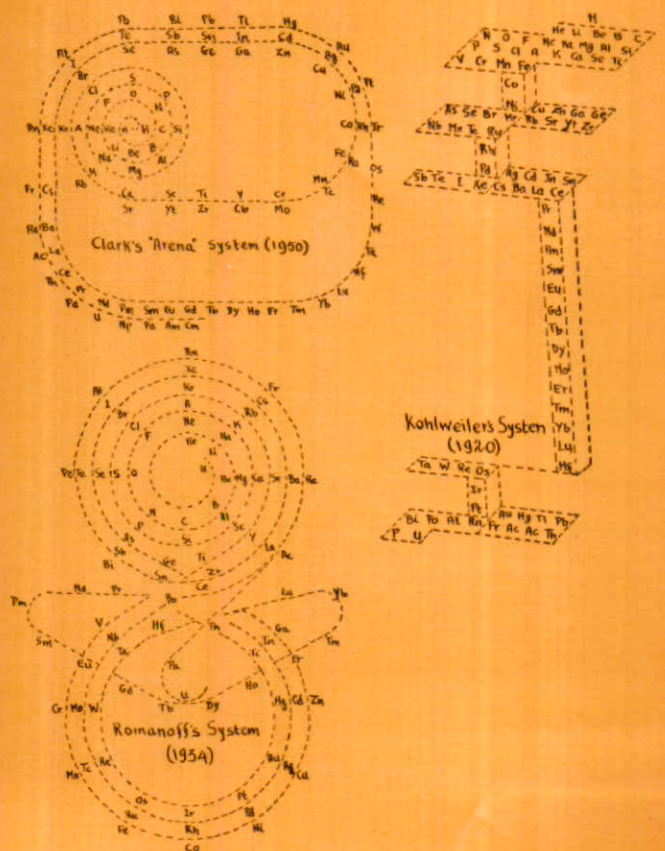
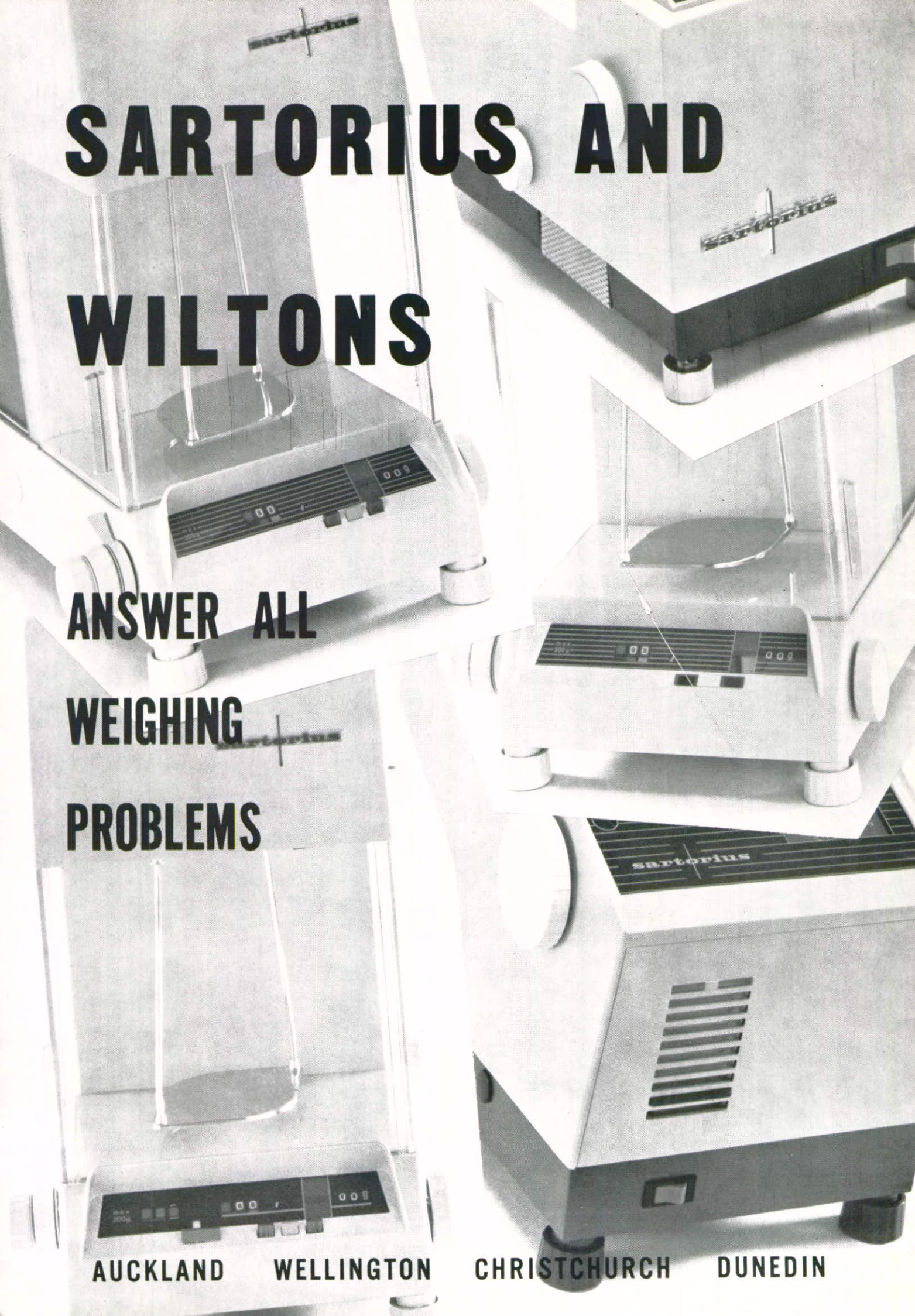


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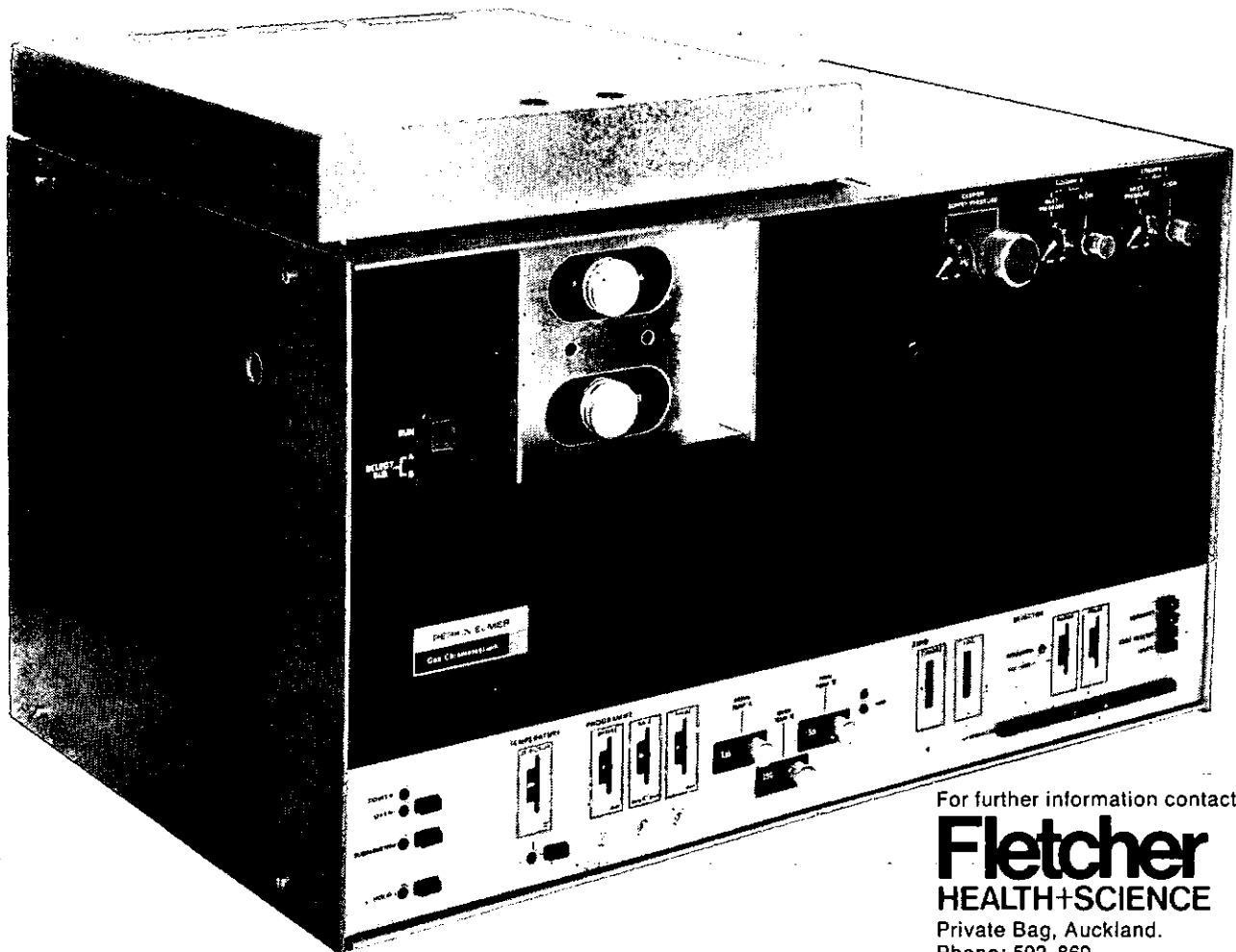
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Comment

Journal Proliferation

A recent letter in "Chemistry in Britain" (1974, 9, 32), signed by eleven eminent chemists expresses considerable concern at the increasing proliferation of new commercial chemistry journals. Although the research journal in its present form undoubtedly has a limited life, that is another matter. There is a more immediate problem. To quote:

1. "Today a publisher can start a journal in almost any part of chemistry and, by charging a high subscription price, can apparently make a profit, relying only on sale to libraries.
2. The new journals generally do not require publication charges from the authors, but subsist on the high subscription prices. Money, which the universities could otherwise use for research, goes to meet the blown-up library costs.
3. We believe that lax refereeing standards are characteristic of some new commercial journals. Such journals necessarily have a vested interest in building up volume to maintain themselves. The quality of new journals needs to be compared carefully with the standards set by other established journals.
4. The compartmentalization of chemistry into more and more specialized sections encourages these new journals and is encouraged by them. Communication among specialists in any one field is thereby facilitated. But our general feeling is that the literature should be so constructed as to deter trends towards overspecialization, and should foster communication among chemists working in different areas."

It cannot be denied that some commercial journals are of good standard and that publishers have in the past detected the wishes of chemists before the learned societies, especially with respect to preliminary communication and specialization. However if the present trend continues, how long will it be before we have a separate journal devoted to each element?

The letter continues by urging positive action and suggests:

1. "That all scientists urge their libraries to exercise the greatest reticence on subscription to new commercial journals. We realize that such a boycott of new literature will lead to some hardship; and some scientific information may take longer to get through. But we feel that there is no quicker way than this to convince publishers.
2. That all scientists refrain from publishing in new commercial journals."

As Dr R. S. Cahn says in his "Survey of Chemical Publications," (The Chemical Society, 1965).

"It is idle to blame the publisher for making as large a profit as he can: it is his business to do so; but it is equally the business of the scientist to prevent excesses. The captive librarian is helpless in this situation for he must buy what his readers require. It is the scientist alone who carries the responsibility and it is his duty to prevent extortion and exploitation."

It is recommended that members and branch committees should discuss this important issue, particularly with reference to the New Zealand situation, and should send comments to the Journal editor for publication in the next issue.

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and Biophysics,
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The Use of Capillary Columns in Gas Chromatography

by J. A. Zabkiewicz

Introduction

Gas chromatography is now a well established technique, but in common with many other separation methods, not all of its possible variants receive equal use or emphasis. One such "specialised" facet of gc is the use of capillary column techniques in a wide variety of problems.

The theoretical explanation for the separation process, in packed gc columns, is contained in the generalised version of the Van Deemter equation as given below, where the height equivalent to a theoretical plate (H) is given by¹:

$$H = A + B/u + Cu \dots \dots [1]$$

- A = a constant (representing the packing uncertainty)
- B = $2\gamma Dg$
- γ = the activity coeff.
- Dg = diffusion coefficient of the solute in the gas phase
- C = a constant (simplified)
- u = linear flow rate of the gas

It is recognised that in difficult separations more resolution may be obtained by increasing the column length, by decreasing the column internal diameter, or by optimising the temperature or flow rate. However, there is a practical limit to all those variables, and beyond them, increased resolution can only be obtained from increased efficiency of the separation process. Since the packing material contributes significantly to any loss in efficiency, (the A term in [1]), elimination of it should lead to a lower, i.e. better, H value. It was this sort of rationalisation which led M. J. E. Golay in 1957 to propose that the equation [2] should apply in the case of

$$H = B/u + (Cg + Cl)u \dots \dots [2]$$

Forest Research Institute, P.B., Rotorua.

case of a thin liquid film (when involved in a partitioning process), distributed over the inner face of a long narrow tube². Construction of such a system (Golay or coated capillary column) proved the theory correct in practice (e.g. typical H_{minimum} 0.5-2.0 mm for packed columns, and H_{minimum} 0.2-1.0 mm for capillary columns¹). A formalised representation (for packed columns) of the variation of the H term with flow rate, and of the individual terms contributing to its total, is shown in Fig. 1. It is evident from this graph that elimination of this A term must cause a significant decrease in H values.

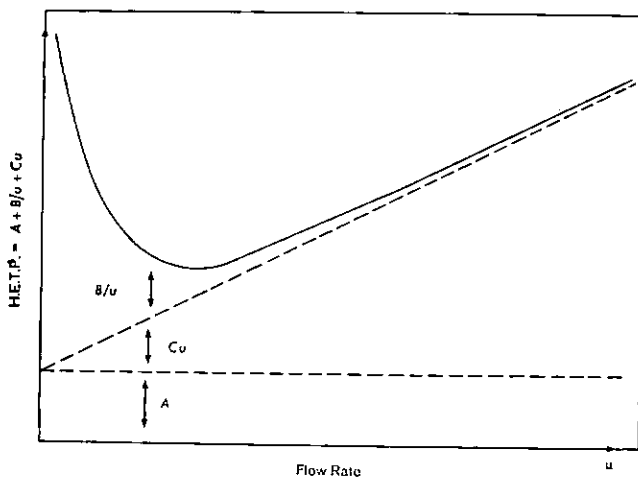


Fig. 1. Diagrammatic representation of the variation of H with flow rate and the component factors affecting its minimum value.

Physical Characteristics and Requirements of Capillary Columns

At present the gc capillary column has two distinct physical variants—the original Golay type, here called coated capillary, and the surface coated open tubular or SCOT capillary. Their physical characteristics are given in Fig. 2. The essential difference is that the SCOT column attempts to overcome the problem associated with maintaining a uniform liquid film on a smooth surface by interposing

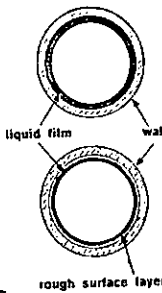
a further rough surfaced layer of a suitable material between the column wall and the liquid film. It also provides a greater surface area as a result, and consequently a higher efficiency of separation (reflected in the fact that they are most commonly available in 17 m length, compared to the coated capillary of 50 m). The wider bore also permits faster flow rates, thereby decreasing analysis times (although hydrogen and helium can also be used to this end in place of the more usual nitrogen). In general, the advantages of high inherent efficiency combined with the great length which can be fitted into a gc oven, make available columns which have in the region of 20,000-50,000 theoretical plates, compared to the usual packed column efficiency of 200-500 plates per foot.

Most capillary columns are made from stainless steel, although previously copper, teflon and nylon have been tried (with inferior results); more recently the glass capillary column has become a practical proposition. However, the present discussion is mainly concerned with the stainless steel version and its characteristics, as the other types are either out of favour or still rather "exotic" and difficult to set up. The problems with glass capillaries in particular involve liquid coating instability, use of teflon couplings, fragility, preferred vertical mounting in the gc oven, and a glass or glass lined injection splitter as well^{3,4}.

The preparation of coated capillary columns is not a difficult process, but requires more care to obtain reproducible and efficient columns. There are various techniques available for depositing the liquid phase from solution onto the inner wall, and since these vary with the liquid used, and with the column type and size, the reader should consult other works for specific details². However, good quality coated and SCOT columns are available commercially (but since the original patents still apply, at present of restricted manufacture).

It will be appreciated that the internal diameter of the column and hence the quantity of liquid phase distributed over it, is less than in packed columns, so smaller sample sizes are mandatory in order to obtain optimum results. This can be achieved with some columns by direct injection (those of 0.75 mm i.d.), but more normally an injection splitter is used, thereby allowing a normal 1-2 μ l injection volume, through only a small percentage of this sample goes onto the column. Again, the design of capillary col-

| | Column material | Length | o.d. | i.d. |
|--------|-----------------|----------------|-------|-------------|
| COATED | steel | (30-150m) | 1.6mm | 0.25-0.75mm |
| | glass | (~50m average) | | |
| | copper | | | |
| | teflon nylon | | | |
| SCOT | steel | (17-50m) | 1.6mm | 0.75mm |
| | glass | (17m average) | | |



CHARACTERISTICS OF CAPILLARY COLUMNS

Fig. 2.

umn injection splitters is of paramount importance for best results; and although commercial units are available, there is still a continuing search for better designs³.

Capillary Columns

Due to their high resolving power, the most useful application for capillary columns is for the analysis of complex mixtures of essential oils, petroleum and oil products, smokes and volatiles in general, waxes, etc. Recent literature frequently describes the separation of hundreds of compounds in the one mixture⁵. This high resolution helps to dispense with tedious and complex fractionation procedures which were previously necessary. A simple example of such an analysis is illustrated in Fig. 3, though in this case even more resolution could have been obtained by the use of linear instead of ballistic temperature programming.

It should be pointed out that because the gc column system is all metal, albeit stainless steel, not all organic substances can be chromatographed without decomposition. It is for this reason that capillary columns are used for the type of extracts mentioned above, rather than with more labile biological extracts. However, it was precisely this lack of general applicability which prompted the development of glass capillary columns for difficult biological samples, and led to the present situation where even steroid type molecules can be chromatographed safely^{6,7,8}.

Two other characteristics of capillary columns can be seen in Fig. 3. Despite the fact that the maximum temperature reached was 175°, little or no baseline drift occurred due to liquid phase bleed. Hence temperature programming with single column operation is quite feasible, unlike that of packed columns where dual column operation is preferred during programming runs. The other characteristic is the typical sharp peak, with only a slight tail on its trailing edge (caused by absorption effects). This is especially useful in trace analysis (see Fig. 4) because instead of small peaks being smeared out along the baseline, small sharp peaks are produced. These can be readily detected by the operator or an automatic integrator (which has to have a distinct change in gradient before it is activated) with a concurrent increase in accuracy.

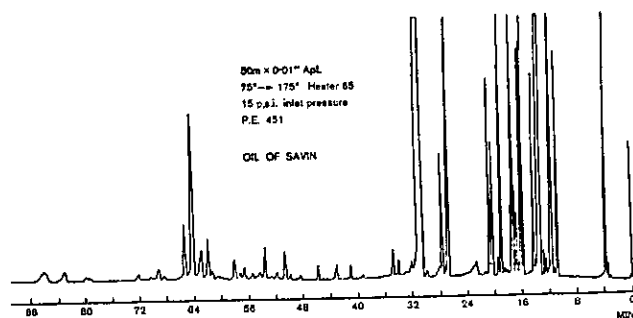


Fig. 3. Temperature programmed analysis of oil of savin on an Ap L capillary column.

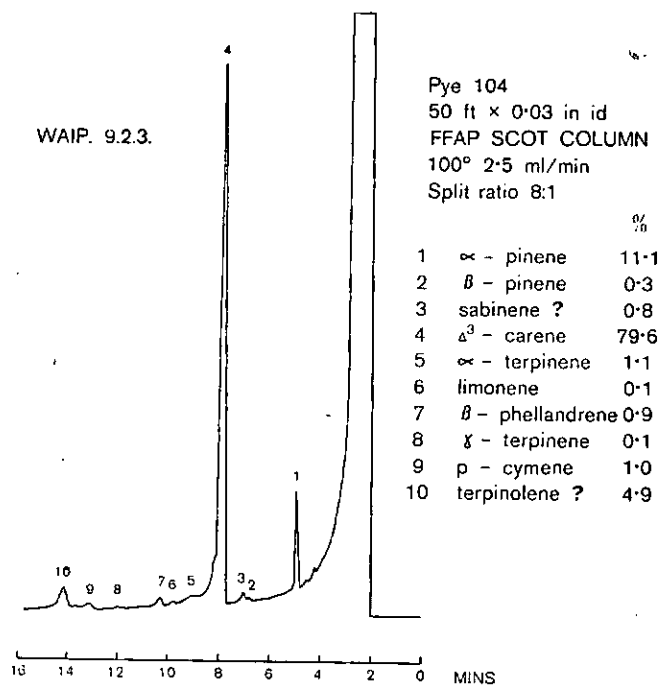


Fig. 4. Analysis of monoterpene constituents of *P. muricata* oleoresin; percentage composition determined with a Chromalog II integrator.

Capillary gc is extremely effective in separating individuals of an isomeric group of compounds, as is illustrated in Fig. 5. The top trace represents the best result that could be achieved with a special packed column; the lower trace was obtained from the analysis of the same components on a SCOT capillary column, when complete resolution was obtained with an equal analysis time. On the packed column, not only was there incomplete resolution, but two compounds overlapped completely.

One final example should suffice to emphasize the vastly higher resolving power of capillary columns. A particularly difficult separation is that of the four menthol isomers (as illustrated in Fig. 6A and B). Again, almost all packed columns gave incomplete resolution, but when this sample was analysed on a capillary column, separation was absolute and facile. However, in the search for a packed column which could separate these isomers, one and only one was found (Cyano P, or more correctly 1,2,3-tris (2-cyanoethoxy)propane) which could effect a separation virtually identical to that of the capillary column. The moral here is that although a capillary column is without doubt very effective, there may still be a particular packed column which can also be used. This is of value when larger quantities of pure substance have to be purified by preparative gc, and the phase used on the capillary column is ineffective. However, this type of example tends to be the exception rather than the rule.

Conclusions

It is difficult to state when capillary columns should or should not be used, but the following list of pros and cons may help to resolve the issue on specific problems.

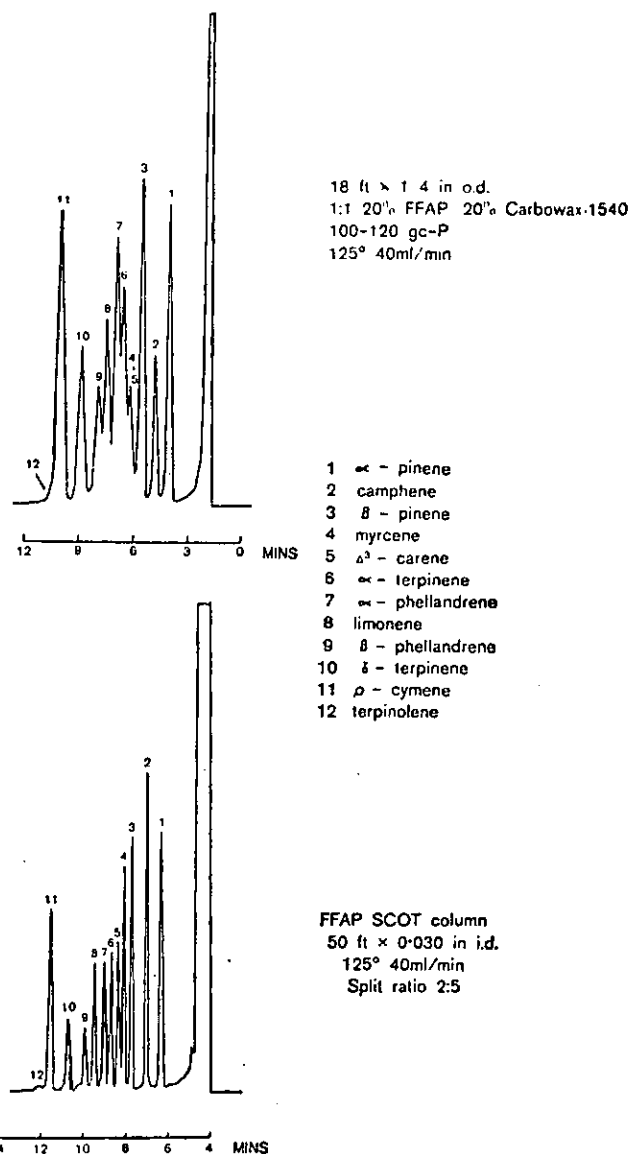


Fig. 5. Analysis of "synthetic" mixture of monoterpenes on a packed column (top trace) and a SCOT capillary column (lower trace).

The advantages of a capillary column lie in its higher resolving power and consequently faster throughput or reduced analysis time. It is probably advantageous to use a capillary column for analyses where the trace components are of more interest than the major compound. Where sample quantity is restricted, then the use of capillaries may be of value as smaller quantities are injected onto capillaries compared with packed ones (particularly if the wider bore type and direct injection is used.) The increased use of gc with mass spectrometry has also drawn attention to the fact that capillary columns can under preselected conditions be connected directly to a mass spectrometer, thereby avoiding all the attendant problems of interfacing the two types of instrument.

Against all these advantages, it must be pointed out that the initial cost of capillary columns is higher, plus the fact that a more expensive splitter/injection port assembly must be used. Operating costs

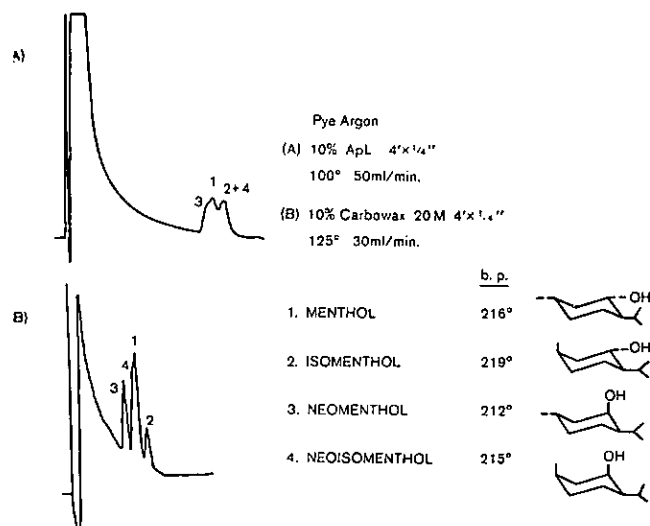


Fig. 6A. Structures of menthol isomers and their separation on conventional packed columns.

may be higher also, as for optimum resolution helium is preferred to nitrogen as carrier gas. A more serious problem is that in general the maximum operating temperatures of coated capillaries (although not SCOT types so much) are somewhat lower than their packed column equivalents. Last but far from least, is the problem that the only ready to use capillary columns available commercially are of metal, so that only compounds which are stable and which tolerate contact with metal can be analysed.

This short article cannot possibly cover all aspects of capillary theory or operation, but many more pertinent references will be found in the literature cited herein.

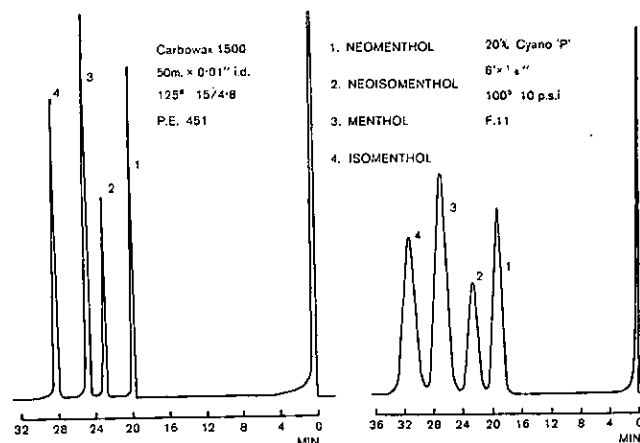


Fig. 6B. Separation of menthol isomers on a capillary and a "special" packed column.

REFERENCES

1. Littlewood, A. B., "Gas Chromatography," 2nd Ed. 198 (1970). Academic Press, London.
2. Ettre, L. S., "Open Tubular Columns," (1965). Plenum Press New York.
3. Grob, K. and Grob, G., *Chromatographia* 5, 3 (1972).
4. Grob, K. and Jaeggi, H. J., *Chromatographia* 5, 382 (1972).
5. Grob, K., *Chemistry and Industry* 248 (1973).
6. Grob, K. and Grob, G., *J. Chromatographic Science* 7, 584 (1969).
7. Novotny, M. and Zlatkis, A., *J. Chromatographic Science* 8, 364 (1970).
8. German, A. L., Pfaffenberger, C. D., Thenot, J-P., Horning, M. G. and Horning, E. C., *Analytical Chemistry* 45, 930 (1973).

NORANDA AWARD

Dr William R. Cullen, Professor, Department of Chemistry, University of British Columbia, Vancouver, is the winner of the Noranda Lecture Award for 1974. The award, established in 1963 by The Chemical Institute of Canada, is for distinguished contributions to physical and inorganic chemistry by an under-40 scientist working in Canada.

Bill Cullen was born in Dunedin, New Zealand in 1933, and was educated at the University of Otago, and at Cambridge University. He went to Canada in 1958 to UBC and has been there

since, apart from two years spent at the University of Bristol (1966-67) and the University of Sussex (1972-73). He has published works on a number of aspects of physical and inorganic chemistry. His Noranda Lecture will deal with the use of spectroscopic tools to elucidate the structures of complex metal carbonyl clusters.

The Chemical Institute of Canada is the 9,000-member national society of chemists, biochemists and chemical engineers working in industry, government and education.

Derivative Formation for Gas Chromatography

by Peter G. Robinson

Introduction

Many compounds which in their free state are not amenable to analysis by gas chromatography because of their low volatility, reactivity or instability can be chemically altered in such a way as to make gas chromatographic analysis possible. This process is termed "derivatisation". Derivatisation reactions are usually aimed at those chemical groups which contain active protons, e.g. hydroxyl, carboxyl and amino groups, but there are some exceptions, such as derivatisation of keto groups to prevent enolisation.

Derivatisation reactions can be broadly classified as follows:

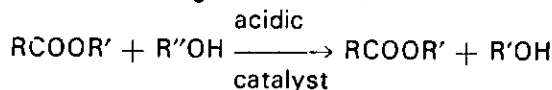
1. esterification
2. silylation
3. derivatisation of keto groups
4. cyclic alkylboronate derivatives
5. alditol acetates.

Esterification

This involves the reaction of a carboxyl group, usually with an alcohol, to form an ester. There are a number of different ways in which this can be done and these are as follows:

1. Esterification using an alcohol and an acidic catalyst

This follows the general reaction:



where R is any organic group, R'' is usually a methyl, ethyl, propyl, iso-butyl or n-butyl group. The acidic catalyst can be HCl, H₂SO₄, BF₃ or BCl₃ and all reagents are usually anhydrous.

Crowell et al¹ used HCl/methanol followed by zinc oxide precipitation of the methanol-insoluble zinc chloride, thus allowing direct chromatography of the methanol solution. Usually however, the prepared esters are extracted into another solvent (diethylether, petroleum ether) before analysis.

There has been considerable debate in the literature over the use of BF₃/methanol. Some authors^{2,3} have reported the formation of artifacts with C₁₈ unsaturated acids while others⁴ report good agreement between this and other methods. Reaction conditions used by the various authors are summarised in Table (1). It appears from this that the reaction temperature has a major effect on the formation of artifacts (which have been tentatively identified as methoxy addition products across the C=C double bonds).

2. Transesterification, either acid or base catalysed

Acid catalysed transesterification follows the general reaction

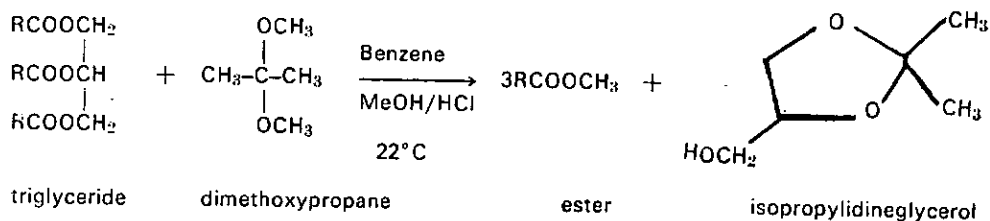
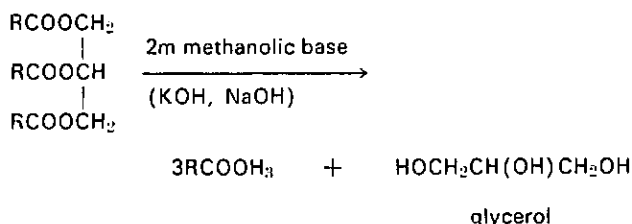


Table 1—Reaction conditions used for BF₃/methanol methylation

| Author | Reaction Temperature (°C) | % BF ₃ | Fatty Acid/Reagent | Artifacts |
|---------------------|---------------------------|-------------------|--------------------|--|
| Lough (1964) | 100 | 50 | 1 g/15 ml | Yes |
| Dawidowicz (1971) | 100 | 14 | 4 mg/1 ml | Yes |
| Metcalfe (1966) | 63 | 6 | 100-200 mg/3 ml | No |
| Klopfenstein (1971) | 120 | 14 | 4 mg/1 ml | Yes (BF ₃) No (BCl ₃) |
| Robinson (1973) | 60 | 14 | 0.5 mg/1 ml | No |

This usually requires standing overnight followed by neutralisation.

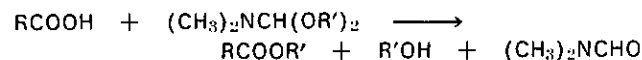
Base catalysed transesterification⁵ is more rapid (about 20 minutes from sampling to analysis)



These methods find particular application in the dairy and natural fats and oils industries where large quantities of triglycerides are present.

3. Use of Dimethylformamidedialkylacetals

The use of these reagents for esterification was first reported by Thenot et al.⁶ Samples were heated at 60°C in DMF-dialkylacetals (or 1:1 reagent and pyridine) for 10 minutes. The proposed reaction is:



The DMF-dialkylacetals have recently been promoted as the "instant esters" reagent,⁷ the "instant" presumably meaning that the esters are derivatised as soon as they are dissolved.

It has recently been reported⁸ that, even if highly pure reagents are used, extraneous peaks are produced in the chromatograms unless all excess reagent is removed. The recommended procedure is to remove the reagent under reduced pressure, dissolve the derivative in *n*-hexane, wash the solution with distilled water and dry over anhydrous sodium sulphate.

The three methods of esterification so far described can be used to prepare any of the esters from methyl to iso-butyl. The next three methods are generally limited to only one type of ester each.

4. The use of diazomethane (or diazoethane)

The use of diazo reagents for the preparation of esters is often criticised because of the dangers involved, both from the explosiveness of the diazo compounds and the carcinogenicity of the reagents. The hazards of explosion can be minimised by preparing the diazoalkane in small quantities as it is needed, rather than in bulk for storage in ether solu-

tion in a deep freeze. A simple apparatus for this is shown in Figure 1.⁹ The use of Diazald (N-methyl-N-nitroso-*p*-toluenesulfonamide), which is relatively non-toxic, also adds to the safety of the method.

Esterification with diazomethane is simple, direct and generally free from unwanted side reactions. Treated with caution it can be as safe as any other method. Diazomethane does not transesterify and saponification must be used if the acids are already esterified.

5. The use of Tetramethylammonium hydroxide (TMAH) or

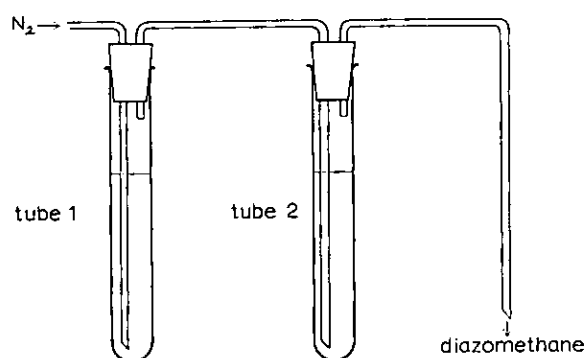
Trimethylphenylammonium hydroxide (TMPAH)

Organic acids may be methylated by pyrolysis of a solution of the acid in TMAH or TMPAH in the injection port of a gas chromatograph.¹⁰ These compounds will also cause methylation of amino groups and this is a standard procedure for the analysis of barbiturates.^{11,12}

6. The use of Boron trichloride/2-chloroethanol or 2,2,2-trifluoroethanol

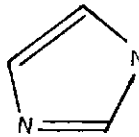
These reagents are used to prepare halogenated esters for analysis with electron capture detectors. Of particular interest is the derivatisation of 2,4-D for analysis,¹² where 2,4-D yields 2-chloroethyl-2,4-D.

FIG 1. Apparatus for generating Diazomethane.



Tube 1 contains diethyl ether to saturate the stream of nitrogen. Tube 2 contains 0.6 ml KOH (1 mg/ml in water), 0.7 ml Et₂O, 7 ml EtOH and 0.4 g Diazald in 1 ml Et₂O (added last). The substrate is dissolved in 10% MeOH in Et₂O and diazomethane is bubbled in until the solution turns yellow.

Table 2—Common Silylating Agents

| Formula | Name | Abbreviation |
|---|---|--------------|
| $(\text{CH}_3)_2\text{SiCl}_2$ | dimethyldichlorosilane | DMCS |
| $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$ | hexamethyldisilazane | HMDS |
| $(\text{CH}_3)_3\text{SiCl}$ | trimethylchlorosilane | TMCS |
| $(\text{CH}_3)_3\text{Si}-\text{O}-\text{C}(=\text{O})-\text{N}(\text{CH}_3)_2$ | N,O-bis-(trimethylsilyl)-acetamide | BSA |
| $(\text{CH}_3)_3\text{Si}-\text{O}-\text{C}(=\text{O})-\text{N}(\text{CH}_3)_2$ | N,O-bis-(trimethylsilyl)-trifluoroacetamide | BSTFA |
| $(\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2$ | trimethylsilyldiethylamine | TMSDEA |
|  | trimethylsilylimidazole | TSIM |

Silylation

The term silylation is usually taken to mean the addition of trimethylsilyl (TMS) groups to a compound but in some cases it may also be used with dimethylsilyl or chloromethyltrimethylsilyl groups. Some of the commonest silylating agents and their abbreviations are shown in Table 2.

In the preparation of most TMS derivatives it is very important that moisture be excluded, as both the reagents and products are susceptible to hydrolysis. An exception to this is the use of TSIM (see later). For the same reason analysis of TMS derivatives cannot be carried out on stationary phases having labile hydrogen atoms, e.g. diethylene glycol succinate (DEGS).

DMCS and HMDS were among the first silylating agents to be put into general use for preparing derivatives for gas chromatography. HMDS has the advantage that HCl is not liberated during derivative formation.

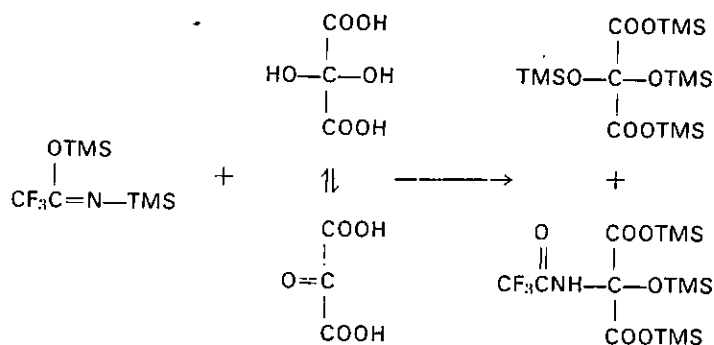
TMCS is often used as a catalyst with either DMCS or HMDS. One of the original reagents for the silylation of carbohydrates, phenols, sterols, etc., was a mixture of HMDS:TMCS:pyridine in a 3:1:9 ratio. This has largely been superceded in the last few years by formulations involving BSA or BSTFA or, more recently still, TSIM and TMSDEA.

BSTFA has become the 'workhorse' silylating reagent and has been used to derivatise aromatic, keto and indole acids, amino acids, their derivatives and metabolites, alkaloids, carbohydrates, narcotics, purines and pyrimidines, phospholipids, prostaglandins, polyols, phenols, pesticides, steroids, vitamins, and even inorganic anions such as phosphate, sulfate, vanadate, arsenate and carbonate. The advantage of BSTFA over BSA is that generally the re-

actions proceed faster and the by-products produced, mono-TMS-trifluoroacetamide and trifluoroacetamide, are more volatile than their BSA analogs.

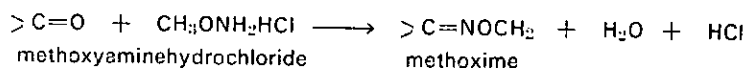
TSIM is a comparatively new silylating reagent which reacts with hydroxyl groups only. It is most useful in carbohydrate analysis and is more resistant to aqueous hydrolysis than other silylating reagents. Because it reacts only with hydroxyl groups it may be used to selectively derivatise certain groups with a molecule, e.g. for an indole amine,¹³ or, in conjunction with other silylating reagents, for steroids¹⁴ as shown in Figure 2.

As with esterification it has been reported that unwanted side reactions can occur. For example it has been found¹⁵ that BSTFA will add to mesoxalic acid to give two products. The proposed reaction is:



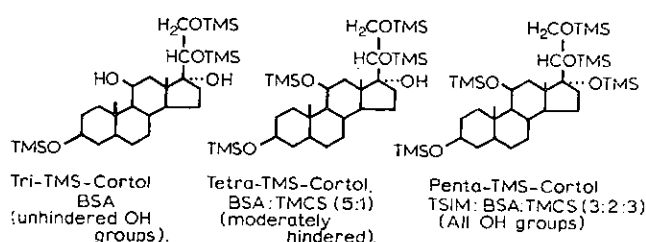
Formation of Derivatives of Ketones

Attempts to analyse some steroids and keto-acids by gas chromatography were initially plagued by the appearance of more than one peak per compound, if any peaks at all. This was found to be due to enolisation of the keto groups in the molecule and the subsequent formation of silyl ethers. The problem was solved by the use of methoxyamine hydrochloride which reacts with keto groups to form methoximes.



More recently O-benzylhydroxylamine hydrochloride has also been used.

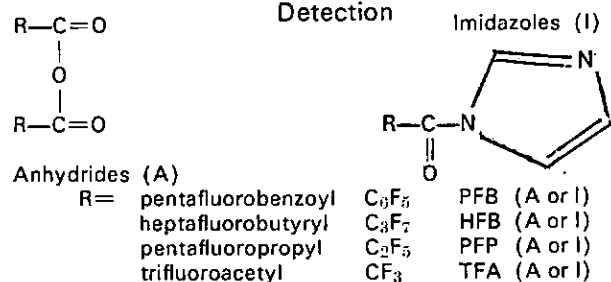
FIG 2. Selective Silylation of Steroids



Special Derivatives for Use with Electron Capture Detectors

Electron capture detectors (ECD's) have a very high sensitivity for atoms or groups which will capture electrons. The best of these are the halogens, in the order $F > Cl > Br > I$. The use of 2-chloroethanol or trifluoroethanol in the analysis of 2,4-D has already been mentioned. Preparation of derivatives for ECD analysis generally involved the addition of a halogenated acyl group. The reagents most commonly used are in two classes, anhydrides and imidazoles, as shown in Figure 3.

Figure 3—Acylating Reagents for Electron Capture Detection



Both classes produce products which are susceptible to hydrolysis. Imidazoles have the advantage that no acids, which could cause hydrolysis, are released during the derivatisation reaction.

In most cases the derivative produced is more volatile than the original compound, even though the acyl groups are quite bulky. The closely bound fluorine atoms are responsible for this effect. Some examples of compounds and the reagents used for their derivatisation are given in Table 3.

Table 3—Compounds and derivatising reagents used with electron capture detectors

| Compound Class | Derivatising Reagent |
|------------------|------------------------|
| Catecholamines | HFBA |
| | TFAA |
| Amines, Drugs | HFBA |
| | HFBI |
| Amines | PFB chloride |
| | PFPA |
| Phenols | PFB Chloride |
| | TFAA |
| Alcohols | Chloroacetic anhydride |
| | TFAA |
| Carboxylic acids | PFB bromide |
| | chloromethyl DMCS |
| | bromoethyl DMCS |
| | chloromethyl DMCS |
| Steroids | HFBA |
| | chloroacetic anhydride |

Cyclic Alkylboronate Derivatives

The use of these derivatives is at the moment mostly confined to steroid analysis. It has been reported¹⁶ that some α -aminoacids, hydroxyamines, ketoacids and diols can also be derivatised. It has been found¹⁷ that the formation of cyclic boronate esters effectively stabilizes corticosteroids for gas chromatographic analysis, the first time this has been possible.

The reaction of the steroid with alkylboronic acid/anhydride is often followed by derivatisation of the

keto groups with methoxyamine hydrochloride or benzyloxyamine hydrochloride.

Formation of Alditol Acetates from Carbohydrates

Because of the large number of hydroxyl groups present, carbohydrates are particularly non-volatile and derivatisation is essential before they can be subjected to gas chromatographic analysis. The formation of TMS ethers is in some cases sufficient, but isomerization can occur. The usual method of circumventing this is to reduce the carbohydrates to alditols with sodium borohydride and then to acetylate the alditol with acetic anhydride.¹⁸ Using this method complete separation of the monosaccharides erythrose, deoxyribose, rhamnose, fucose, ribose, arabinose, xylose, deoxyglucose, mannose, galactose and glucose was obtained in 42 minutes on a 3 m column containing 3% ECNSS-M.

Summary

Some of the many methods used to prepare compounds for analysis by gas chromatography have been discussed, including esterification, silylation and some more specific reactions.

Derivatisation is not always necessary and a large number of compounds and mixtures can be chromatographed directly. On the other hand, some mixtures require not only derivatisation but extensive clean-up procedures and every step which is introduced leads to some loss of sample. Thus the aim in gas chromatography must be to develop methods involving as few steps as possible between sampling and analysis.

REFERENCES

- E. P. Crowell, S. M. Aronovic and B. B. Burnett, *J.Chrom. Sci.* 9 (5): 296 (1971).
- A. K. Lough, *Biochem.J.* 90: 4c (1964).
- E. A. Dawidowicz and T. E. Thompson, *J.Lipid.Res.* 12: 636 (1971).
- L. D. Metcalfe, A. A. Schmitz and J. R. Pelka, *Anal.Chem.* 38 (3): 515 (1966).
- B. O. Christopherson & R. L. Glass, *J.Dairy Science* 52: 1289 (1968).
- J. P. Thenot, E. C. Horning, M. Stafford and M. G. Horning, *Anal.Letters* 5: 217 (1972).
- 'Alkyl-8 Reagents', Pierce Chemical Company, Rockford, Illinois, U.S.A. (1973).
- Chromatography Catalog, 1974, Supelco Inc. Bellefonte, Pennsylvania, U.S.A.
- H. Schlenk and J. L. Gellerman, *Anal.Chem.* 32 (11): 1412 (1960).
- D. T. Downing and R. S. Greene, *Anal.Chem.* 40 (1): 827 (1968).
- R. F. Skinner, E. G. Gallaher and D. B. Predmore, *Anal.Chem.* 45 (3): 574 (1973).
- D. W. Woodham, W. G. Mitchell, C. D. Loftis and Collier, *J.Agr.Food.Chem.* 19: 186 (1971).
- M. G. Horning, A. M. Moss, E. A. Boucher and E. C. Horning, *Anal.Lett.* 1: 311 (1968).
- 'Handbook of Silylation', Pierce Chemical Company, Rockford, Illinois, U.S.A. (1972).
- S. P. Markey, *J.Chrom.Sci.* 11 (8): 417 (1973).
- C. J. W. Brooks and I. MacLean, *J.Chrom.Sci.* 9: 18 (1971).
- G. M. Anthony, C. J. W. Brooks, I. MacLean and I. Sangster, *J.Chrom.Sci.* 7: 623 (1969).
- J. S. Sawardeker, J. H. Sloneker and A. Jeanes, *Anal.Chem.* 37: 1602 (1965).

Proton Induced X-Ray Fluorescence Analysis And Its Uses in Measuring Air Pollution

by D. C. Robinson, N. E. Whitehead and G. E. Coote

Introduction

The last few years have seen the development of high resolution lithium drifted silicon X-ray detectors which have transformed non-dispersive X-ray fluorescence into a powerful tool for the analysis of trace elements. The technique has been widely discussed in the last year or two (Cookson et al.,¹ Floccini et al.,² Gordon and Kramer,³ Larson et al.,⁵ Rudolph et al.,⁷ Watson et al.,⁸ Young,¹⁰). Johansson et al.⁴ discuss detecting amounts as small as 10^{-12} g and concentrations of parts per 10^6 . There has also been much discussion of the advantages of various ionizing methods: bombardment by protons or heavier ions; irradiation by X-rays both from radioactive sources and from X-ray tubes; and irradiation from electrons. It is not always easy to reconcile the various claims because of the large number of parameters involved, the varying criteria used for detectability, and differing experimental conditions.

The Institute of Nuclear Sciences has recently purchased a Si(Li) detector with resolution of 185 eV at 5.9 keV, and we have embarked on a programme to detect trace elements. We plan to use both proton induced and X-ray induced fluorescence; this paper is concerned only with the former. We will describe the technique and illustrate one of its many possible applications—analysis of air filters. These were supplied by the Department of Health and consisted of a strip of filter paper $1\frac{1}{2}$ " wide with discs of aerosol matter at 2" intervals. Each disc represented two hours' collection time or about 2.5 cubic metres of air, and the set covered an uninterrupted 32 hour period. They were collected on a July week day in Christchurch. It was possible to use the clean spaces between the discs of aerosol material as blanks. We were interested firstly in what elements we could detect, and secondly in whether we could see significant variations within the period.

The results presented here, while interesting, are only preliminary, but they do illustrate the possibilities of the technique. Detailed meteorological data will be necessary before useful conclusions can be drawn. Furthermore, results are presented on lead and bromine only, because of the high and variable blank levels for other elements in the filter paper.

Description of the method

In X-ray fluorescence analysis some external source of radiation is used to ionize the elements in the sample which then emit characteristic X-rays. These are detected by an energy-sensitive detector. Their energies uniquely determine the various parent elements, while their intensities are proportional to the amounts present.

In our work the external source was a beam of protons from the Institute's 3 MV Van de Graaff accelerator. The filters were put in the accelerator vacuum system exactly as they were received, i.e., with no sample preparation beyond cutting the strip of filter paper into suitably sized pieces. They were mounted on a piece of carbon to improve electrical conductivity. The detector, of lithium drifted silicon, protected by a 12 micron beryllium window, was mounted within the vacuum system about 8 cm from the filters. Pulses from the detector were amplified and then analysed and stored in a Kicksort 4096 channel analyser. Only 512 channels were used for each spectrum. Beam currents varied between approximately 0.04 and 0.10 μ A and the maximum counting rate was approximately 3000 per sec. This, in the absence of pileup rejection electronics, was close to the maximum which could conveniently be handled. Typically each spectrum was accumulated for about 3 minutes. The peak areas in each spectrum were extracted using our PDP-11/20 computer. The programme used (McCallum⁶), although still under development, allows almost completely automatic analysis which takes about 10 minutes for each spectrum. Conversion of the peak areas to weight of element present can be approached either

by using standards or by calculation from published values of cross sections, absorption coefficients, fluorescent yields, etc. We have investigated both these approaches; above $Z = 20$ the calculated results have a mean deviation from the experimental ones of 35% which is adequate for a preliminary experiment. Valuable features of the technique are that it allows simultaneous determination of a large number of elements, and that the X-ray yields from the elements vary smoothly with atomic number. When using proton excitation the major source of background and hence the major determinant of the limit of detectability is almost invariably bremsstrahlung from electrons knocked out by the protons. Since the maximum energy that an incident proton can deliver to a free electron is

$$E_{\text{max}} = \frac{4 m_e}{M_p} E_{\text{inc}}$$

where m_e and M_p are the electron and proton masses and E_{inc} is the incident proton energy, this bremsstrahlung spectrum has a cut-off at about $E_{\text{inc}}/500$. Above this energy background can still arise from accelerator-produced X-rays, room background and direct proton bremsstrahlung, but it is much lower. Hence detectability tends to be higher for elements with X-rays above this energy. An absorber is necessary between the target and detector to prevent scattered protons from reaching the detector. The resultant X-ray absorption is responsible for a sharp drop in the detected yield of X-rays from light elements. Reduction of the beam energy to 1.0 MeV allows this absorber to be removed, as at this energy the 12 micron beryllium window will stop the protons. Consequently the detected yield for light elements is much improved, but that for heavier elements is reduced because their ionisation cross section is reduced. These considerations mean that best sensitivity for light elements (Na - Cl) is ob-

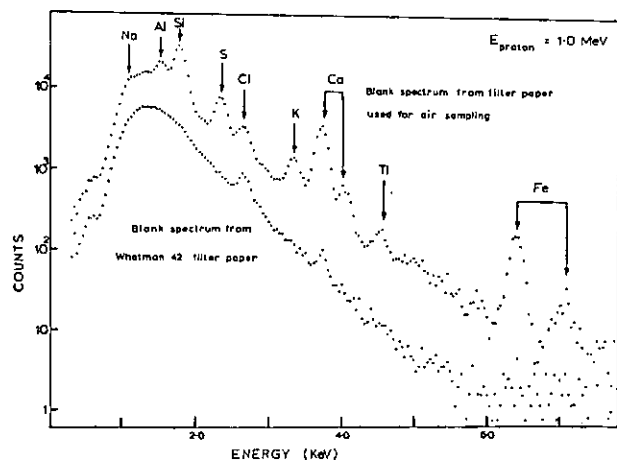


Figure 1—Blank X-ray spectra taken with a proton energy of 1.0 MeV. The upper curve was obtained from the bombardment of an unused part of the filter paper used in the air sampling. A large number of peaks are visible. The lower curve was obtained from bombardment of Whatman No. 42 filter paper. The only obvious peaks are from chlorine and calcium. This spectrum has been displaced by a factor of approximately 2.5 so that the two curves may be compared. Both took about $3\frac{1}{2}$ minutes to accumulate and both display the characteristic bremsstrahlung background shape.

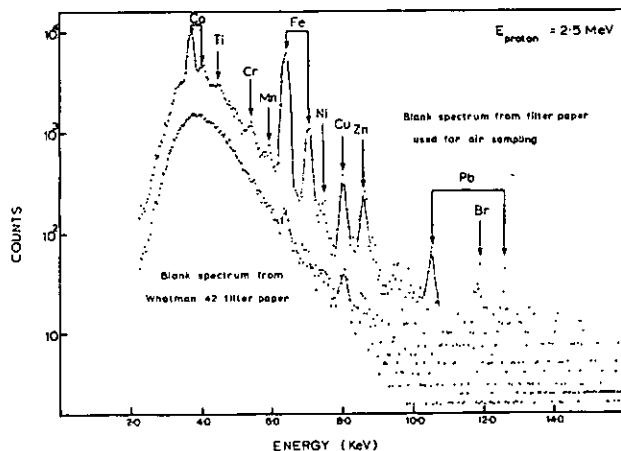


Figure 2—Blank X-ray spectra taken with a proton energy of 2.5 MeV and an additional absorber. At this energy sensitivity for the heavier elements is enhanced but the bremsstrahlung background extends to a higher energy. As in fig. 1 the lower spectrum has been displaced by a factor of about 2.5 so the two curves may be compared.

tained at low proton energies and for heavier elements at high proton energies.

Results

Two series of measurements were done, one using a proton energy of 2.5 MeV and the other of 1.0 MeV. Unfortunately the filter paper used for collecting the air samples contained a large number of contaminants. X-rays from all of the following elements were seen from supposedly blank or clean filter paper: sodium, aluminium, silicon, sulphur, chlorine, potassium, calcium, titanium, manganese, iron, nickel, copper, zinc, bromine and lead. Most of these are probably present in the filter paper itself, but some may have been deposited through contamination by handling or prolonged contact with dirty air. Figs 1 and 2 are blank spectra obtained respectively at 1.0 and 2.5 MeV compared with spectra obtained by bombarding pieces of Whatman No. 42 filter paper. Only small amounts of chlorine, calcium, iron, copper and zinc can be seen on the Whatman paper. We have found No. 44 paper is even cleaner. As a further comparison fig. 3 shows the spectrum obtained from a piece of glass fibre

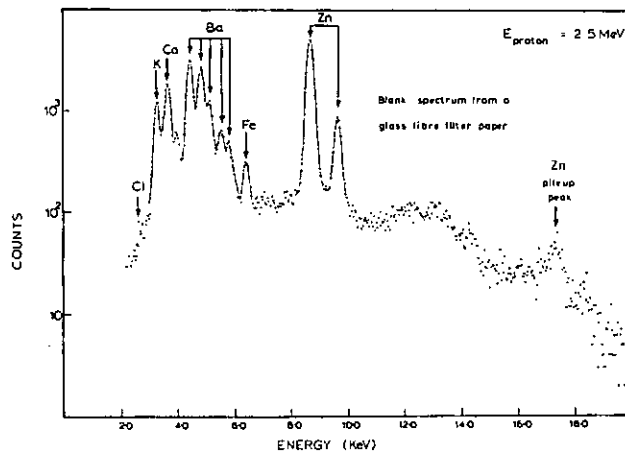


Figure 3—X-ray spectrum obtained from an unused glass fibre filter paper.

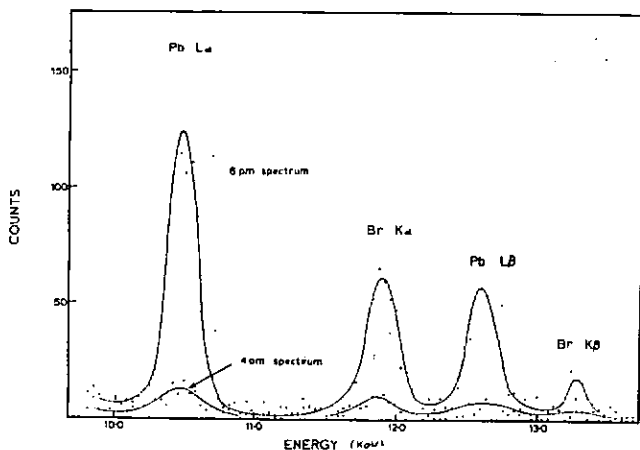


Figure 4—Portions of spectra obtained by 2.5 MeV proton bombardment of the aerosol material collected at 6 p.m. and 4 a.m.

filter paper. The large amounts of zinc and barium make it unsuitable for use with this technique. The background bremsstrahlung and its sudden reduction at very low energies due to absorption can clearly be seen in these spectra. Unfortunately the blank values were not only high but variable as well, and significant information could be extracted only for lead and bromine. Concentrations of these two elements showed very marked variation throughout the 32 hour period. Fig. 4 shows the most interesting region of a high lead (1800 hrs) and low lead (4044 hrs) spectrum plotted on a linear scale. Analysis of the complete set of air filters resulted in Figs 5 and 6 showing respectively the lead and bromine variations with time. The error bars represent statistical errors only, and although the error on the absolute calibration could be as high as 50% it is quite certain that the overall picture correctly represents the concentration differences on the filter papers.

Conclusions

Proton induced X-ray fluorescence is a sensitive and useful technique for the analysis of trace elements. Our work illustrates that with a bombarding time of a few minutes one can measure most of the elements in the periodic table down to weights of around 100 ng/cm^2 (10^{-7} g/cm^2). Given our experi-

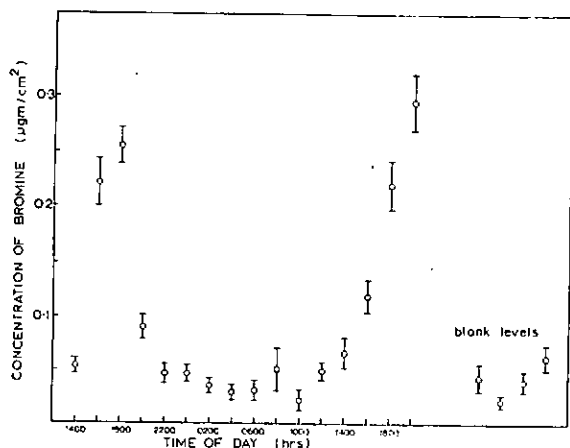


Figure 5—Lead variations throughout the 32 hour period.

mental conditions, the most sensitive region is centred on nickel ($Z = 27$) for which the minimum detectable quantity is 10 ng/cm^2 (10^{-8} g/cm^2). This involves detecting K X-rays. The least sensitive region, apart from elements lighter than sodium which cannot be detected at all, is centred around cadmium ($Z = 48$) where the detection limit is about 300 ng/cm^2 . For heavier elements the L X-rays are detected and the minimum detectable weight improves again to about 40 ng/cm^2 around tantalum ($Z = 73$). In this context the minimum detectable weight means that the resulting peak area is three times the standard deviation of the background under it. These detectability figures, of course, apply specifically to the conditions we used for these experiments, i.e., with the sample material on filter paper of 8 mg/cm^2 thickness. Under different conditions they could be completely different. In particular, changes in the beam energy or the absorber material would alter both the detectability limits and the positions of greatest sensitivity. Again, if the sample material could be spread on very thin carbon or plastic film, the sensitivity figures could be improved greatly because the bremsstrahlung background would be reduced. Finally, improvements in detectable limits can always be achieved by counting for longer periods or by using higher beam currents, although the latter may introduce count rate problems.

The results of this experiment show that the concentrations of lead and bromine in the air change throughout a day. Wedberg et al. (1973) point out that airborne lead may come either from industry or from automobile traffic, while bromine comes almost exclusively from the latter. Hence a constant lead-bromine ratio suggests that both elements are originating from motor vehicles. This appears to be the case in the present work. However further work and closer examination of prevailing meteorological conditions are necessary for further elucidation of the system.

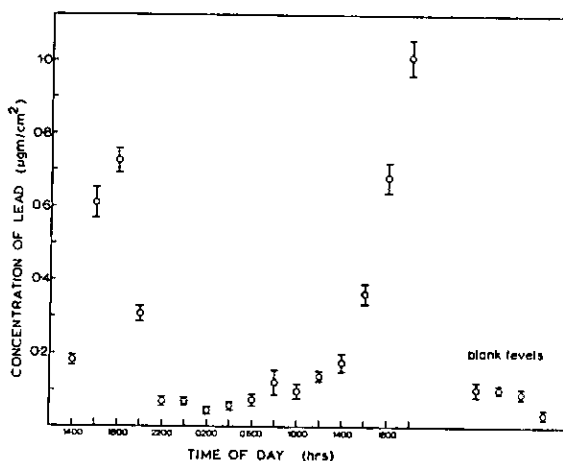


Figure 6—Bromine variations throughout the 32 hour period.

ACKNOWLEDGMENTS

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REFERENCES

1. J. A. Cookson; M. Ivanovich; F. D. Pilling (1972): Analysis using proton-induced X-rays. *AERE-PR/NP/18*: 62.
2. R. G. Floccini; P. J. Feeny; R. J. Sommerville; T. A. Cahill (1972): Sensitivity versus target backings for elemental analysis by alpha excited X-ray emission. *Nuc. Instr. Meth.* 100, 397.
3. B. M. Gordon; H. W. Kramer (1971): On the development of a system for trace element analysis in the environment by charged particle X-ray fluorescence. *BNL* 16182.
4. T. B. Johansson; R. Akselsson; S. A. E. Johansson (1970): Trace analysis at the 10^{-12} level. *Nuc. Instr. Meth.* 84, 141.
5. H. T. Larson; R. B. Liebert; D. Miljanic; V. Valkovic; T. Zabel; G. C. Phillips (1972): Trace analysis of biological materials by charged particle induced X-ray excitation and elastic scattering. *Bull. Am. Phys. Soc.* 17(4), 548.
6. G. J. McCallum (1973): *Institute of Nuclear Sciences Computer programmes*. Pp. 114, 115.
7. H. Rudolph; R. A. Ristinen; W. R. Smythie; A. Alfrey; S. R. Cantiguglia (1972): A proton-induced X-ray study of trace element transfer in hemodialysis. *Bull. Am. Phys. Soc.* 17(4), 548.
8. R. L. Watson; J. R. Sjurseth; R. W. Howard (1971): An investigation of the analytical capabilities of X-ray emission induced by high energy alpha particles. *Nuc. Instr. Meth.* 93, 69.
9. G. H. Wedberg; K. C. Chan; B. L. Cohen; J. O. Frohlinger (1973): X-ray fluorescence measurements of the lead/bromine ratio in an urban atmosphere. *Bull. Am. Phys. Soc.* 18(4), 580.
10. F. C. Young (1972): Trace element analysis by proton-induced X-ray excitation. *J. Wash. Acad. Sci.* 62(2), 153.

Inorganic Analysis To-day

by H. Keyzer

To demand that inorganic analysis be placed contemporaneously requires reference to the past and invites comments to the future. Only a handful of readily recognizable elements were known to the ancients—Ag, Au, C, Cu, Fe, Hg, Pb, S, and Sn. As was added at about 1250 A.D. then Bi, P, Sb, and Zn were added about 1700 A.D.

The medieval bankers' houses of Europe in search of mineral wealth provided the impetus for inorganic analyses more rigorous than those advanced by alchemy. Names like Albertus Magnus became legendary (he discovered As) and methods for inorganic analyses began to appear.

The course of the discovery¹ of elements to this day is represented in Fig. 1.

Several interesting features appear:

A viable classification of elements was constructed before a little over half the elements were known. This led via many systems (amongst others, Clarke's Arena, the Romanoff Mindbender and Kohlweiler's Leaning Tower (cover)) to the comfortably stable and familiar Periodic Table of today.

Recently the discovery (in this case synthesis) of new elements continues apace with the addition of a new element approximately every two and a half years. Albert Ghiorso and his collaborators in Cali-

fornia have been the outstanding workers in this area. In the last decade they have added the element Lawrencium 103 (1961), Rutherfordium 104 (1969) and in 1970³ element 105 for which they proposed the name Hahnium (after the German scientist who discovered nuclear fission). Analysis took early

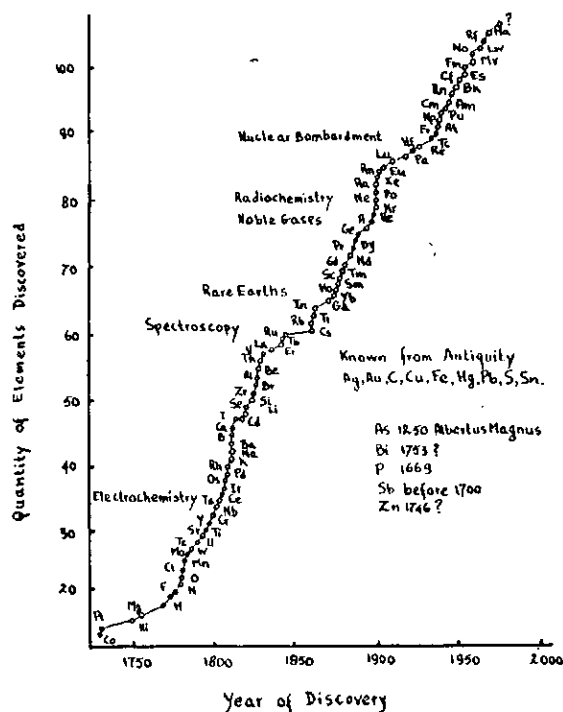


Fig. 1—Quantity of elements discovered versus year of discovery. Adapted and extended from ref. 1.

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advantage of new discoveries, chemical and physical; rudimentary instrumentation was in evidence.

With knowledge of chemical properties and chemical systems expanding, inorganic analysis became preoccupied with precise and accurate quantitative determination of elements in a sample and many laborious schemes were devised, as some of us remember ruefully. The leading *motif* in inorganic analytical research can be expressed by the unattainable ideal:

"To determine non-destructively, *in situ*, without pretreatment, instantly and quantitatively, every element in state and distribution in an infinitesimal sample"

and for those who would quibble, one might add—"without expense".

This definition is perforce a *non-sequitur* and one should advance pragmatically.

Inorganic analysis today can be arbitrarily divided into:

chemical methods (to which reference will be made only when essential), and instrumental methods, sub-divided into: thermal methods, electrical methods, spectroscopic methods, and radioactive or nuclear methods.

Thermal methods cover both thermogravimetric and differential thermal analysis. The former as an analytical tool is severely restricted. Differential thermal analysis, introduced by Le Chatelier in 1887 commenced strictly with W. P. White's¹ paper in 1920 and received due attention for the next 25 years, but remained restricted to insoluble contaminants. This method, which measures the heat content of a sample as a function of changing temperature, is comparatively "blind" in that it can be employed gainfully only for indiscriminate contaminant concentration. A sensitivity of 10^{-5} g/g is sometimes attainable. The progress of its utility reached peak interest in 1960.

In terms of sensitivity, as is the case with many penetrating methods, a marriage of principles often leads to a superior result. So, in the determination of trace impurities in metals, electrical resistivity versus temperature yields sensitivities readily of 10^{-8} , particularly at low temperature. The resistivity does not fall to zero at 0°K in a metal because chemical impurities and lattice defects act as scattering centres for charge carriers. The displacement of the resistivity curve is a function of such sites. Hence, the ratio of resistivities at room and liquid helium temperatures is often used as a simple measurement for the purity and perfection of a metal crystal. Although special cases exist,² e.g. individual doping with Ag, Fe or Ni in a Cu host, this method is also comparatively "blind". This method is of fundamental importance in the analysis of high purity materials provided by zone refining and other processes of crystal growth which have led to the semiconductors and therefore to dramatically improved detectors, circuitry and computers.

For electrochemical systems, especially those capable of discriminating elements with a sensitivity of about 10^{-6} , the obvious example is that of polarography which grew from the d.c. falling drop methods to include numerous adaptations such as the rotating electrode and a.c. fields. This relatively simple method serves to determine a tremendous range of elements providing they are reducible or oxidizable. The popularity of this tool based on comparative simplicity and low cost was evident in industry where interest peaked at about 1954. Note that greater interest now attaches to biological applications.

Although polarography enjoys respect in the scientific community, its popularity as an analytical device has been eclipsed by the advent of the specific ion electrode which boasts a sensitivity of a fraction of a part per million (ppm). This electrode takes advantage from the mobility of a particular ion in an otherwise immobile host-lattice, e.g. F^- in LaF_3 . Many electrodes are selective in that interferences may arise from other ions³ present. It is the aim of research in this area to increase the specificity of the exchange membrane. Hence so-called liquid membrane electrodes have been introduced such as the calcium electrode. Here an inert porous membrane is in contact with two reservoirs, one of which contains the reference solution and reference electrode, and the other which contains a solution of a long chain polymer with a phosphate group to which calcium is ionically bonded. The polymer is tailored to confer upon it the property of relative immobility. Other electrodes are of the composite type, where an insoluble salt of interest is dispersed in a silicone rubber⁴ or epoxy¹⁰ matrix. Specific ion electrodes appear to hold the promise of a simple method to rapidly determine anions which have been orphans from an instrumental point of view. In our laboratory we have attempted to produce membranes from quaternary ammonium polymers with negative specific counterions. So far, insoluble compounds with I_3^- ¹¹ and $Cr_2O_7^{2-}$ ¹² have been obtained which appear to have desired properties.

Spectroscopy, the method of UV-visible absorption, must be alluded to as a viable analytical tool primarily for the reason of low-cost. The sensitivity of this method compared with others is disappointing, but becomes more acceptable by improving the technique with suitable organic reagents of the coordination type, (such as the familiar 8-hydroxyquinoline, o-phenanthroline, aluminon and a host of Schiff bases) all designed to create specificity and increased sensitivity of analysis. Even so, sensitivity is rarely better than 10^{-5} attainable. Detectability is enhanced by utilizing concentrating techniques such as chromatography, ion-exchange and specific reagents, but this applies equally to many other instrumental methods.

An indispensable technique for analysis is emission spectroscopy. This method must have been the first ever used by man as he lurked near his fire and observed coloured flames, but it could not be established to meet analytical demands until New-

ton used the prism and Wollaston added the slit in 1802. The latter also noticed black lines in the solar spectrum; Fraunhofer measured them in 1818 and Bunsen and Kirchoff explained them. Such a complicated plethora of spectral lines attended elemental emission that it became known as the "forgotten method" in the period 1885-1924. In 1926 Gerlach introduced the internal standard and the popularity of this technique was assured as industry utilized it extensively from 1930 onwards. In 1960 the ruby laser as an auxiliary volatilizing method was introduced. Emission data were made amenable by high speed photographic emulsions, superlative gratings, photocounting densitometers and the use of computers. However, the technique is inexorably losing ground as a universal analytical method. In 1965 Chemical Abstracts lists 455 publications and 335 in 1970. This decrease must have its roots in competition from other modern analytical methods, for it is inconceivable that emission spectroscopy will not remain a tool *per force* for stellar research.

The introduction of atomic absorption spectroscopy made viable by Walsh¹³ in the 1950's has given the analyst a relatively low basic-cost instrument. The technique is sensitive to fractions of ppm, and the common interferences abounding in flame emission photometry are absent because the concern is now with excitation from the ground state of a neutral atom. The tremendous interest which attaches to this method is shown by the variety of atomization devices utilized:¹⁴ flame atomization (air-acetylene, acetylene-nitrous oxide), sputtering chamber, L'vov furnace, flash discharge lamp, laser sampling, plasma sources (16,000°K), solid propellant atomization. Particular interest applies to the L'vov furnace which, it is claimed, can cause a sensitivity of 10^{-5} g* to be achieved. This furnace consists of a Ta lined graphite tube into which the sample is placed. An external auxiliary electrode then causes a short circuit and the sample is progressively volatilized. Another point of interest is the possible use of atomic absorption spectroscopy as a dating device. Zaidel and Korennoi¹⁶ attempted to use the Li doublet at 6707Å (0.15Å spacing) for this purpose. The hollow cathode illumination source consisted of Li enriched in one isotope. However the method is rife with interference and not likely to be widely applicable as yet.

X-ray fluorescence is the term coined for the production of characteristic secondary X-rays from the transition of higher "shell" electrons to vacant lower shell orbitals. The vacancies in the inner orbitals may be effected by knocking out the electrons with primary X-rays or a stream of energetic electrons, the former being termed the X-ray fluorescent method, whereas the latter comes under the heading of electron microprobe analysis. A high speed, modern X-ray fluorescence instrument with a programmable computer is a boon to holistic geo-

logical and metallurgical determinations. The peculiarity of the microprobe gives it the limits of detectability comparable with the touch stone of inorganic analysis: neutron activation.

One of the most sensitive methods of modern analysis is isotopic dilution, in which a species of known radioactivity is added to a sample and after mixing homogeneously the species is isolated and measured. This method is one of the most selective available to the chemist.

Modern activation analysis is classed into excitation by fast neutrons, slow neutrons, γ - and other charged particles.

A typical n-activation event is given by bombardment of one isotope Sb, which decays with γ -emission of characteristic energy, 1.18 MeV.

Another isotope decays with 2 γ -emissions respectively of 0.061 and 0.075 MeV. These are far less energetic than those in the previous decay. The 1.18 MeV species is the one analysed in the neutron generator. Neutrons are produced by accelerating deuterium nuclei through a 150,000V electric field to impinge upon a target which emits neutrons to irradiate the sample. The γ - or β -emission of the converted sample is then monitored and counted with multichannel analysers.

Some 75 elements are accessible to neutron activation. The n-generator activates about $10^{-14}\%$ of the sample and many isotopes produced decay back to their previous state. The limit of sample size is about 10^{-6} g and the sensitivity in many cases is 10^{-5} microg. with a relative error of 1-3%. This method can therefore be regarded as non-destructive. By comparison, n-activation in a reactor with slow neutrons does not lead to efficient capture cross-sections and the sample is adversely affected by the heat and γ -radiation in the pile.

n-Generation analysis is so reliable that it usually provides acceptable forensic evidence. In this context it is worthwhile to point to the acceptance of utilizing rare earths in harmful drugs for source and date markers¹⁷. Many of the rare earths have high detectability but are difficult to separate chemically, hence addition to a drug of a specific mixture of rare earths makes the previously mentioned identification entirely feasible. The quantity of added mixture would be virtually infinitesimal and presumably harmless.

Particle scattering is also a useful modern analytical tool particularly for remote control situations. Alpha scattering involves measuring the energy spectra of α -particles scattered backwards from atomic nuclei of the sample, and of protons obtained from the nuclear reactions of α -particles with some of the lighter elements. Such spectra give quantitative information on all major elements excepting H, He and Li.

Instrumentation of this kind was used on Surveyor missions²⁰. A typical experiment consisted of obtaining data for one hour in transit on a known sample

*Note: Dr J. Aggett¹⁵ disputes this figure and his work with carbon filaments fully justifies his view.

and comparing it with preflight data. This showed that the analytical device had survived the launching and that background radiation was low enough to permit experimentation. Two hours after the lunar landing the known sample was again monitored, and engineering data were returned for one hour. Systems were still "go". Then the sensor head was released by remote command and suspended 0.5 m above the lunar surface to monitor cosmic radiation, solar protons and possible surface radiation. For three hours background spectra were taken and then the sensor was lowered to the surface. After a specified period the device was moved and the analytical process repeated. Signals were sent to the Jet Propulsion Laboratory via Robledo, Spain, for computer analysis. Information was obtained on C, O, Na, Mg, Al, Si, the 'Ca' elements (atomic number 28-45) and the 'Fe' elements (atomic number 45-65) which were in line with later Apollo 11 findings. A review of terrestrial testing of lunar samples can be found in a publication by Reese²¹. On reading this, one is struck by the fact that the main methods of inorganic analysis utilized for this purpose were predominantly neutron activation and mass-spectrometry.

Mass spectrometry is perhaps one of the best inorganic analytical tools now available but the high cost of acquisition, rigorous vacuum requirements and tremendous maintenance and operational costs makes this method virtually unattainable to many normal institutions. To my knowledge only one county institution, the Los Angeles County museum, boasts such a high-cost giant. This instrument is expected to pay for itself because the fees are high to collectors who wish to ensure that they have acquired a genuine Rembrandt at \$10,000/in². A mass spectrometer was also utilized in Surveyor²⁰.

After this brief catalogue of methods there will be no time to mention the application of laser spectroscopy to pollutant monitoring of SO₂, N₂O₄, O₃, CO and other molecules in urban atmospheres using the city as a sample cell. It is not possible to discuss atomic fluorescence spectroscopy or nuclear quadrupole, nuclear magnetic resonance, Mossbauer spectroscopy or any of the boggling array of other methods. We have no time to discuss new sources, new detectors, automation and computers but one prediction that can be made is that the introduction of the tunable laser will dramatically alter the scene of inorganic analysis and reaffirm the tremendous power of man.

Apollo 11 returned 22 kg of lunar sample, 40% of which was divided into 1500 samples and sent to principal investigators. This caused one investigator to declare that "We have samples coming out of our ears!"²¹ In this light it is sobering to be shown a text book example that effort alone will not keep man at the pinnacle of achievement. Observe and compare Figs 3 and 4. For the sake of mankind and his continuity in our troubled environment and short projected existence, it is essential that man urgently acquires accurate analytical data. Some 60 elements

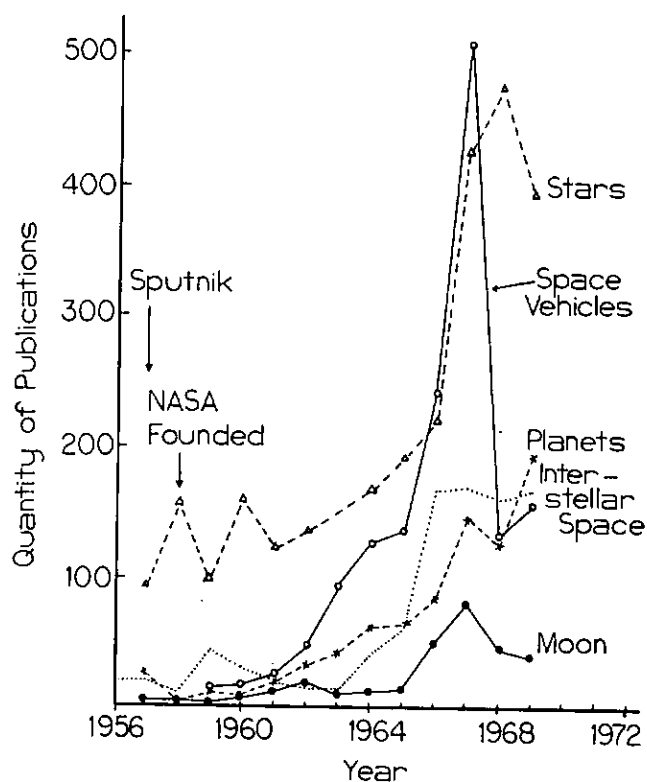


Fig. 3—NASA, the Spur to Research (ref. 22).

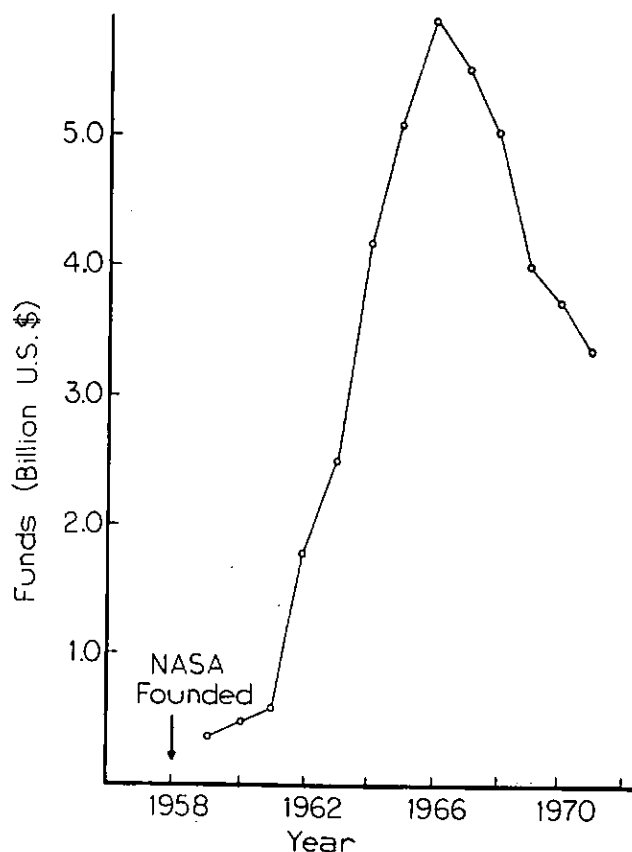


Fig. 4—The NASA budget (ref. 22) cf Fig. 5.

are found in mammalian tissues²². How many are essential? How many are adventitious? How are they distributed and how utilized? Pb, Cd, Sn, are necessary but their function is undetermined. Co is essential to vitamin B₁₂ synthesis and Se in vitamin E production; Zn associates with prostate phenomena, Mo is needed for the mammalian utilization of Cu. How limited is our knowledge! Thus not only do we need to know what happens extra-terrestrially, but how and where the elements occur in the soil, water and air about us, in flora and fauna, in the things we eat and use, in man himself and particularly how they dispose him to his end.

Table 1—Comparison of X-ray Fluorescence and Electron Microprobe Methods (From Ref. 17)

| Method | XRF | EMP |
|---------------------------------|--------------------|---------------------|
| Lowest Atomic Number Accessible | 9 (Fluorine) | 5 (Boron) |
| Precision for Major elements | 1% | 3-5% |
| Relative Detectability | 1 ppm | 100 ppm |
| Absolute Detectability | 10 ⁻⁸ g | 10 ⁻¹⁴ g |
| Cost (Approximate) | \$50,000 | \$100,000 |

REFERENCES

- H. Goldwhite and R. C. Adams, *J.Chm.Ed.*, 47, 808 (1970).
- J. W. Van Spronsen, "The Periodic System of Chemical Elements", Elsevier, New York (1969).
- Meeting of the American Physical Society, Washington D.C., April 27, 1970.
- W. P. White, *J.Physic.Chem.*, 24, 393 (1920).
- W. Forman and H. Keyzer, Thermal Analysis Literature Survey, unpublished work.
- N. B. Hannay, "Solid State Chemistry", Prentice-Hall, Englewood Cliffs, New Jersey (1967).
- H. Keyzer and W. Schneider, Polarography Literature Survey, unpublished work.
- T. M. Florence, *Proc. R.A.C.I.*, 37, 261 (1970).
- E. Pungor, *Anal.Chem.*, 39, 28A (1967).
- M. Mascini and A. Liberti, *Anal.Chim.Acta.*, 47, 339 (1969).
- H. Keyzer, A. Rembaum and R. F. Landel, "Polymeric Organic Halogen Salts", Patent application, California Institute of Technology (1971).
- H. Keyzer, unpublished work.
- A. Walsh, *Spectrochim.Acta.*, 7, 108 (1955); *J. New Zealand Inst. Chem.*, 30, 7 (1966); "Advances in Spectroscopy", Vol. II, Thompson, H. W., Ed., Interscience, New York (1961).
- W. Slavin, "Atomic Absorption Spectroscopy", Interscience, New York (1968).
- J. Aggett, New Zealand Institute of Chemistry Conference, Victoria University of Wellington, August 24, 1972.
- A. N. Zaidel and E. P. Korennoi, *Opt.Spectry*, 10, 299 (1961); *Zadovsk Lab.*, 29, 1449 (1963).
- S. Siggia, "Survey of Analytical Chemistry", McGraw-Hill, New York (1968).
- Private Communication, D. Gollnick, Department of Physics, California State University, Los Angeles (1971).
- D. A. Skoog, and D. M. West, "Principles of Instrumental Analysis", Holt, Rinehart and Winston, New York (1971).
- J. S. Whittick, R. F. Muraca and L. A. Cavanagh, *Analytical Chemistry Instrumentation*, National Aeronautics and Space Administration, Special Publication 5083, Washington (1966).
- K. M. Reese, *J.Anal.Chem.*, 42 (6), 27A (1970).
- H. Keyzer and V. Kubo, unpublished work based on Chemical Abstracts.
- H. J. M. Bowen, "Trace Elements in Biochemistry", Academic Press, London (1966); D. R. Williams, "The Metals of Life", Van Nostrand Reinhold, London (1971).

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Duties will include the setting up of laboratory services, analyses of boiler water, fuel, lubricating oils, sea water etc., corrosion monitoring and pollution surveys. The Senior Chemist will head a team of assistants who will carry out this work and other duties associated with water treatment works.

In addition to the salary quoted, there are extra benefits, including free family passages, children's school passages, paid leave, children's educational allowances, subsidised accomodation, free medical attention, income tax at low local rates and a terminal gratuity of 25 percent. Appointment will be on agreement for 2½ years.

Please apply to Hong Kong Appointments Officer, British High Comission,
P. O. Box 1047, Wellington, giving brief details of qualifications and experience.

BRANCH NEWS

Auckland

Professor R. E. F. Mathews, Professor of Cell Biology in the University of Auckland has been elected a Fellow of the Royal Society of London.

Mr A. H. Lewin has been appointed a director of Cadbury Schweppes Hudson Ltd., with particular responsibility for the Papakura biscuit factory and the potato crisp operations of the company. He is currently President of the N.Z. Institute of Food Science and Technology.

Mr P. L. Chappell, General Manager, N.Z. Starch Ltd., Auckland, has been responsible for the building and commissioning of a plant for the manufacturing of glucose from maize starch. The cost of this plant, which is now in production, approached \$1m; because of corrosion problems at high temperatures much of it is constructed of titanium.

Dr E. G. Bollard, FRSNZ, has been appointed Director of the Plant Diseases Division, D.S.I.R., Mt. Albert. Dr J. D. Atkinson has retired.

Dr D. A. Heatherbell also of the Plant Diseases Division will shortly be going overseas to visit fruit research establishments abroad. He will be attending the Congress of the International Union of Food Science and Technology (IUFOST) at Madrid in September.

The Auckland Branch of the N.Z. Institute of Food Science & Technology, after canvassing a number of firms in the food industry, has set up a fund to assist staff and students at Massey University in obtaining equipment for research. This fund has been named the Brooker Fund in honour of S. G. Brooker, first Chairman of the Branch and a past President of the N.Z.I.C.

Wellington

D.S.I.R.—Chemistry Division

Dr H. P. Rothbaum left in April on a trip to the U.S.A., England, Italy, France and Israel where he will investigate mineral extraction processes.

Mr G. Down leaves for England in June in order to study for his Ph.D. At the University of Bristol he will investigate some aspects of plant hormone chemistry under the supervision of Dr J. MacMillan.

Ms C. Brewer, who has a B.Sc. (Hons.) degree in Biochemistry from the University of Surrey, has joined the Forensic Section. She was formerly with the Haematology Department of St George's Medical School, London, and will help further the work of Chemistry Division on the grouping of blood stains.

Institute of Nuclear Sciences

Dr J. R. Hulston briefly visited laboratories in Europe and America in March to study recent developments in the instrumentation of isotope mass spectrometers. This trip precedes the purchase of a solid source mass spectrometer for the Institute in the coming year.

Dr C. J. Adams is at present spending 6 months at Leeds University where he is studying recent developments in geo-chronological techniques.

Soil Bureau

Dr K. R. Tate recently returned to Soil Bureau after spending a year at the Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, where he worked on aspects of the origin and function of organic matter in soils.

Mr A. Metson attended the symposium "Sulphur in Australasian Agriculture" at A.N.U., Canberra, in February.

Victoria University of Wellington— Chemistry Department

Professor Duncan will be on leave until 15/6/74; Professor Tomlinson is acting Head of Department in his absence.

Dr A. F. M. Barton has been appointed to the staff of the School of Mathematical and Physical Sciences, Murdoch University, Perth, Western Australia, as senior physical chemist.

Dr R. J. Speedy has been appointed to a temporary lectureship until the end of 1974.

The Department of University Extension is running a series of seminars on "Chemistry and the Community" on Saturdays, 22nd June, 27th July, 24th August and 21st September from 9 a.m.-12 noon. Topics to be discussed will include the chemistry of clays and glazes, the chemistry of garden nutrients, common household chemicals, corrosion, polymers, glasses, liquid crystals, colour chemistry, luminescent devices, the hydrogen-based economy, and alternative sources of energy.

The annual course offered by the Faculty of Science's Analytical Facility was held on Wednesday, 20th March. The programme included lectures on atomic absorption and X-ray fluorescence, as well as special lectures on sampling procedures and the electron microprobe. Professor W. E. Harvey discussed mass spectrometry with special reference to the g.l.c.-m.s.-data-processing equipment recently ordered by the Facility. The course was attended by 45 people representing different Departments within the University, D.S.I.R., Wellington Hospital and Industry.

Institute prizes for 1973 have been awarded to Miss M. R. Blakely, Miss C. M. Todd and Miss L. Coleman; it is noted with a certain anxiety that in recent years young ladies have been monopolising these prizes.

Manawatu

The April meeting of the Branch was addressed by Dr T. D. Thomas on "Lactic Acid Bacteria: Cornerstone of one of New Zealand's Major Industries."

Mr R. Chittenden has been appointed to the Branch Committee as a replacement for Mr G. M. Ryburn. Mr Chittenden is Production Manager at Unilever N.Z. Ltd., Palmerston North.

D.S.I.R., Applied Biochemistry Division

Dr R. W. Bailey has been appointed Director of the Applied Biochemistry Division of the D.S.I.R. in succession to Dr G. W. Butler, who recently became deputy Director-General of the Department.

Dr Bailey has been leader of the Division's carbohydrate group for the past several years. His work on carbohydrates in pasture plants and the ruminant digestive system has contributed to the Division's general studies of pasture quality, animal nutrition, and bloat. Recently he has been concerned also with studies of carbohydrates in seaweed and wood wastes, and in the interdepartmental investigation of kikyuu poisoning in Northland.

Born in Nelson in 1923, Dr Bailey graduated M.Sc. with honours in Chemistry at Canterbury University in 1944;

Canterbury

On April 2, Dr P. K. Foster addressed the Branch on the subject "Management in Industry and Research."

This year's Chemistry in Action lecture to senior school pupils was attended by over 200 6th and 7th Formers. Professor Tomlinson of Victoria University, spoke on "Chemistry, Electricity and Energy."

The topic for the Teachers Evening held on April 29 was "What do Chemists do all day." Mr Dennis Hogan of the Chemistry Division of DSIR described aspects of the water analysis, and of the background of the people engaged in this work. Dr W. S. Simpson and Mr D. B. Early of the Wool Research Organisation, described the activities of chemists engaged in developing wools modified by polymer deposition.

On May 6, Dr S. Woodhead spoke to the Christchurch Biochemical Society on the subject of the biochemistry of phenylalanine ammonia lyase.

Lincoln College

Michael Wilson who has recently completed studies towards a Ph.D. at Auckland University, has been appointed as Lecturer in Chemistry.

worked for some years in research units of the Department of Agriculture; completed his Ph.D. in carbohydrate chemistry at Birmingham University in 1955; and joined the then Plant Chemistry Division of the D.S.I.R. in Palmerston North in 1958. He was elected Fellow of the Royal Society of New Zealand in 1969 and of the Institute of Chemistry in 1962.

Massey University

Professor R. L. Scott, Chairman, Department of Chemistry, University of California, Los Angeles, visited the Department of Chemistry, Biochemistry and Biophysics. He is an authority on the theory of liquids and liquid mixtures.

Dr K. W. Jolley has returned from a trip to Japan where he was investigating recent developments over the Fourier Transform N.M.R. machine on order for Massey.

Industry

Mr G. M. Ryburn has moved to Auckland. He was General Production Manager at Unilever's ice cream factories at Palmerston North and Papatoteo and has taken up a similar position in Auckland. He was Chairman of the Manawatu Branch last year.

Wool Research Organisation

Dr W. S. Simpson who is Section Leader in the Wool Science section left on May 17 for visits to Fiji, Japan, Europe and the United Kingdom, where he will be engaged in discussions on research and development activities relevant to the interests of the Organisation, before returning to New Zealand at the end of June.

Christchurch Hospital

Dr Michael Lever has joined the Department of Clinical Biochemistry. He will be working on the application of fluorimetric techniques in an Autoanalyser.

John Harman is in London at Newcross Hospital doing toxicology studies on a Churchill Fellowship. He will be spending some time in Cleveland before returning to New Zealand.

DSIR Chemistry Division

Miss J. B. Ross retired from a career in chemistry with DSIR on May 8. Miss Ross completed her studies at Canterbury College in 1937, graduating MSc. 2nd Class Honours. Her first position was with Davis Gelatine Ltd. in Christchurch. In May 1946, she joined the Coal Section of Dominion Laboratory, under W. G. Hughson, working on calorific values, sulphur determinations and mine airs. In 1950/51 she expanded her interest in gas

analysis at the British Coal Utilisation Research Association, and sulphur in fuels at the Gas Research Laboratory in Dorset. Miss Ross applied gas chromatography to the study of natural gas samples, including Kapuni gas which was discovered in September 1959. In 1963-64 her interest in toxic gas analysis took her to the Gas Chromatography section of the DSIR, Warren Spring Laboratory at Stevenage. In 1970 Miss Ross transferred to Christchurch, where, in addition to periodic gas investigations she developed an interest in food analysis.

Otago

The chairman, Mr J. L. Grigg spoke at the March meeting on the subject of 'Molybdenum in Plant and Animal Nutrition'.

At a special meeting to which local industrial personnel were invited, Mr J. Gilmour, Director of the Testing Laboratory Council of New Zealand (TELARC) discussed the background to the setting up of this organisation and its aims, methods and scope.

The national president, Dr P. Foster, spoke to the branch at two meetings on the 18th April concerning the topics "Technician membership of the Institute of Chemistry" and "Management in Production and Research".

Chemistry Department

Dr R. A. J. Smith recently spent a week in Tokyo, Japan at the invitation of JEOL (Japan) to inspect and assess their developments in Fourier Transform NMR spectrometers.

Dr R. Colton, Reader in Inorganic Chemistry, University of Melbourne, and at present on sabbatical leave in the Chemistry Department, Canterbury University, visited the department for two days in April and during this time presented a seminar on the topic of halide and carbonyl chemistry of heavy transition metals.

Professor R. L. Scott, Professor of Chemistry, University of California and a former Mellor Visiting Professor in the Otago Chemistry Department, revisited the department on the 8-10th May on his way to the RACI 5th National Convention in Canberra. During this time he gave a seminar on the topic 'Simple analytic equations of state for gas mixtures'.

A number of staff attended a recent meeting of all university personnel interested in assisting in environmental investigations. This was organised by Mr A. G. Fricker who is Coordinator of the Otago University Technical, Advisory and Consulting Service.

Biochemistry Department

The department was shocked at the sudden death of Dr Jan Nielsen on 8th March of this year.

University of Canterbury

Dr A. G. Williamson of the Department of Chemical Engineering has been appointed to a Chair within the Department. Professor Williamson graduated from Canterbury University College in 1954, and has held positions at Reading University and the University of Otago. He joined the staff of the Department of Chemical Engineering at the University of Canterbury in 1967. His research interests are in the thermodynamics and statistical mechanics of solutions and in the thermodynamics of membrane processes. Professor Williamson has played an active part in the affairs of the Canterbury Branch of the Institute being Chairman and Delegate to Council in 1972.

Dr C. R. Slack from the Plant Physiology Division of D.S.I.R., Palmerston North, visited the department in April and gave a seminar on the topic "The C-4 pathway of photosynthesis—a current view".

Professor P. Berquist from the Cell Biology Department, University of Auckland, also made a visit in early May and gave a seminar on 'Mutations preventing Episome Replication in *E. coli*'.

Dr G. Bailey has returned from a trip to the U.S.A. where he presented a paper to the 3rd International Conference on Isoenzymes held at Yale University, 18-20th April, 1974. During his trip he also visited a number of biochemistry departments and assessed availability of post doctoral positions and observed current research in protein chemistry.

Dr M. R. Grigor has joined the department as a lecturer. Dr Grigor undertook a B.Sc. (Hons.) in Chemistry at Canterbury University and then moved to the MRC Nutrition Project at Otago University where he completed his Ph.D. In 1971-72 he undertook post doctoral research with Dr F. Snyder, Medical Division, Oak Ridge Associated Universities, Tennessee on the topic of lipid metabolism in mammalian systems.

Pharmacology Department

The Otago Pharmacological Association entertained Professor C. Dollery, Professor of Clinical Pharmacology, Postgraduate Medical School, University of London, while he was on a recent visit sponsored by the MRC. During his stay a seminar was arranged on the topic 'Catechol amines'.

Pharmacy Department

Mr W. H. Thomas has left on sabbatical leave. Rather than spending his time at one institution he is visiting a large number of pharmaceutical manufacturers in the United Kingdom and the Continent where he will be observing the manufacture of sterile solutions for intravenous fluids.

**PROGRAMME 1974 N.Z.I.C. CONFERENCE, AUCKLAND
CHEMISTRY SERVES SOCIETY**

| | | | |
|---|---|--|---|
| Monday, 26 August Registration, 9.00-10.30 a.m. | Tuesday, 27 August Easterfield Address, 9.00-10.30 a.m. | Wednesday, 28 August Biochemistry Guest Lecturer, Dr W. H. Elliott, University of Adelaide, 9.00-10.30 a.m. | Thursday, 29 August Visiting Lecturer, Dr H. J. Moore, Hannah Research Institute, Industrial Group |
| TEA 10.30-11.00 a.m. | | | |
| Registration, 11.00-12.30 p.m. Biochemistry / Group | Fats Symposium: - Inorganic; Physical Groups | Professionalism Symposium: Chromatography; Physical Groups | Social Responsibility Symposium: Chromatography Group |
| LUNCH 12.30-2.00 p.m. | | | |
| Opening Ceremony, 2.00 p.m. | Fats Symposium and Specialist Analytical; Chromatography; Chem. Educ.; Organic Groups | Professionalism Symposium Biochemistry; Chem. Educ.; Organic; Electrochemistry; Inorganic Groups | Social Resp. Symposium: Biochemistry; Chem. Educ.; Electrochemistry; Inorganic; Organic Groups |
| TEA 3.00-3.30 p.m. | | | |
| Analytical; Biochemistry; Industrial; Inorganic; Organic; Physical Groups 3.30-5.30 p.m. | Fats Symposium: Analytical; Biochemistry; Chem. Educ.; Organic; Physical Groups 4.00-5.00 p.m. | Professionalism Symposium: Biochemistry; Electrochemistry; Inorganic; Organic; Chem. Educ.; Groups | Social Resp. Symposium: Biochemistry; Industrial; Organic Groups. Winning Student Paper 5.00-5.30 I.U.P.A.C. 5.30-6.00 p.m. |
| TEA 3.30-4.00 p.m. | | | |
| Social Hour, 5.30-6.30 p.m. | Vice-Chancellor's Buffet, 5.45 p.m. | N.Z.I.C. Annual General Meeting, 5.00 p.m. | Social Hour, 6.00-7.30 p.m. |
| Guest Lecturer, Dr A. Walsh, C.S.I.R.O., 8.00 p.m. | Mercury Theatre, 8.00 p.m. | Presidential Address, Dr P. K. Foster, 8.00 p.m. | Conference Dinner, 7.30 p.m. |

SYMPOSIA PROGRAMMES

Science and Technology of Fats

Chairman: Dr F. B. Shorland, Victoria University, Wellington.

Symposium Plenary Lectures

- 11.00-11.45 "THE CHEMISTRY OF FATS"
Mr S. G. Brooker, Abels Ltd., Auckland.
- 11.45-12.30 "THE BIOCHEMISTRY OF FATS"
Dr J. C. Hawke, Massey University.

Invited Speakers

- 2.00- 2.30 "MODIFICATION OF THE PHYSICAL PROPERTIES OF BUTTER"
Mr R. S. Jebson, N.Z.D.R.I., Palmerston North.
- 2.30- 3.00 Mr R. Norris, N.Z.D.R.I., Palmerston North.
- 3.00- 3.30 "EXTRACTION OF OIL SEEDS USING THE EXPELLER PROCESS"
Mr A. J. D. Robb, Fletcher Industries Ltd., Dunedin.
- 4.00- 4.30 "FATS AND THE PHYSICIAN"
Assoc. Professor P. J. Scott, Medical School, Auckland University.
- 4.30- 5.00 "POST-PRANDIAL THOUGHTS ON FATS"
Assoc. Professor Marion Robinson, University of Otago.

Professionalism

Chairman: Dr D. R. Llewellyn, Vice-Chancellor,

Symposium Plenary Lectures

- 11.00-11.35 "FACTORS INFLUENCING SCIENTIFIC POLICY-MAKING IN GOVERNMENT"
Dr A. T. Johns, Director-General, Ministry of Agriculture & Fisheries.
- 11.15-12.30 Professor A. M. Kennedy, University of Canterbury.

Invited Speakers

- 2.00- 2.45 "CHEMISTRY: TUBS, TEST TUBES & THEORY—A PROFESSIONAL MIX"
Mr J. G. Fletcher, A.T.I.
- 2.45- 3.30 "SOME THOUGHTS ON THE ORGANIZATION OF SCIENCE IN N.Z."
Dr F. B. Shorland, Victoria University Wellington.

4.00- 4.30 "CHEMISTRY & FOOD PRODUCTION IN THE FUTURE"
Mr D. J. Higgins, Kempthorne Prosser & Co. Ltd., Dunedin.

4.30- 5.00 "SOLIDARITY IN A SCIENCE-BASED PROFESSION"
Assoc. Professor G. A. Wright, University of Auckland.

Social Responsibility

Chairman: Professor J. Vaughan, University of Canterbury.

Symposium Plenary Lectures

- 11.00-11.45 "THE OPTIONS OF MANKIND'S FUTURE"
Professor A. T. Wilson, University of Waikato.
- 11.45-12.30 "WHERE THE BUCK STOPS"
Dr R. B. Mann, University of Auckland.

Invited Speakers

- 2.00- 2.45 "CHEMISTRY AND CONSERVATION"
Dr A. F. Wilson, N.Z. Forest Products, Tokoroa.
- 2.45- 3.30 "THE DISPOSAL OF INDUSTRIAL WASTES"
Dr M. E. U. Taylor, Auckland Regional Authority.
- 4.00- 4.30 "THE QUALITY OF SCIENTIFIC EVIDENCE"
Dr T. J. Sprott, T. J. Sprott & Associates, Auckland.
- 4.30- 5.00 "CHEMICAL INFORMATION"
Dr W. S. Metcalfe, University of Canterbury.

Guest Lectures

- "ATOMIC ABSORPTION SPECTROSCOPY" by Dr A. Walsh, F.R.S., F.A.A.
- "THE VECTORIAL TRANSPORT OF PROTEINS ACROSS CELL MEMBRANES" by Professor W. H. Elliott, F.A.A.
- "ASPECTS OF LIPID METABOLISM IN THE RUMINANT ANIMAL" by Dr J. H. Moore, F.R.I.C.

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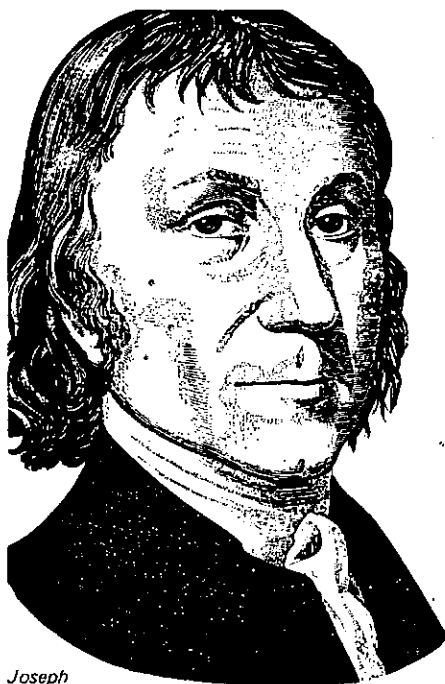
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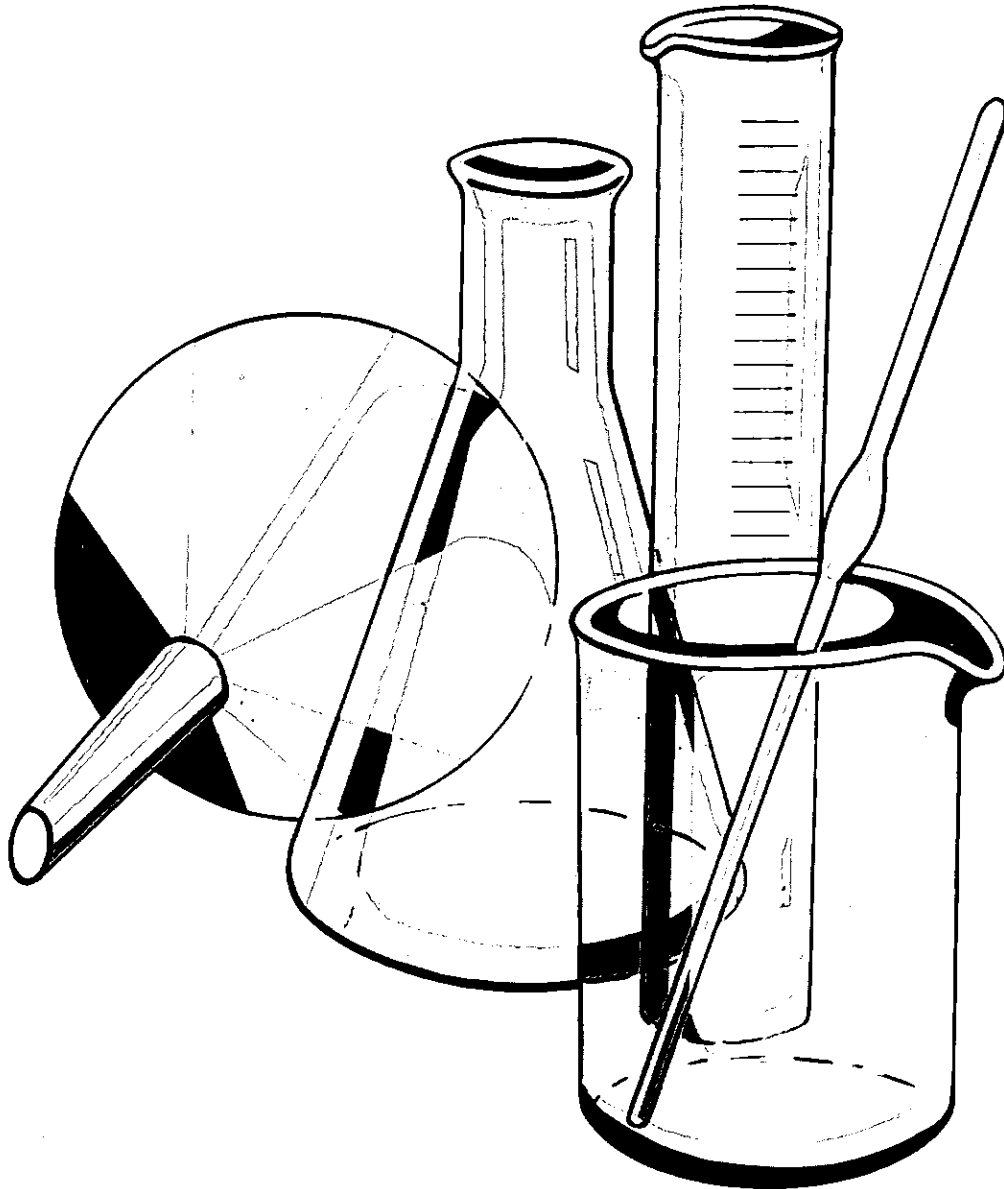
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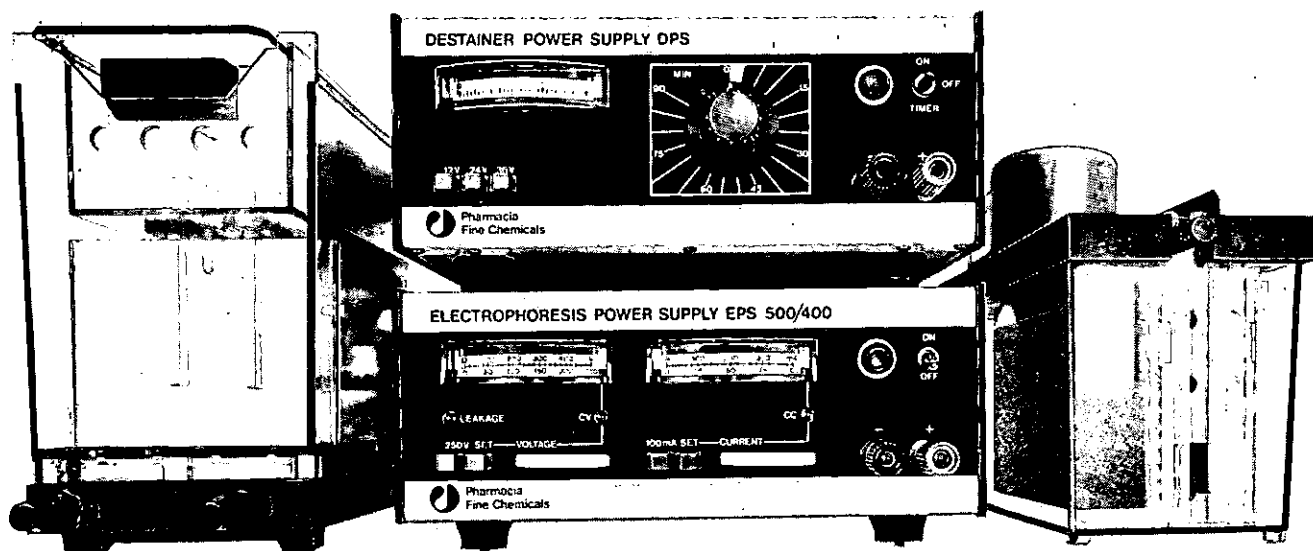
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