean conc.	S. D.	Mean conc.	S. D.	Mean conc.	S. D.
50 mg kg^{-1}/1	2.52	0.320	1.54	0.055	1.13[b]	0.020	0.62	0.172	0.23	0.091
50 mg kg^{-1}/2	2.66[a]	0.329	1.50	0.124	0.99[b]	0.151	0.52	0.021	0.29	0.045
100 mg kg^{-1}/1	6.29	0.187	3.67	0.187	3.40	0.209	1.71	0.178	1.18	0.024
100 mg kg^{-1}/2	7.27	0.187	4.05	0.210	3.31	0.116	2.29	0.139	1.61	0.120
150 mg kg^{-1}/1	6.34	0.156	6.13[a]	0.078	4.51	0.103	3.13	0.392	1.93	0.074
150 mg kg^{-1}/2	7.77	0.414	6.07[a]	0.694	4.55	0.158	2.92	0.060	1.97	0.105
175 mg kg^{-1}/1	7.09[a][b]	0.668	5.73[a]	0.592	3.85	0.015	2.81	0.106	1.64	0.080
175 mg kg^{-1}/2	7.84[b]	0.900	5.65[a]	0.263	4.29	0.226	2.72	0.076	2.24	0.048
300 mg kg^{-1}/1	9.65[b]	1.204	9.48	0.176	6.83	0.620	6.83	0.121	3.37	0.025
300 mg kg^{-1}/2	12.00[b]	1.761	10.97[a]	1.774	6.42	0.665	6.02	0.236	4.51	0.127

[a] mean of triplicate analyses

[b] mean of quadruplicate analyses

all other values, mean of duplicate analyses

Table Al. 29. Carvone headspace concentrations (mg m^{-3}) of potatoes in 10 kg boxes, 10, 26, 60 and 97 days after treatment.

Sample	10 days		26 days		60 days		97 days	
	*Mean conc.	S. D.	Mean conc.	S. D.	Mean conc.	S. D.	Mean conc.	S. D.
100 mg kg^{-1}/1	3. 68	0. 146	1. 02	0. 049	0. 45	0. 114	0. 18	0. 001
100 mg kg^{-1}/2	2. 49	0. 610	0. 85	0. 063	0. 38	0. 043	0. 13	0. 008
500 mg kg^{-1}/1	20. 84	0. 332	8. 06	0. 463	2. 58	0. 285	1. 33	0. 113
500 mg kg^{-1}/2	12. 84	0. 718	3. 91	0. 334	2. 06	0. 019	0. 74	0. 033

* mean of duplicate analyses

Table A1.30. Pulegone headspace concentrations (mg m^{-3}) of potatoes in 10 kg boxes, 10, 27, 60 and 98 days after treatment.

Sample	10 days		27 days		60 days		98 days	
	*Mean conc.	S.D.	Mean conc.	S.D.	Mean conc.	S.D.	Mean conc.	S.D.
100 mg kg^{-1}/1	5.14	0.569	2.12	0.016	0.54	0.016	0.14	0.052
100 mg kg^{-1}/2	6.37	0.347	3.70	0.169	0.97	0.107	0.66	0.063
500 mg kg^{-1}/1	38.33	0.127	11.69	0.686	2.76	0.064	1.52	0.023
500 mg kg^{-1}/2	38.76	0.790	20.23	0.832	8.02	0.310	5.23	0.404

* mean of duplicate analyses

Table Al. 31. Citral headspace concentrations (mg m^{-3}) of potatoes in 10 kg boxes, 11 and 27 days after treatment.

Sample	11 days		27 days	
	*Mean conc.	S. D.	Mean conc.	S. D.
100 mg kg^{-1}/1	0.16	0.016	0.35	0.190
100 mg kg^{-1}/2	0.20	0.031	0.13	0
500 mg kg^{-1}/1	3.02	0.295	0.95	0.158
500 mg kg^{-1}/2	3.86	0.450	1.15	0.196

* mean of duplicate analyses

A1. 5. 1. 3. DISCUSSION

5 kg samples of treated tubers were used, as this would provide a large free volume above the sample. The porous polymer pre-columns were inserted 40 mm into the boxes. At this position the headspace samples were taken from a point 35 mm above the tubers. With the boxes half-full there was a free headspace volume above the potato samples of approximately 9 dm^3. Removal of two 45 cm^3 samples should not cause dilution effects. On occasions when duplicate sample variation was high, a third or fourth sample was taken.

The thermal desorption-injection unit made rapid analyses possible. Using the desorption and chromatographic conditions described, an interval of five minutes separated each sample injection.

Analysis of citral was unsatisfactory and was discontinued after 27 days. The sample of citral was derived from natural sources and consisted of a mixture of two geometric isomers, geranial and neral (Merck Index, 1976). The chromatographic conditions adopted allowed adequate resolution of the isomers, although it was not ideal. However, it was found that, when preparing precolumns containing standard solutions of citral (A1. 3. 3. 1.), unless the Wade, precolumn connecting coupling, was kept cool (30°C), citral appeared to break down. This was shown by the appearance of a third peak in the chromatogram. Standard solutions injected either directly into the gas chromatograph or via the thermal desorption-injection device, showed no evidence of a breakdown product. Empty precolumn temperatures of 240°C did not appear to cause any breakdown. It was also noted that one of the isomers appeared more susceptible to breakdown than the other, i. e. the peak area of only one isomer was reduced when the third peak was detected. Using a desorption temperature of 150°C, and keeping the precolumn coupling hand-hot, no breakdown of standard solutions occurred. The values of citral (Tables A1. 26, A1. 27 and A1. 31) were calculated from the peak area of the least susceptible isomer, assuming that the head-

space concentration of the isomers was equal. When the headspace of boxes of citral treated potatoes was analysed, the levels were low (compared to pulegone and carvone). The peak areas of both isomers were similar. The chromatogram also showed a peak with the same retention time as the previously observed breakdown product. The desorption and chromatographic conditions had been shown not to induce breakdown of standard solutions. Therefore, the low levels of citral must have been due in some part to breakdown (oxidation) of both isomers in the sample box.

Recovery of 1, 4 - dimethylnaphthalene, carvone, citral and pulegone from porous polymer precolumns (Table Al. 26) was considered satisfactory. They showed that the thermal desorption-injection device did not affect sample recovery. Recoveries less than 100% can also be due to the method by which the porous polymer precolumn standards were prepared. Therefore, the lower recovery values, particularly those of pulegone cannot be considered to be due wholly to the thermal desorption-injection device.

The sampling rates adopted, ensured that porous polymer precolumn adsorption rate exceeded the adsorption rate with no flow (Table Al. 27).

For some samples the precision of analysis was not as good as that obtained during naphthalene headspace studies (Tables Al. 28, Al. 29, Al. 30, Al. 31 and Al. 16). Porous polymer precolumn standards, showed no loss in precision using the thermal desorption-injection device (Table Al. 26). The loss in precision was therefore considered to be due principally to the handling of each potato sample before headspace analysis. Removing the box from its storage position, placing it on the table, and inserting the porous polymer precolumn, all caused the walls of the box to bend, and thus alter its volume. Such changes in volume would alter the homogeneity of the headspace.

A1. 5. 1. 4. CONCLUSIONS

The procedure adopted provided a rapid, convenient means of headspace analysis. Results using porous polymer precolumn standards show no loss in accuracy or precision using the thermal desorption-injection device, compared to direct desorption analysis of naphthalene (A1. 4. 4. 4.). The headspace values were therefore accurate. However, the precision of the headspace analysis was less than in the naphthalene studies. This was thought to be due principally to handling the boxes prior to headspace analysis. Sealing the box before sampling (A1. 5. 2.) may help.

A1. 5. 2. HEADSPACE ANALYSIS OF 5 kg POTATO SAMPLES TREATED WITH TECNAZENE AND CHLORPROPHAM

Two headspace experiments were conducted. In the first experiment, headspace concentrations of chlorpropham and tecnazene were studied concurrently with the 1, 4 - dimethylnaphthalene, carvone, citral and pulegone headspace experiment (A1. 5. 1.). The experiment lasted for fourteen weeks at $9^{o}C$.

In the second experiment, the headspace of samples treated with two different commercial formulations of tecnazene, were compared for two weeks at $9^{o}C$.

A1. 5. 2. 1. METHODS

Treatment of potato sample

Commercial formulations of tecnazene and chlorpropham were applied to 5 kg samples of potatoes, cv. Maris Peer.

Chlorpropham was applied at 10 mg kg^{-1}; 0.1 cm^{3} Mirvale 50 AC, 500 mg cm^{-3} a. i. (Ciba-Geigy (UK) Ltd., Cambridge) was mixed overnight with 12. 5 g alumina, and then evenly dusted over the tuber sample.

Two commercial formulations of tecnazene were studied; Fusarex, 3% a.i., (ICI, Plant Protection, Yalding, Kent) and Hortag granules, 6.32% a.i., (BBW (Horticultural Requisites) Ltd., Sway, Hants.). They were applied at rates recommended by the manufacturers; Fusarex 4.5 g kg^{-1} (135 mg tecnazene kg^{-1}) and Hortag granules 0.5 g kg^{-1} (32 mg tecnazene kg^{-1}).

Each treatment was duplicated. The boxes were stored singly on a shelf in the temperature controlled room. Their relative positions did not alter throughout the period of storage.

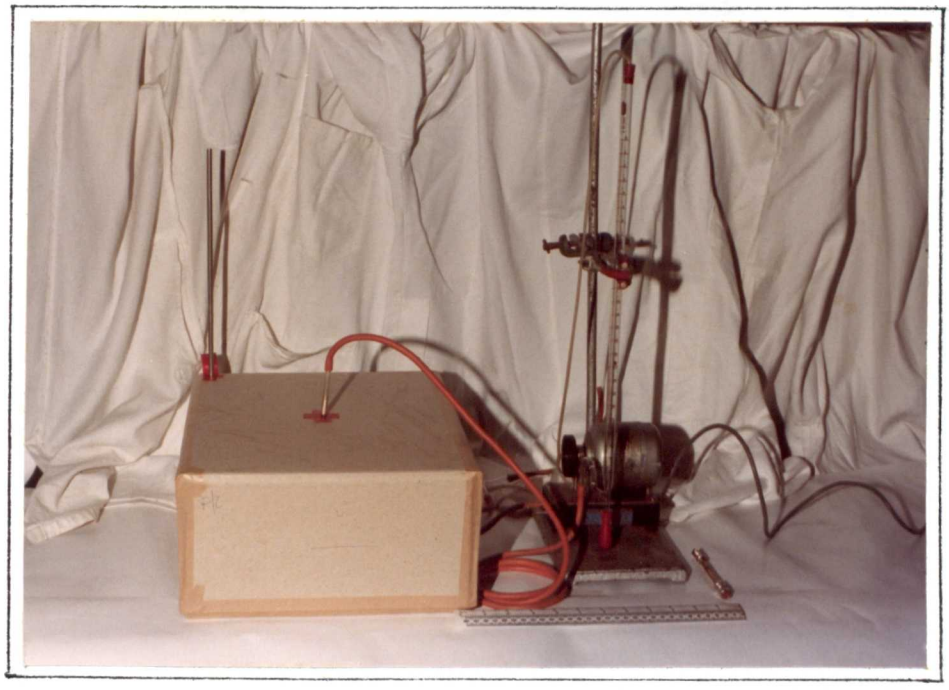
Headspace sampling

In the first experiment, chlorpropham samples were analysed on one occasion, 15 days after treatment, tecnazene samples were analysed on three occasions, 16, 61 and 98 days after treatment.

In the second experiment, tecnazene samples were analysed on two occasions, 1 day and 16 days after treatment.

24 hours before sampling, all gaps between the box and its lid were sealed using adhesive tape. Then each box was removed from its storage position and placed on a table in the temperature controlled room. Two, 6.35 mm diameter holes were made in the box lid, one at the centre, the other at one corner. A 200 mm x 6.35 mm o.d. x 4.0 mm i.d., stainless steel tube was inserted in the hole at the corner of the box. The tube extended to the base of the box. Headspace samples were taken by porous polymer precolumn, from the hole in the centre of the box. The porous polymer precolumn was inserted 40 mm into the box (Plate A1.06).

Plate A1. 06. Headspace sampling method. Chlorpropham and tecnazene treatments in 10 kg boxes.



The porous polymer precolumn was connected to a 20 cm^3 bubble meter by 6. 5 mm o. d. x 3. 2 mm i. d., rubber tubing. Air was drawn through the precolumn and bubble meter by a small diaphragm pump (Dymax Mk II, Charles Austen Pumps Ltd., Weybridge, Surrey), connected to the bubble meter by similar rubber tubing. The pump was run for one hour before sampling commenced.

Sample volumes of 1 dm^3 were removed at a rate of 60 cm^3 min^{-1}. Sample volume was measured by determining the sampling rate for 10 cm^3, using a stopwatch, and calculating the time required for 1 dm^3. The rate was measured at the beginning, during and at the end of sampling. Sampling rate was adjusted to 60 cm^3 min^{-1}, by a constricting valve (Hoffman clip) in the rubber tubing connecting the pump and bubble meter. At a sampling rate of 60 cm^3 min^{-1}, the maximum error in time measurement for 10 cm^3 was 0. 5 s. Consequently, the maximum error in volume measurement for 1 dm^3 was + 52. 6 or -47. 6 cm^3.

After sampling, the stainless steel tube was removed. The holes in the lid were sealed with PVC tape. The porous polymer precolumn was sealed with Wade couplings. In the first experiment, the adhesive tape sealing the box, was also removed.

Porous polymer precolumn analysis

Chlorpropham and tecnazene were analysed by direct desorption onto the analytical column (A1. 3. 2. 2.). The best analysis conditions for each chemical were determined using porous polymer precolumns to which had been added, known amounts of standard solutions (A1. 3. 3. 1.). Standard solutions of each chemical in hexane (1 mg cm^{-3}) were prepared, and stored in a refrigerator. Tecnazene(Koch-Light, Colnbrook, Bucks., England) and chlorpropham (Sigma, St. Louis, USA) were used. 0. 5 mm^3 aliquots of standard solution were injected using a Hamilton series 7001 microlitre syringe.

Chlorpropham:- Desorption conditions; 240°C, 5 min, 60 cm^3 min^{-1}. Chromatographic conditions; Helium 60 cm^3 min^{-1}, 5% OV17 on 100 - 120 mesh GCQ in 1 m x 6. 35 mm o. d. x 3. 2 mm i. d., glass column; 5 min isothermal 125°C, increasing to 200°C, 49°C min^{-1}, 5 min isothermal 200°C; Detector 250°C; Injector 240°C.

Tecnazene:- Desorption conditions; 240°C, 5 min, 60 cm^3 min^{-1}. Chromatographic conditions; Helium 60 cm^3 min^{-1}, 5% OV17 on 100 - 120 mesh GCQ in 1 m x 6. 35 mm o. d. x 3. 2 mm i. d., glass column; 5 min isothermal 125°C, increasing to 200°C, 49°C min^{-1}, 6 min isothermal 200°C; Detector 250°C; Injector 240°C.

A1. 5. 2. 2. RESULTS

Table Al. 32. Peak area of chlorpropham and tecnazene standard solutions injected via a heated empty glass precolumn and trapped by the analytical column.

Sample number	Sample	Mean peak area (mm^2)	S. D.
6	0. 5 µg chlorpropham	289. 5	4. 77
9	0. 5 µg tecnazene	265. 2	4. 39

Table Al. 33. Tecnazene headspace concentration (mg m^{-3}) of potatoes in 10 kg boxes, 16, 61 and 98 days after treatment with Fusarex (4. 5 g kg^{-1}). First experiment.

Sample	16 days		61 days		98 days	
	*Mean conc.	S. D.	Mean conc.	S. D.	Mean conc.	S. D.
Box 1	0. 63	0. 007	0. 41	0. 004	0. 47	0. 037
Box 2	0. 50	0. 014	0. 41	0. 001	0. 45	0. 006

* mean of duplicate analyses

Table Al. 34. Tecnazene headspace concentration (mg m^{-3}) of potatoes in 10 kg boxes, 1 and 16 days after treatment with Fusarex (4. 5 g kg^{-1}) or Hortag granules (0. 5 g kg^{-1}). Second experiment.

Sample	1 day		16 days	
	Mean conc.	S. D.	Mean conc.	S. D.
Fusarex box 1	0. 29	0. 021	0. 32[b]	0. 046
Fusarex box 2	0. 23	0. 008	0. 33[c]	0. 016
Hortag box 1	0. 28[a]		0. 07	0. 001
Hortag box 2	0. 27	0. 005	0. 07	0. 001

[a] single analysis

[b] mean of triplicate analyses

[c] mean of quintriplicate analyses

all other values, mean of duplicate analyses

A1. 5. 2. 3. DISCUSSION

Chlorpropham and tecnazene could not be analysed using the thermal desorption-injection unit. Standard solutions of chlorpropham and tecnazene were not quantitatively recovered when injected via the thermal desorption-injection unit. The operating temperature of the unit, and the temperature of the hot oil bath, were not sufficient to promote rapid volatilization of the standards. Chlorpropham standard solutions injected via the unit were not recovered using the operating conditions previously described (A1. 3. 2. 3.). However, by heating the unit's cold trap for 5 minutes and retrapping on a cold analytical column, with subsequent analysis, the chlorpropham standards were recovered. Although recovery of tecnazene standards using similar operating conditions (A1. 3. 2. 3), was much better, the resultant chromatograms had broad tailing peaks.

Analysis by direct desorption of porous polymer precolumns (A1. 3. 2. 2.) was therefore adopted. The desorption and chromatographic conditions were designed to provide rapid sample analysis with sharp sample peaks, well resolved from compounds of secondary interest.

Standard solutions of chlorpropham and tecnazene were analysed by injecting via a heated empty glass precolumn, and trapping on the analytical column (A1. 3. 2. 2), using the conditions described (A1. 5. 2. 1.). The analyses were reproducible (Table A1. 32) and show that the analytical methods will accurately quantify chlorpropham and tecnazene desorbed from porous polymer precolumns. Recovery of chlorpropham and tecnazene standards from porous polymer precolumns (A1. 3. 3. 1.) exceeded 94%.

Chlorpropham will thermally decompose at high temperatures, particularly in the presence of metal surfaces (Romagnoli and Bailey, 1966). Breakdown of chlorpropham occurred when standards were injected via an empty glass precolumn at 270^{o}C. There was evidence

that when Wade couplings became excessively hot, some breakdown occurred, although the extent of this effect was masked by the high background levels also produced (Al. 3. 2. 1.).

Reproducibility of chlorpropham analyses was improved if several injections of chlorpropham solution preceeded the first analysis.

Chlorpropham was not detected in 1 dm^3 headspace samples above treated tubers. (Detection limit 0. 05 μg chlorpropham). Larger volumes of headspace would be necessary to accurately determine chlorpropham concentration. As this would cause dilution problems, chlorpropham analysis of 10 kg boxes was discontinued.

1 dm^3 sample volumes were necessary for accurate tecnazene analysis. The headspace sample was taken from a position 35 mm above the tubers. The free volume above the potato sample in each box was approximately 9 dm^3. Sealing the box with adhesive tape, and inserting an air-leak extending to the base of the box was intended to help minimize dilution effects. Air entered the box from a point as far from the porous polymer precolumn as possible. Any air entering the box would have to pass over treated tubers and hopefully become saturated with tecnazene. Without sealing the box it is conceivable that outside air which was not saturated with tecnazene, would enter and be extracted through the porous polymer precolumn.

Headspace analysis of boxes containing tecnazene treated tubers was satisfactory. Porous polymer precolumns, connected second in series (Al. 1. 2. 3.) did not contain tecnazene (Detection limit 0. 01 μg). The results (Tables Al. 33 and Al. 34) showed that analyses were precise, with no apparent sign of dilution effects. The analyses were more precise than those of 1, 4 - dimethylnaphthalene, carvone, citral and pulegone (Al. 5. 1.). Sealing the boxes and larger sample volumes may be a means of improving headspace sample homogeneity.

A1. 5. 2. 4. CONCLUSIONS

Headspace sample volumes larger than 1 dm^3 are necessary for chlorpropham analysis. Accurate headspace analysis of chlorpropham in 10 kg capacity potato boxes is therefore *not* possible.

Tecnazene headspace analysis of 10 kg potato boxes was accurate and precise, using 1 dm^3 sample volumes.

Headspace sampling of 10 kg potato boxes appeared to be improved by sealing the box, and removing larger headspace volumes.

A1. 5. 3. HEADSPACE ANALYSIS OF CHLORPROPHAM AND TECNAZENE IN COMMERCIAL POTATO STORES

Headspace concentrations of chlorpropham were determined in two commercial potato stores. One was a 3, 000 tonne, 1 tonne box store (United Biscuits Ltd., Grimsby), and the other a 4, 000 tonne bulk store (Cadbury Schweppes Foods Ltd., Catterick Bridge). Tecnazene headspace concentrations were determined in the 4, 000 tonne bulk store over a period of 38 days following treatment. The tecnazene headspace concentrations of the bulk store were compared to the tecnazene headspace concentration of a 30 dm^3 glass tank in the laboratory.

A1. 5. 3. 1. METHODS

Headspace sampling

Headspace samples were taken by connecting porous polymer precolumns to a small diaphragm pump (Capex Mk II, Charles Austen Pumps Ltd., Weybridge, England) by 1. 5 m x 3. 2 mm i. d. x 6. 5 mm o. d., rubber tubing (Plate A1. 07).

8. 5 dm^3 sample volumes were taken. Sample volume was measured by two methods. In the first method a gas meter (George Wilson Industries Ltd., Coventry, England) was used to measure the total sample volume passing through the porous polymer precolumn. The pump was connected to the gas meter which in turn was connected to the porous polymer precolumn. In the second method, the gas meter and a stopwatch were used to measure the sampling rate through a porous polymer precolumn. The pump was connected to the porous polymer precolumn which in turn was connected to the gas meter. The sampling rate for 2. 8 dm^3 sample volumes was determined in the laboratory. When sampling in the potato store the porous polymer precolumn was connected to the pump and the time required for 8. 5 dm^3 was calculated from the sampling rate.

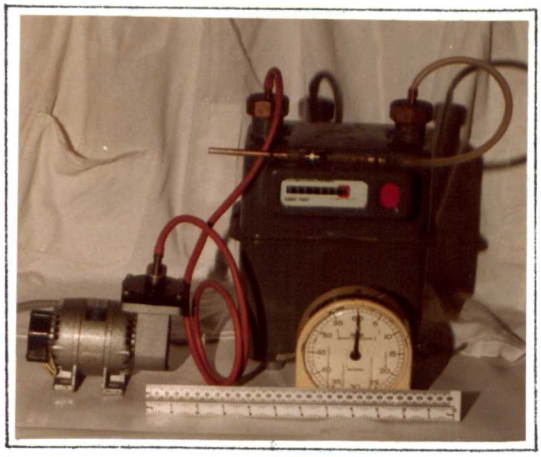


Plate A1. 07. Headspace sampling method. Chlorpropham and tecnazene treatments in commercial potato stores.

3, 000 tonne box store sampling conditions

Headspace sample volume was measured directly by the gas meter. A 8. 5 dm^3 headspace sample was taken from a point 25 mm above the potatoes held in a one tonne box. The sampling rate was 0. 4 dm^3 min^{-1}. In addition, a 1 dm^3 sample at 75 cm^3 min^{-1} was taken using the method outlined in Section A1. 5. 2. 1. Three boxes were studied. The first box was at ground level, near the central passage, the second box was at ground level in a corner of the store, and the third box was at the highest level, near the central passage. The store was held at 10°C.

4, 000 tonne bulk store sampling conditions

Headspace sample volume was determined from the sampling time and sampling rate.

Headspace samples were taken from three points, 1 m above the potato stack. The three sampling points were all at a position approximately equidistant from the East and West ends of the store. The first point was 5 m from the South wall, the second 10 m from the North and South walls, and the third 5 m from the North wall.

Samples were taken 6 hours, 24 days and 38 days after treatment with tecnazene. In addition, the potatoes had been treated with chlorpropham 3 days before the third sampling date.

Tecnazene was applied at 37. 5 mg kg^{-1}, as Hortag granules (BBW (Horticultural Requisites) Ltd., Sway, Hants.). Chlorpropham (Taterpex, Mirfield Agricultural Chemicals Ltd., Mirfield, Yorks) was applied at 10 - 20 mg kg^{-1}.

On the first sampling date, the store was sealed and the air inside recirculated for 6 hours before sampling commenced. On the second and third sampling dates, the air inside was recirculated for 9 hours, before sampling commenced. The recirculating fans were not operating during sampling.

Details of the sampling conditions are given in Table A1. 35.

30 dm^3 glass tank

The headspace of a 30 dm^3 glass tank containing tecnazene was studied. Headspace sample volume was determined from the sampling rate and sampling time. The tank was of similar design to the 54 dm^3 tank used previously (A1. 4 and A1. 3. 3.), incorporating a stainless steel air leak, and a mercury in glass thermometer. 10 g of tecnazene (Koch-Light, Colnbrook, Bucks, Englad) were placed in the tank. The tank was held at 9°C. Headspace samples were taken from a point 64 mm from the top of the tank.

Porous polymer precolumn analysis

Chlorpropham and tecnazene were analysed by direct desorption onto the analytical column (A1. 3. 2. 2.).

The best analysis conditions were determined using porous polymer precolumns to which had been added known amounts of standard solutions (A1. 3. 3. 1.). Standard solutions of each chemical in hexane (1 mg cm^{-3}) were prepared, and stored in a refrigerator. Tecnazene (Koch-Light, Colnbrook, Bucks, England) and chlorpropham (Sigma, St. Louis, USA) were used. 0. 5 mm^3 aliquots of standard solution were injected using a Hamilton series 7001 microlitre syringe.

Chlorpropham:- Desorption conditions; 240°C; 5 min, 60 cm^3 min^{-1}. Chromatographic conditions; Helium 60 cm^3 min^{-1}; 5% OV17 on 100 - 120 mesh GCQ in 1 m x 3. 2 mm i. d. x 6. 35 mm o. d. glass column;

5 min isothermal 125°C, increasing to 200°C, 49°C min^{-1}, 5 min isothermal 200°C; Detector 250°C; Injector 240°C.

Tecnazene:- Desorption conditions; 240°C, 5 min, 50 cm^3 min^{-1}. Chromatographic conditions; Helium 50 cm^3 min^{-1}; 5% OV17 on 100 - 120 mesh GCQ in 1 m x 3.2 mm i.d. x 6.35 mm o.d. glass column; 5 min isothermal 125°C, increasing to 200°C, 49°C min^{-1}, 6 min isothermal 200°C; Detector 250°C; Injector 240°C.

Analytical conditions were altered for samples containing both tecnazene and chlorpropham in major amounts.

Tecnazene and chlorpropham:- Desorption conditions; 200°C, 50 cm^3 min^{-1}. Chromatographic conditions; Helium 50 cm^3 min^{-1}; 5% OV17 on 100 - 120 mesh GCQ in 1 m x 3.2 mm i.d. x 6.35 mm o.d. glass column; 2 min isothermal 30°C, increasing to 125°C, 49°C min^{-1}, 125°C increasing to 200°C, 7°C min^{-1}, 2 min isothermal 200°C; Detector 200°C, Injection temperature same as oven temperature.

A1.5.3.2. RESULTS

Table Al. 35. 4,000 tonne bulk store sampling conditions.

Time after treatment with tecnazene	Potato stack temperature (°C)	Number of samples	Sample volume (dm^3)	Mean sampling rate ($dm^3 min^{-1}$)	S. D.
6 hours	13	6	8. 5	0. 7	0. 37
24 days	9	6	8. 5	0. 5	0. 08
38 days	9	8	8. 5	0. 5	0. 15

Table Al. 36. Time taken to sample 2. 8 dm^3 through four porous polymer precolumns.

Precolumn number	Number of 2. 8 dm^3 samples	Mean time (s)	S. D.	*Confidence limit (s) ($p < 0.05$)
1	9	158	6. 3	$\pm$ 4. 8
2	6	170	4. 6	$\pm$ 4. 9
3	7	257	10. 8	$\pm$10. 0
4	7	217	8. 7	$\pm$ 8. 0

* calculation of confidence limit

$$\bar{x} = \pm t \frac{s}{\sqrt{n}}$$

Table Al. 37. Tecnazene headspace concentration of 4, 000 tonne bulk store and 30 dm^3 glass tank.

Number of samples	Temp. (°C)	Sample Volume (dm^3)	Sample	Mean conc. (mg m^{-3})	S. D.
6	13	8. 5	Bulk store: 1st date	0. 22	0. 040
6	9	8. 5	2nd date	0. 17	0. 010
8	9	8. 5	3rd date	0. 12	0. 007
12	9	2. 8	Glass tank	0. 16	0. 018

Table Al. 38. Chlorpropham headspace concentration in 3, 000 tonne box store and 4, 000 tonne bulk store.

Sample	Number of samples	Temp. (°C)	Mean conc. (µg m^{-3})	S. D.
Box store:				
1st box	1	10	62	
2nd box	1	10	33	
3rd box	1	10	21	
Bulk store	8	9	55	4. 5

A1. 5. 3. 3. DISCUSSION

The box store experiment was a preliminary exercise in which sampling techniques were tested for the first time. Headspace concentrations of chlorpropham were too low for accurate determination using 1 dm^3 samples. Chlorpropham concentrations in three, 8. 5 dm^3 samples were variable (Table A1. 38). The samples were taken at three different positions in the store, which could have accounted for the variability. On the other hand, the sampling method could have been at fault.

Some laboratory investigations were conducted to determine any sources of error, particularly those of sample volume measurement. It was found that the gas meter performed erratically when connected between the porous polymer precolumn and diaphragm pump. Sample volumes of 8. 5 dm^3 registered by this meter were 18 to 40% greater than the values registered by a meter connected to the other end of the porous polymer precolumn, open to the atmosphere. The gas meter and two other meters of similar design were tested by connecting them singly and in series to a diaphragm pump with their inlet ports open to the atmosphere. Sample volumes up to 57 dm^3 were measured. The volumes registered by the meters all agreed within 5% of one another. These results showed that provided their inlet ports were open to the atmosphere, the meters accurately measured the volume of air passing through them. When connected between the porous polymer precolumn and diaphragm pump they were operating under reduced pressures, which caused erratic measurements.

For the bulk store analysis it was considered that sample volumes would be more accurately measured if the sampling rate through each precolumn was determined. The sampling time would be accurately measured by a stopwatch. This method had already proved successful in previous 10 kg box headspace studies (A1. 5. 2.). Sampling

rate through each precolumn was determined using sample volumes of 2.8 dm^3, measured by the gas meter and stopwatch. Sampling rates of approximately 0.5 dm^3 min^{-1} were obtained when two porous polymer precolumns were connected in series. The accuracy of this method was determined by studying the sampling rate of four precolumns (Table A1.36). The results indicate that for volumes of 2.8 dm^3, errors in volume measurement should not often exceed $\pm$ 100 cm^3 ($p < 0.05$).

This method of sample volume measurement proved quicker and simpler to operate in the potato store. In the box store experiment, it had been found that one of the major limitations to sampling was the time taken to set up and operate experimental apparatus. As time in the bulk store was limited, it was important that sampling procedures should be rapid.

The bulk store was an ideal situation for assessing the headspace analysis method. The store was sealed and the air recirculated for 6 or 9 hours before sampling. This would provide a large homogeneous headspace with little chance of dilution problems caused by removing 8.5 dm^3 headspace samples. Variations in concentration values, therefore, would be caused by loss of precision in the sampling method.

Tecnazene headspace concentrations from the bulk store and the 30 dm^3 glass tank are given in Table A1.37. Headspace samples taken from three different positions in the store all contained similar concentrations of tecnazene. The values are combined in Table A1.37. On the second and third sampling dates more care was taken when determining sampling rate. This and an experience factor account for the greater precision compared to the first sampling date. Porous polymer precolumns connected second in series (A1.1.2.3.), did not contain any tecnazene (detection limit 0.01 μg). The close agreement between levels found in the potato store and 30 dm^3 glass tank also helped confirm the accuracy of the method.

Desorption and chromatographic conditions were altered when both tecnazene and chlorpropham were present in major amounts. The desorption heater, detector heater and injector heater temperatures were all reduced. This was to guarantee that thermal decomposition of chlorpropham did not occur (Romagnoli and Bailey, 1966). The chromatographic conditions allowed for a longer desorption period at analytical column temperatures which trap tecnazene and chlorpropham. These conditions also improved resolution between tecnazene and chlorpropham.

Chlorpropham headspace concentrations are given in Table Al. 38. Analysis of porous polymer precolumns second in series (Al. 1. 2. 3.) showed that they did not contain chlorpropham (detection limit 0. 01 μg). The values generally agree with the levels detected in the preliminary box store experiment. However, it is worthy of note, that chlorpropham levels in both the box store and bulk store are much lower than the reported levels found in a similar commercial potato store (Filmer and Land, 1978).

Al. 5. 3. 4. CONCLUSIONS

Headspace analyses of bulk potato stores containing chlorpropham and tecnazene were accurate and precise.

Headspace sample volume was determined by measuring the sampling rate and sampling time. This proved an effective, simple method, especially for use in some of the less accessible parts of a potato store.

CHAPTER A2

MEASUREMENT OF DIMETHYLNAPHTHALENE RESIDUES IN TREATED POTATO TUBERS

A2.1 INTRODUCTION

A method was developed to determine residue levels of dimethylnaphthalene in treated potato tubers. It was considered important that reliable residue values should be determined as they would provide an essential step towards determining whether or not treated tubers would be fit for human consumption.

No routine residue analysis method for dimethylnaphthalene had been published.

The general principles adopted in the analysis were the same as those used in previously reported tecnazene residue analyses (Dalziel and Duncan, 1974; Dalziel, 1978). The finer details of the method had to be adapted to suit the particular requirements of dimethylnaphthalene.

A representative potato sample was macerated to a fine pulp and then homogenized with ethanol. Hexane was added and the mixture blended for a further period. By blending in ethanol before adding hexane, the formation of a stable emulsion was avoided. Dimethylnaphthalene was extracted by the hexane. The hexane extract was then passed through an alumina column to remove most of the plant residues. Plant residues were removed as they interfered with quantitative detection of dimethylnaphthalene, reducing the overall sensitivity of the method. After the alumina clean-up, the concentration of dimethylnaphthalene in the hexane extract was determined using gas chromatography.

Dimethylnaphthalene residues in treated potato tubers were determined during storage seasons 1976-77 and 1977-78. In storage

season 1976-77, two experiments were conducted. In the first preliminary experiment residue levels of 1, 4-dimethylnaphthalene were determined in a 10 kg batch of tubers. In the second experiment residue levels of dimethylnaphthalene 99% pure isomer mixture were studied in tubers taken from the assessment and development experiments conducted during that storage season (Chapters 2 and 3). In storage season 1977-78, residue levels of 1, 4-dimethylnaphthalene were determined in tubers taken from 10 kg batches of treated tubers. These tubers were treated with the sole intention of studying residue levels.

A2.2 MATERIALS

Chemicals

Glass distilled hexane (Rathburn Chemicals, Walkerburn Ltd.) was used for extraction and alumina clean-up procedures.

Absolute alcohol (Burroughs Ltd.) was used for the extractions.

1, 4-dimethylnaphthalene (Koch-Light) and dimethylnaphthalene 99% pure isomer mixture (Aldrich) were used to treat the tubers. Standard solutions of these chemicals in hexane were used in the analyses.

All other chemicals used were of the highest quality available.

Acidic, neutral and basic alumina (Woelm) were used.

Equipment

Electric mincer (Bauknecht, West Germany).

Electric blender (MSE-Ato-mix).

Buchi (Switzerland) rotary evaporator.

Pye SP 1800 spectrophotometer.

Pye series 104 gas chromatograph.

Hamilton series 7000 syringe.

A2.3 RESULTS AND DISCUSSION

A2.3.1 DESCRIPTION OF THE ANALYTICAL METHOD

Several experiments were conducted to determine the best conditions under which low residue levels of dimethylnaphthalene could be quantitatively recovered from treated tubers. As a result, the most suitable method was developed. The following discussion is a description of the analytical method in which the results of the experiments are considered at the appropriate point in the sequence of analytical steps.

Tuber samples

10 kg batches of tubers were studied. The tubers were treated by the methods outlined in the assessment and development experiments (Chapters 2 and 3). 1 kg samples were taken from each 10 kg batch. The 1 kg samples were stored at -20°C until analysed. In the 1977-78 experiment, it proved more convenient to macerate the tubers immediately after sampling and then store c. 300 g of macerate at -20°C.

Extraction

Each 1 kg sample was thoroughly washed and then macerated using an electric mincer. After mixing, c. 100 g of macerate was accurately weighed out and then homogenized with 100 cm^3 ethanol for 1 minute in a high-speed blender. 100 cm^3 hexane were added to the homogenate and the contents blended for a further 2 minutes. The blender contents were filtered under reduced pressure through Whatman No. 1 filter paper and the vessel rinsed out with two separate 50 cm^3 portions of hexane which were passed in turn through the filter pad. The filtrate was transferred to a separating funnel by two separate 10 cm^3 hexane washing treatments to attain quantitative recovery. 100 cm^3 of saturated sodium chloride were added and after vigorous shaking the aqueous layer was discarded. The hexane layer was

washed in turn with 200 cm^3 of 10% (w/v) sodium carbonate solution followed by 200 cm^3 deionized water after which the hexane layer was collected and dried over anhydrous sodium sulphate. After filtering off the sodium sulphate and washing the filter contents with 100 cm^3 of hexane the combined filtrate was reduced in volume to 5 cm^3 using a rotary evaporator.

Clean-up on alumina

Alumina columns were prepared by pouring a slurry of alumina in hexane into a glass column of dimensions 300 mm by 9 mm diameter and fitted with a glass sinter. The columns were packed to a depth of 150 mm.

Basic, acidic and neutral alumina of varying activity grades were studied to determine the optimum chromatographic conditions for 1, 4-dimethylnaphthalene. The retention volume of dimethylnaphthalene from these columns was determined by U. V. spectrophotometry at 228 nm.

Neutral alumina, deactivated by 3% water (w/w) was found to be most suitable. Under these conditions, the retention volume of 1, 4-dimethylnaphthalene was sufficient to allow separation from those plant residues which were immediately eluted from the column, while on the other hand avoiding unnecessarily large time-consuming volumes of eluting solvent.

The hexane extract plus washings were applied to the column and the flow regulated to 1. 0 cm^3 min^{-1} with hexane as eluting agent. The flow rate was most easily regulated by a constant head reservoir system attached to the column by Teflon tubing. After discarding 25 cm^3 of effluent, the subsequent 100 cm^3 were collected. The solvent was then removed using a rotary evaporator. The volume was finally adjusted to exactly 5 cm^3 by quantitative transfer of the reduced extract to a 5 cm^3 volumetric flask.

Solvent removal under vacuum by rotary evaporator

It was found that temperature and vacuum conditions during solvent removal were of considerable importance. Unless both these conditions were controlled, dimethylnaphthalene could be removed with the solvent. The effect of vacuum control at constant temperature on loss of dimethylnaphthalene from the rotary evaporator can be seen in Table A2. 01.

Table A2. 01. Loss of dimethylnaphthalene when removing hexane solvent using a rotary evaporator. Method; 1 mg 1, 4-dimethylnaphthalene added to 35 cm^3 hexane. Hexane then removed until solution volume c. 4 cm^3. Solution then accurately adjusted to 5 cm^3 using a volumetric flask. Concentration of dimethylnaphthalene determined by gas chromatography.

Number of samples	Rotary evaporator conditions		% Recovery of dimethylnaphthalene	
	water bath temperature (°C)	vacuum control[a]	mean	S. D.
6	24 ± 0. 5	No	84. 2	1. 8
10	24 ± 0. 5	Yes	100. 9	3. 5

[a] The vacuum source was a water pump. When there was no vacuum control the water pump was operating at its maximum capacity. The vacuum was controlled by including a fine adjustable air leak and a mercury manometer between the vacuum pump and rotary evaporator. The pump operated at maximum capacity and the air leak adjusted until only a slow steady trickle of hexane was seen to be removed from the solution. Slow, controlled removal of hexane was maintained by constantly monitoring the mercury manometer and adjusting the air leak when necessary.

The results showed that quantitative recovery of dimethylnaphthalene was obtained only when both temperature and vacuum conditions were controlled.

Solvent temperature was best controlled using a large volume, thermostatically controlled water bath. Vacuum conditions were controlled using a mercury manometer and adjustable fine air leak. A water pump was used in the 1976-77 experiments. Unfortunately,

using this type of pump, the vacuum had to be constantly monitored due to fluctuations in water pressure. However, a mechanical pump (Charles Austen) provided a more suitable constant vacuum source in the 1977-78 experiments. By circulating ice-cooled water through the rotary evaporator condenser coils, solvent removal could be hastened. This was achieved by using a small peristaltic pump.

It was also important that all the solvent was not removed. Otherwise dimethylnaphthalene was lost. Presumably this was due to the heat of evaporation of hexane keeping the solution cool. For this reason, the extract solutions were not reduced to volumes less than c. 4 cm^3.

Clearly, the best temperature and vacuum conditions were those which permitted rapid evaporation of hexane without removal of dimethylnaphthalene. The best temperature and vacuum conditions were determined by analysing the contents of the evaporated solvent reservoir of the rotary evaporator. The conditions were adjusted until dimethylnaphthalene was no longer detected in the evaporated solvent reservoir. U. V. spectrophotometric methods were used to detect dimethylnaphthalene in the evaporated solvent.

In the 1977-78 experiments, for example, using a mechanical vacuum pump, the optimum temperature and vacuum conditions were $31 \pm 0.5^{o}C$, with a pressure of 470 mm mercury.

Detection of dimethylnaphthalene

Gas chromatographic and U. V. spectrophotometric methods were used to detect and quantify dimethylnaphthalene.

U. V. methods were capable of detecting dimethylnaphthalene at levels of 0.1 $\mu g\ cm^{-3}$ in solution. 1, 4-dimethylnaphthalene absorbed strongly at 228 nm. U. V. methods provided a rapid, convenient means of detecting dimethylnaphthalene in fractions of effluent from alumina

columns and in the evaporated solvent reservoir of the rotary evaporator. In most of these analyses it was only necessary to know whether or not dimethylnaphthalene was present. Quantitative detection of dimethylnaphthalene by U. V. methods was not used principally because plant residues eluted along with dimethylnaphthalene from the alumina column caused interference at 228 nm.

Gas chromatographic methods were used to quantify dimethylnaphthalene. Samples of 0. 5 mm^3 purified extract were injected into a gas chromatograph equipped with a flame ionization detector.

1, 4-dimethylnaphthalene was analysed using silanized glass columns containing (a) Tenax GC or (b) 5% OV17. The chromatographic conditions were,

(a) Helium 40 cm^3 min^{-1}; Tenax GC 60 - 80 mesh in 1 m x 3. 2 mm i. d. x 6. 35 mm o. d. glass column; oven temperature 240°C; detector 300°C; injector 280°C.

(b) Helium 40 cm^3 min^{-1}; 5% OV17 on 100 - 120 mesh GC Q in 1 m x 3. 2 mm i. d. x 6. 35 mm o. d. glass columns; oven temperature 180°C; detector 250°C; injector 240°C.

The preliminary 1, 4-dimethylnaphthalene analysis in season 1976-77 used Tenax GC. In the 1977-78 analyses 5% OV17 was used. Both chromatographic conditions were suitable for quantitative determination of 1, 4-dimethylnaphthalene. The conditions using 5% OV17 were more rapid.

Dimethylnaphthalene isomer mixture was analysed using (a) a conventionally packed column containing Tenax GC and (b) a S. C. O. T. glass capillary column containing OV17. The chromatographic conditions were,

(a) Helium 40 cm^3 min^{-1}; Tenax GC 60 - 80 mesh in 1 m x 3. 2 mm i. d. x 6. 35 o. d. column; oven temperature 240°C; detector 300°C; injector 280°C.

(b) Helium 3 cm^3 min^{-1}; 73 m OV17 S. C. O. T. glass capillary column; oven temperature 160°C; detector 250°C; injector 250°C.

The 1 m Tenax GC column was unable to resolve the dimethylnaphthalene isomer mixture. Chromatograms using this column consisted mainly of one asymmetric peak. However, by using the 73 m OV17 S. C. O. T. capillary column the isomer mixture was shown to consist mainly of 8 isomers, the isomer in greatest amount being 1, 6-dimethylnaphthalene. When quantifying dimethylnaphthalene using the 1 m Tenax GC column peak heights only were measured. When using the capillary column, the concentration of dimethylnaphthalene was measured using the area of the 1, 6-dimethylnaphthalene peak.

Determination of recovery factors

For the determination of recovery factors, 1 mg amounts of dimethylnaphthalene were applied at various stages in the residue analysis procedure. The results are shown in Table A2. 02.

Table A2. 02. Recovery of 1 mg amounts of dimethylnaphthalene, added at various stages in the residue analysis procedure.

Chemical	Stage in residue analysis procedure	Number of samples	% Recovery	
			mean	S. D.
1, 4-dimethyl-naphthalene	a	3	96. 5	1. 0
	b	5	97. 4	0. 7
	c	5	84. 5	2. 5
dimethylnaphthalene isomer mixture	c	6	68. 6	1. 7

[a] 1 mg dimethylnaphthalene added to a 3% deactivated neutral alumina column.

[b] 1 mg dimethylnaphthalene added to 150 cm^3 washed, hexane extract of 100 g macerated potato tubers.

[c] 1 mg dimethylnaphthalene added to 100 g macerated tubers prior to blending with hexane.

The results showed that only small amounts of 1, 4-dimethylnaphthalene were lost during the rotary evaporator and alumina column stages. The presence of potato tuber hexane extract did not affect the recovery of 1, 4-dimethylnaphthalene. The principal source of loss of 1, 4 dimethylnaphthalene was considered to be during the homogenizing stage, when heat generated by the high speed blender caused evaporative loss of 1, 4-dimethylnaphthalene. Recoveries of 1, 4-dimethylnaphthalene from macerated tubers prior to blending with hexane were precise. All subsequent residue analyses of tubers treated with 1, 4-dimethylnaphthalene were considered to be 84. 5% efficient.

The results using dimethylnaphthalene isomer mixture showed considerable loss during the analytical procedure. The recoveries were, however, remarkably precise. Loss of dimethylnaphthalene isomer mixture, which was greater than 1, 4-dimethylnaphthalene could be caused by differing adsorption of the isomers on alumina. Dimethylnaphthalene isomers have differing retention behaviour on alumina columns (Popl et al., 1974). As the alumina column conditions were set for 1, 4-dimethylnaphthalene it is possible that some other isomers were not recovered from the alumina column. Selective removal of certain isomers by the alumina column could account for low recovery rates with no loss in precision. Differing volatility of the isomers (Osborn and Douslin, 1975) could also cause low recovery rates through loss at the rotary evaporation stage. Further experiments would, however, be necessary to confirm these theories. All subsequent residue analyses of tubers treated with dimethylnaphthalene isomer mixture were considered to be 68. 6% efficient.

The minimum detectable residue level of 1, 4-dimethylnaphthalene was in the order of 1 - 10 $\mu g\ kg^{-1}$.

A2. 3. 2 RESIDUE LEVELS OF DIMETHYLNAPHTHALENE FOUND IN TREATED TUBERS

The residue levels of dimethylnaphthalene in treated tubers are presented in Tables A2. 03 and A2. 04.

The first residue experiment involving several samples studied tubers treated with dimethylnaphthalene isomer mixture. The results are presented in Table A2. 03.

Table A2. 03. Residue levels of dimethylnaphthalene isomer mixture found in treated tubers. Storage temperature 10°C.

Cultivar	Application rate (mg kg^{-1})	Treatment time (weeks)	Airing time (weeks)	Residue level (mg kg^{-1})	
				mean[c]	S. D.
Maris Peer[a]	100	16	3	1. 45	0. 16
	100	16	8	1. 31	0. 22
	300	16	3	3. 57	1. 39
	300	16	8	3. 17	0. 52
Red Craigs[a]	100	16	3	1. 61	0. 16
Royal	100	16	8	0. 66	0. 00
	300	16	3	8. 85	2. 00
	300	16	8	1. 36	0. 04
Record[b]	200	14	5	0. 73	0. 23
	300	14	5	1. 15	0. 13
Redskin[b]	200	14	5	0. 48	0. 05
	300	14	5	3. 49	0. 70

[a] Storage season 1976-77. Samples taken from first development experiment (Chapter 3).

[b] Storage season 1976-77. Samples taken from second development experiment (Chapter 3).

[c] Mean of duplicate 100 g samples taken from 1 kg potato macerate. Corrected for recovery factor.

The results were not considered to be reliable for two main reasons - (a) The recovery rate of 1 mg amounts of dimethylnaphthalene isomer mixture was low, and (b) the precision of some duplicate analyses was poor. However, although the absolute values of these

analyses were questioned, they could be used qualitatively. Generally they showed the effects of increasing residue levels with higher application rates, and decreasing residue levels with longer airing times.

Because of doubts in the accuracy of the dimethylnaphthalene isomer mixture residues, another residue experiment was conducted during the following season. In this experiment, 1, 4-dimethylnaphthalene was used for three main reasons. The recovery rate of 1, 4-dimethylnaphthalene was considered to be reliable. The analysis would, therefore, be accurate. Gas chromatographic analysis would be easier and quicker as there was no need to resolve a complex isomer mixture. Gas chromatographic analysis would be more sensitive as the total dimethylnaphthalene residue would consist of one isomer peak instead of several smaller isomer peaks.

The results are presented in Table A2. 04.

Table A2. 04. Residue levels of 1, 4-dimethylnaphthalene found in treated tubers.

Cultivar	Application rate ($mg\ kg^{-1}$)	Treatment time (weeks)	Airing time (weeks)	Residue level ($mg\ kg^{-1}$)	
				mean[c]	S. D.
Maris Peer[a]	100	12	0	3. 77	0. 39
		12	7	2. 69	0. 37
		16	0	3. 08	0. 23
		16	1	3. 19	0. 01
	300	16	0	11. 03	0. 01
		16	1	11. 22	0. 21
Record[b]	100	18	0	3. 35	0. 43

[a] Storage season 1977-78, temperature 9°C.

[b] Storage season 1976-77, temperature 10°C.

[c] Mean of duplicate 100 g samples taken from 1 kg potato macerate. Corrected for recovery factor.

It was considered that the results were accurate and that duplicate analyses of the same potato macerate were precise. The results also

agreed with the residue levels of 1, 4-dimethylnaphthalene found in the first preliminary experiment of storage season 1976-77.

A2.4 CONCLUSIONS

When determining residues of volatile pesticides in plant material, loss through evaporation can occur during the isolation procedure. Therefore, careful control of temperature and vacuum are necessary when removing solvents using a rotary evaporator.

A successful method was developed for determining trace levels of 1, 4-dimethylnaphthalene in potato tubers. The method included carefully controlled temperature and vacuum conditions during solvent removal by rotary evaporation. The method was shown to be sensitive, accurate and precise.

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