

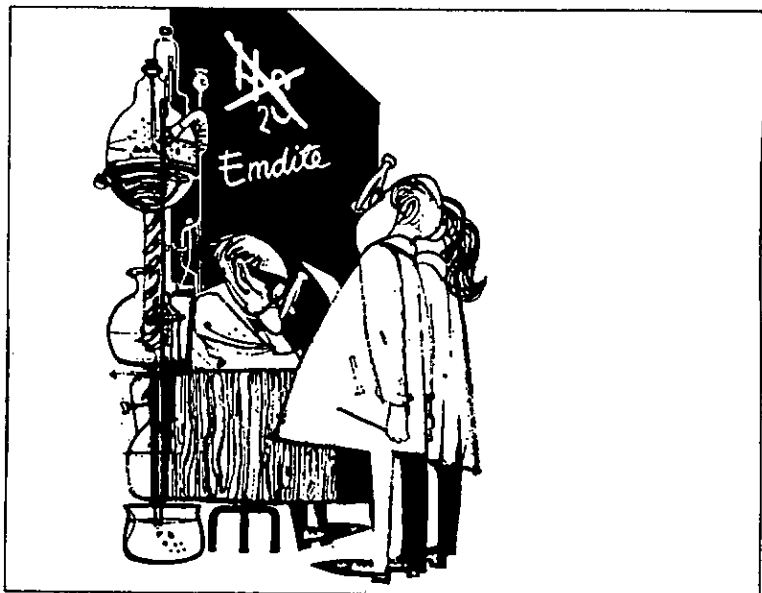
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1. Hart, K.K., Hill, A.G. and Savage, B., J. Roy. Inst. Chem., 1964, 418-23 (reprints are available on request).

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JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

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JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

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EDITORIAL

The year 1966 should see new developments for the N.Z.I.C. In his presidential address Professor Siemon made a case for the involvement of chemists in the community. The Minister for Science pleaded for enlightenment and explanation of those extraordinary titles of the papers given at conference. "Have you told the people what you are doing?" he asked. "Have you told them what these papers mean?" The A.G.M. asked Council to look into the matter of public relations, and Council is doing so.

The Institute has done an excellent job in recent years in its relations with sixth form chemistry students. This is a good foundation for the future, but is very limited. It does nothing for the non-chemistry students, and nothing for the adult members of the community who are chemically illiterate.

Picture the plight of the common man, average age forty, with average schooling to school certificate level. His schooling was limited by the times, not by his intelligence. His present world is quite unrelated to the one when he did his test-tube experiments in school. Twenty-five years later he lives in a different world. The pressures are different, the demands are different. As a member of a democratic community he is expected to think sensibly about problems of fluoridation, insecticides, feeding the world's population, selective weedkillers, and overpopulation; he is buffeted by arguments about the despoiling of the countryside for the production of power as at Aratiatia and aluminium at Manapouri; he is annoyed by having to eat poor quality bread and can't see why the baker can't do better; he sees huge expenditure on rocket research and space travel while we have not yet learned to cope with what we have on earth; he feels threatened by hormones, laser beams, atomic energy, electronics, genes and automation, and is surrounded by TV, plastic bags and cellotape. What connection have these with iron filings and sulphur in a test-tube?

Chemistry is largely responsible for the development of this modern world, changing it beyond his understanding. No real effort has been made to help him gain any understanding. And lack of understanding leads to fear and mistrust. Is it any wonder that he is confused by science? That the word science is often a nasty word? That he does not trust scientists and thinks of them as eggheads who are not human?

Chemists have a responsibility to the community not only to explain their work, but to help educate the adult population to appreciate the part science plays in modern life.

CANTERBURY HONOUR FOR CHEMIST



The University of Canterbury has appointed to its first personal chair Dr. L. F. Phillips, Branch Editor of the Canterbury Branch, N.Z.I.C. Dr. Phillips will take up his new position in February 1966, continuing to work in the Chemistry Department in his special field of upper atmosphere chemistry for which he has an international reputation.

Dr. Phillips is a Canterbury graduate who won a Shell Commonwealth scholarship, then a Ph.D. at Cambridge University. He held a post-doctoral fellowship at McGill University, Canada, before returning to Canterbury to join the staff of the Chemistry Department. The Royal Institute of Chemistry awarded him the Easterfield Medal, 1965, for outstanding quality and originality in chemical research. The United States Air Force Office of Scientific Research has awarded him in the last few years more than 50,000 dollars in grants. The New Zealand Universities' Research Committee has granted him nearly £4,000 since 1962.

Dr. Phillips was born in 1935, is married and has one child. One of his hobbies is demonstrated below.

THE SLAVE

My parents both objected strongly
When I said my sole ambition
Was to be a poet, wrongly
Had I hoped for their auspicion,
Hence my uninspired position.

"Modern poets" said they, "sever
Life from hope, ignore tradition,
Are really too profound, and never
Use their terms with true precision—
Here, read this on nuclear fission."

So you see me in the white
Ascetic garb of the technician,
Never hear me speak of light,
It's quanta now, and my volition
Suffers sore from inhibition.

Thus it is I often mutter
(While the teeth in geared collision
Earn for me my bread and butter)
Words that pierce with steeled incision.
Do not view me with suspicion.

L.F.P.

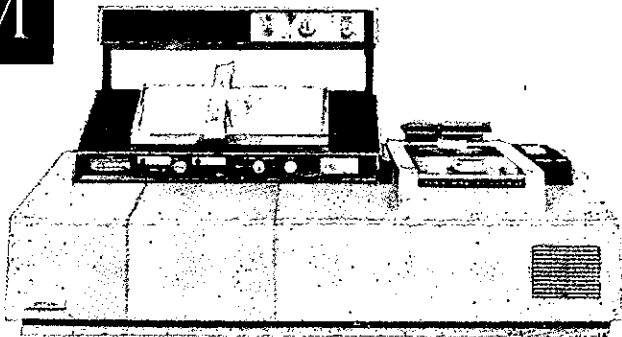
If Canty's given you a chair
You surely must have shown a flair
For quanta, upper atmospheric.
May your jam be now poetic.

Ed.

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Spectrophotometer

For faster and even more efficient operation Unicam offer a set of automation accessories.

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Facilities are provided for the automatic interchange of up to 4 sample and 4 reference cells, automatic re-cycling over any preselected wavelength range and automatic recording at predetermined time intervals.

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SP.800A—Double beam recording ultraviolet and visible spectrophotometer with linear wavelength scale 190-700 $m\mu$. Complete with tungsten and deuterium lamps, automatic lamp interchange, fused silica prism in thermostatted monochromator, automatic slit programme, attenuator combs giving linear absorbance scale 0-2A, photomultiplier detector and automatic gain control, integral flat bed recorder, holders for standard cells in both normal and second sample position with two 10 mm. stoppered silica cells with case, instruction manual, 300 sheets chart paper, ring binder for completed spectra, test filters for wavelength and stray light, two absorbance scale attenuators, set of fuses and one spare pen.

SP.800B—As SP.800A but with linear wavelength scale 190-850 $m\mu$ and special red sensitive photomultiplier.

SP.800C—As SP.800A but with linear wavelength scale 52,500 cm^{-1} to 14,000 cm^{-1} .

SP.800D—As SP.800A but with linear wave-number scale 52,500 cm^{-1} to 11,500 cm^{-1} and special red sensitive photomultiplier.

This elegantly styled instrument automatically records absorbance against wavelength or wave number throughout the ultraviolet and visible region of the spectrum. One of four different models may be selected to suit the applications in hand.

Performance

Wavelength (SP.800A, SP.800B)

Accuracy $\pm 0.4 m\mu$ at 200 and 250 $m\mu$,
 $\pm 2 m\mu$ at 500 $m\mu$.

Reproducibility $\pm 0.1 m\mu$ at 200 and 250 $m\mu$, $\pm 1 m\mu$ at 500 $m\mu$.

Wavenumber (SP.800C, SP.800D)

Accuracy $\pm 40 cm^{-1}$ at 50,000 cm^{-1} ,
 $\pm 80 cm^{-1}$ at 20,000 cm^{-1} .

Reproducibility $\pm 15 cm^{-1}$ throughout range.

Photometric

Accuracy $\pm 0.02A$

Reproducibility $\pm 0.005A$

Absorbance Zero Flatness

$\pm 0.01A$ (adjustable)

Resolution

190-370 $m\mu$, 0.1-0.4 $m\mu$; 370-700 $m\mu$, 0.4-2.0 $m\mu$.

Stray Light Less than 1% at 200 $m\mu$.

Sample Compartment

9.4 \times 4.9 \times 4.8 inches high.

24.0 \times 11.0 \times 12.5 cm high.

Overall Instrument

Dimensions

37 \times 23 \times 15½ inches, 211 lb weight.

94 \times 59 \times 40 cm, 96 kg weight.

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SOME RECENT ADVANCES IN ATOMIC ABSORPTION SPECTROSCOPY

by

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*Division of Chemical Physics, Commonwealth Scientific and Industrial
Research Organisation, Melbourne, Australia*

Introduction

During the past two years there has been a dramatic increase in the application of atomic absorption spectroscopy to chemical analysis, and there are now more than a thousand laboratories throughout the world carrying out analysis by this method. This number is expected to increase by a further thousand within the next twelve months. It might be presumed that this remarkable upsurge in the demand for atomic absorption equipment has resulted from some notable recent advances in technique, but this is by no means the case. The instrumentation and methods now used are basically similar to those described several years ago but it is only recently that commercial equipment which fully exploits these known techniques has become available. The demand for such equipment is now so large that the doubt, suspicion and disbelief which greeted the early papers on atomic absorption methods of chemical analysis has completely disappeared. Indeed, the buoyant claims now being made by some enthusiastic users of such methods are read with awe by at least one of the authors of these papers!

The widespread adoption of atomic absorption spectrophotometry to chemical analysis has naturally resulted in the publication of a vast amount of information regarding specific analyses and this is of the utmost value to the analyst. However, excellent summaries of such work are readily available and will therefore not be discussed in this paper, which will be restricted to an account of investigations carried out by our group in Melbourne since the last Colloquium Spectroscopicum Internationale. In confining my remarks to the work of this particular group it is, of course, by no means intended to imply that advances being made elsewhere are not of more significance, but rather that it seems preferable to discuss only those projects about which I have some first-hand information, and accounts of which have either not yet been published or have only been published within the past few weeks.

Production of Atomic Vapour

It is convenient to discuss our work in relation to the three main components of a typical atomic absorption spectrophotometer, viz: the flame for converting some of the sample solution into an atomic vapour; the atomic spectral lamp which emits a spectrum of the element to be determined; and the equipment for the isolation and measurement of the intensity of one or more of the resonance lines emitted by the lamp.

It has been known for many years that the central problem in atomic absorption methods of chemical analysis is that of converting the sample for analysis into an atomic vapour. Thus, in 1957, Russell, Shelton and Walsh¹ stated: "At the present state of its development, by far the most serious difficulty in the atomic absorption method is due to the difficulties in atomising various elements. For example, highly oxidisable elements such as aluminium, silicon, hafnium, etc., are not atomised in the air/coal-gas flame used in this work and thus are not detectable in absorption. Similarly many other elements will not be completely atomised, thus decreasing the sensitivity and providing a serious obstacle to accurate absolute analysis. In this respect the cyanogen/oxygen flame, which has a temperature of about 4,600°C and has recently been applied by Baker and Vallee to emission methods, may prove to be extremely valuable. This problem of complete atomisation of the sample seems to us to be the outstanding problem at the present time." Commenting on this last statement Allan², in 1961, remarked: "It still is." In considering this problem of the production of atomic vapour it cannot be stressed too strongly that the inability to produce a detectable concentration of free atoms for the highly oxidisable elements is not the only, nor indeed the major problem. More important is the fact³ that "other elements are only partially atomised thus resulting in loss in sensitivity and the possibility of chemical interference due to variation of the degree of atomisation of one element with the concentration of other elements, radicals or compounds in the solution". It will be obvious that all chemical interferences would be eliminated if the sample were completely atomised.

Until recently the progress made in producing improved flames has been so discouraging that completely new lines of attack have been proposed. Lvov⁴ has developed an arc furnace, and Gatehouse and Walsh⁵ have reported on a cathodic sputtering technique. Both these approaches are so much more inconvenient than flames that neither can be regarded as pro-

viding a satisfactory basis for a generally suitable method of analysis.

Fortunately in 1962 Fassel *et al.*^{6, 7} showed that much improved atomisation of several metals could be obtained by direct injection of the solution, usually in organic solvents, into fuel-rich oxyacetylene flames. These results were confirmed by Slavin and Manning⁸ and by Dowling, Chakrabarti, and Lyles^{9, 10}. This type of flame, however, is unpleasantly noisy and Amos and Thomas¹¹ developed a pre-mixed flame of acetylene and enriched air (50 per cent oxygen) which successfully atomised aluminium and other metals. However, this flame is potentially dangerous since the high burning velocity results in a danger of flash-back if the fuel flow is reduced too much.

TABLE I
CHARACTERISTICS OF FLAMES SUITABLE FOR ATOMIC
ABSORPTION SPECTROSCOPY

Gas Mixture	Maximum flame speed, cm sec. ⁻¹	Maximum temperature, °C
Air/propane	82	1,925
Air/acetylene	160	2,300
50% oxygen—50%nitrogen/acetylene	640	2,815
Oxygen/acetylene	1,130	3,050
Nitrous oxide/acetylene	180	2,955
Nitric oxide/acetylene	90	3,080
Nitrogen dioxide/acetylene	160	?

Following a consideration of the characteristics, listed in Table I, of various flames which could prove suitable for atomic absorption spectroscopy, my colleague Dr. J. B. Willis¹² investigated the nitrous oxide/acetylene flame, since this gives the same temperature as the enriched air/acetylene flame but has a much lower burning velocity. Allan¹³, at the Third Australian Spectroscopy Conference in 1961, had previously reported on some experiments with a nitrous oxide/acetylene flame but his preliminary results were discouraging and he did not pursue his investigations further.¹⁴

Amos and Willis summarised their conclusions as follows: "We believe that either the 50 per cent oxygen-50 per cent nitrogen/acetylene or the nitrous oxide/acetylene flame affords a simple and effective means of determining the refractory-oxide metals with good sensitivity, using a standard atomic absorption instrument. We feel that, though the two flames are almost identical in performance, the nitrous oxide/acetylene one is

better suited for commercial application on account of its greater safety margin, and because nitrous oxide, unlike special oxygen/nitrogen mixtures, is readily available commercially."

Table II gives the results obtained by Amos and Willis,¹⁵ who also reported that both flames eliminate some chemical interference such as that of aluminium on magnesium and of phosphorus on calcium. For example, aluminium/magnesium ratios as high as 1,000 had no effect on magnesium absorption, whilst calcium absorption was not affected by a concentration of phosphorus two hundred times greater than that of the calcium.

TABLE II
SENSITIVITIES USING ENRICHED AIR/ACETYLENE
AND NITROUS OXIDE/ACETYLENE FLAMES

Metal	Wavelength, Å	N ₂ -O ₂ -C ₂ H ₂ (Amos)	N ₂ O-C ₂ H ₂ (Willis)
Al	3,093	1	1
B	2,497	100	100
	2,498	—	50
Be	2,349	0.03	0.03
Hf	3,072	20	—
Nb	3,580	30	—
Si	2,516	10	5
Ta	2,715	33	—
Ti	3,643	4	3.5
V	3,184	4	1.5
W	2,944	—	12
	2,947	17	18
Zr	3,601	9	—

— Not yet measured.

It must not, of course, be expected that these new flames will completely eliminate chemical interferences in all analyses, but they undoubtedly represent a major advance in the whole technique of atomic absorption analysis, since they greatly extend its scope and increase its accuracy with only a minor modification to existing equipment, i.e. replacement of the burner with one designed for use with high temperature flames.

As far as the analysis of solutions is concerned, it is indeed becoming increasingly difficult to visualise a method of producing an atomic vapour which is as simple, rapid, convenient, and effective as the flames now available. However, it is salutary to bear in mind that existing techniques are restricted to the

analysis of solutions and there is as yet no satisfactory method in sight for the direct analysis of solids.

Atomic Spectral Lamps

Atomic spectral lamps used in atomic absorption spectroscopy must emit spectra of stable intensity, free from background, and in which the resonance lines have half-widths of the order of 0.01Å. The most widely used lamp is the sealed-off hollow-cathode tube, in which the cathode consists of, or contains, the element whose spectrum it is required to emit. Lamps for some forty elements are now available and these now satisfactorily fulfil many of the requirements for atomic absorption spectroscopy.

In operation, the current in conventional hollow-cathode lamps is usually adjusted to the maximum consistent with the line-width requirements and is not, in general, increased beyond the point where the line-width shows a significant increase as indicated by peak absorption measurements. Experience with these lamps indicates that as far as the resonance lines are concerned, the onset of broadening is in most cases due to self-absorption or self-reversal. If such broadening is to be prevented, the vapour pressure of the metal atoms liberated from the cathode must be kept low. Thus there does not appear to be much possibility of achieving much increase in intensity of the resonance lines emitted by a hollow-cathode lamp if the line-width is not to be increased by absorption broadening.

Sullivan and Walsh¹⁶ have stated that the basic limitations of the conventional hollow-cathode lamp arise from the fact that the one electrical discharge is used to produce the required atomic vapour by cathodic sputtering and also to excite this atomic vapour. Consequently, any attempt to increase the excitation, as for example by means of a higher current or lower pressure of the filler gas, will inevitably be accompanied by a higher pressure of metal vapour with the resultant danger of absorption broadening. This limitation is surmounted in the high-intensity hollow-cathode lamp¹⁶ by using one electrical discharge to produce by cathodic sputtering the optimum pressure of atomic vapour, and a second electrical discharge electrically isolated from the first, to produce the necessary excitation. In this manner, the excitation and therefore the intensity, can be increased without increasing the vapour pressure. Thus there is no accompanying increase in self-absorption or self-reversal.

A typical electrode assembly is shown in Fig. I, in which A and C are the anode and cathode respectively of the primary discharge, whilst BB are the booster electrodes of the auxiliary discharge. To ensure that the boosting discharge passes essentially through the atomic vapour produced by the primary discharge, BB are surrounded by shields SS in which are openings OO. These ensure that the boosting discharge passes through the region at the mouth of and in the interior of the hollow-cathode, and effectively excites in that region the atomic vapour produced from the walls of the hollow-cathode by cathodic sputtering. Whilst the auxiliary electrodes can be of metals such as tungsten or nickel, oxide-coated cathodes, electrically heated if necessary, are preferable since they lower the voltage across the boosting discharge. This avoids excessive heating and difficulties due to cathodic sputtering from the auxiliary electrodes. An interesting feature of these lamps is that atoms in the negative glow of the hollow-cathode discharge are excited in the positive column of the subsidiary discharge.

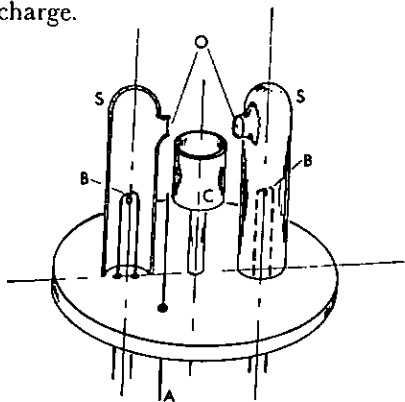


FIG. 1

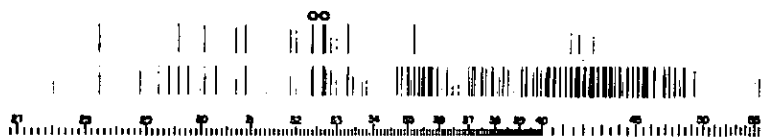


FIG. 2



FIG. 3

Typical spectra obtained with such lamps are shown in Figs. 2 and 3. In each case there is a remarkable increase in intensity of the resonance lines and it can be demonstrated by peak absorption measurements that this increase is obtained without any increase in line width. Increases in intensity by factors of thirty to one hundred have been obtained for a wide range of metals.

A vitally important property of these lamps is that the boosting discharge is essentially of low energy (about 20V) and consequently results in virtually no additional excitation of the rare gas or of spectral lines of the metal ions. This is of great value in cases where it is difficult to isolate the required resonance line from neighbouring ion lines. Examples of this are in the determination of nickel and cobalt where interfering lines result in curvature of the calibration curves, shown in Figs. 4 and 5, when using a conventional hollow cathode lamp. When a high-intensity lamp is used the resonance line of the neutral atom is enhanced with respect to the interfering ion line, and a linear calibration curve results. The new lamps are also particularly valuable in the determination of elements such as iron, for which a small spectral slit-width must be used to isolate the most sensitive line, thus resulting in a poor signal/noise ratio when using conventional hollow-cathode lamps.

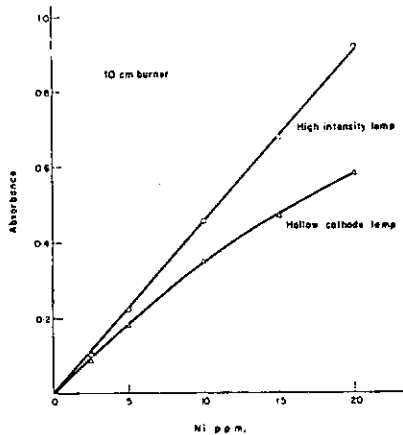


FIG. 4

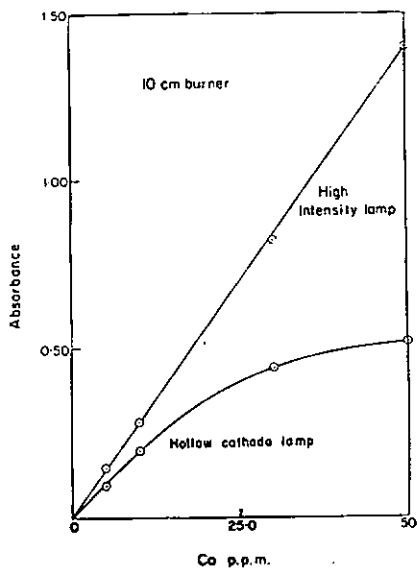


FIG. 5

A detailed study of the application of these high-intensity lamps to atomic absorption analysis for a wide range of metals has not yet been made, but their high-intensity, stability, and enhancement of resonance lines with respect to other lines seem certain to prove of value in many analyses. However, possibly a more important feature of the high-intensity lamps is that these have made possible two new approaches to the isolation of the strongest absorption line. These are described below.

Isolation and Detection of Resonance Lines

An essential feature of an atomic absorption spectrophotometer is the equipment for isolating and measuring the intensity of one or more of the lines in the spectrum emitted by the atomic spectral lamp. The line selected is usually that which shows the highest sensitivity in absorption. Such lines are usually those which involve a transition between an excited state and the ground state of the neutral atom, and are commonly referred to as resonance lines. Strictly, the term should be restricted to transitions to or from an upper level which can undergo a transition to or from no lower level except the ground state.

(i) Selective Modulation of Resonance Lines

A well-known method of "isolating" a given region of a spectrum is by means of periodic interposition at a given frequency of an absorbing medium in a light beam, thus producing a modulated signal at all wavelengths which lie within the region of absorption of the medium. By using an A.C. detection system tuned to the same frequency one obtains an output-signal vs wave-length curve corresponding to the absorption spectrum. This principle is widely used in infra-red gas analysers. Alkemade and Milatz^{17,18} have shown that the same principle can be used to isolate a given atomic resonance line by using as the selective absorber a flame into which is sprayed the salt of the metal whose resonance line is to be isolated. This system involves periodic moving of components, such as rotating or oscillating mirrors, to obtain periodic absorption by the flame.

Bowman, Sullivan and Walsh¹⁹ have recently developed an alternative method of modulating atomic resonance lines which uses a sputtering cell²⁰ to produce the necessary atomic vapour. The principle of the method is shown in Fig. 6. Light from an unmodulated atomic spectral lamp is passed along the axis of a discharge tube, the open-ended hollow-cathode of which consists of the element whose resonance line(s) it is required to

SELECTIVE MODULATION OF RESONANCE LINES
SCHEMATIC DIAGRAM



FIG. 6

isolate. The power-supply to the discharge is modulated and thus the concentration of atomic vapour within the cathode is pulsating. This provides modulation of the resonance lines emitted by the lamp. No other lines are modulated since they are not absorbed by the vapour in the sputtering cell. The emerging light beam is passed through a monochromator or filter and the tuned detection system only gives an output signal for those lines which have been modulated.

In general this modulation technique cannot be operated successfully without a monochromator or filter, since the output signal due to non-resonance lines emitted by the sputtering cell and the noise due to unmodulated radiation from the spectral lamp would be prohibitive. It is also essential to ensure that any signal due to resonance lines emitted by the sputtering cell is negligible compared with the modulated signal it is desired to measure. This condition is readily fulfilled when a high-intensity hollow-cathode lamp of the type described earlier is used as the light source. If necessary, the modulator can be incorporated in the same envelope, which is the same size and shape as that of a conventional hollow-cathode lamp.

The performance of this selective modulation system is illustrated by Fig. 7 which shows the spectra obtained from a nickel high-intensity hollow-cathode lamp, and from the same lamp when used in conjunction with a nickel modulator of the type described. It can be seen that even with a spectral band-pass of 7\AA the modulation technique completely isolated the resonance line as 2320.06\AA . By correct choice of the current through the modulating discharge, any modulated signal due to the resonance line at 2321.38\AA can be reduced to a negligible value.

Fig. 8 shows the calibration curves obtained using this modulation technique with an atomic absorption spectrophotometer

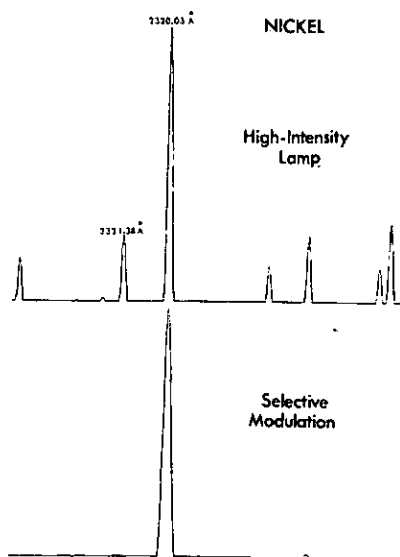


FIG. 7

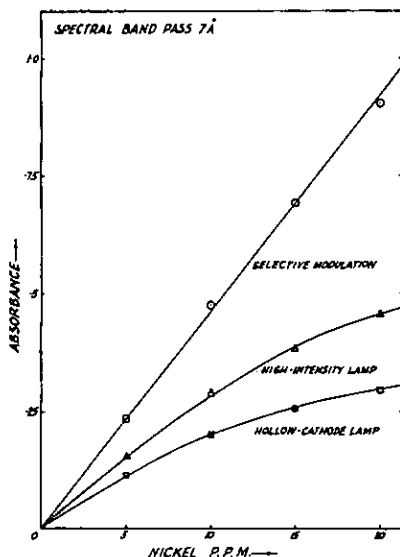


FIG. 8

having a spectral band-pass of 7Å. The slope of the calibration curve obtained using a high-intensity lamp is steeper than that obtained with a hollow-cathode lamp since the former preferentially excites the resonance lines, but the curvature indicates that at the band-pass used there is some interference from non-resonance lines. The linear calibration curve obtained with the selective modulation technique shows that the atomic resonance line has been completely isolated.

Bowman, Sullivan and Walsh¹⁹ have reported similar results for the determination of iron and cobalt, and state that one of the main advantages of the modulation technique is that it permits the use of monochromators of low resolution for the isolation of atomic resonance lines. An associated advantage is that the requirements for the stability of the wave-length-setting of the monochromator can be correspondingly relaxed.

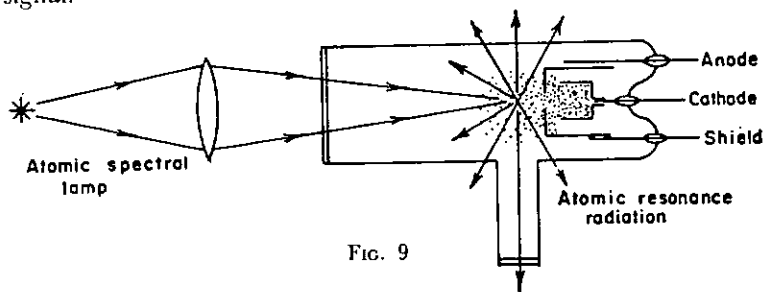
(ii) Resonance Monochromators

When radiation is absorbed by an atomic vapour the absorbed energy is usually converted to thermal energy. However, if the vapour is under the appropriate conditions of pressure and temperature, some of this absorbed radiation may be re-emitted. This "resonance radiation" was first detected in 1905 by R. W. Wood, whose early work clearly showed that its intensity was

proportional to the intensity of the resonance lines in the exciting radiation. It has thus been known for a long time that in principle, resonance radiation provides a convenient method of measuring the intensity of the resonance lines in a spectrum. Until recently, however, studies of resonance radiation have been largely restricted to metals having an appreciable vapour pressure at below the softening point of glass or silica, since only for these metals were satisfactory light sources available.

In 1959 Russell and Walsh²⁰ published spectra of the resonance radiation from copper and chromium vapour produced by cathodic sputtering and stated: "The possibility suggests itself of using an atomic vapour produced in this manner as a means of isolating a signal due to resonance lines, in just the same way as in the well-known method of isolating the $\text{Hg } 2537\text{\AA}$ line by illuminating mercury vapour by the mercury spectrum, the re-emitted radiation then consisting primarily of the 2537\AA resonance line. Such a method would provide a resolution of the order of 0.01\AA and would be highly specific. The fact that the resonance radiation is weak is compensated to some extent by being able to avoid the limitations imposed by the usual slit and entrance pupil of a monochromator."

Sullivan and Walsh²¹ have recently reported on some results obtained using the experimental arrangement illustrated schematically in Fig. 9. Radiation from a high-intensity hollow-cathode lamp falls on a resonance lamp in which the atomic vapour is produced by cathodic sputtering by a conventional hollow-cathode discharge. Some of the resonance radiation, which is emitted in all directions, is collected through a side arm and is detected by a photomultiplier. The power supply to the illuminating lamp is modulated whilst that to the resonance lamp is unmodulated. Thus by use of an A.C. detection system any radiation emitted directly by the resonance lamp does not produce an output signal.



This arrangement provides an extremely effective method of producing resonance radiation, even from metals of high melting point, since the cathodic sputtering phenomena occurs even at room temperature. It was shown that by interposing a flame between the two lamps it was possible to determine magnesium and copper by atomic absorption measurements, without the necessity for a conventional monochromator. For magnesium the calibration curve, shown in Fig. 10, was identical with that obtained for the same flame by the usual type of atomic absorption spectrophotometer, as shown in Fig. 11, the resonance radiation consists

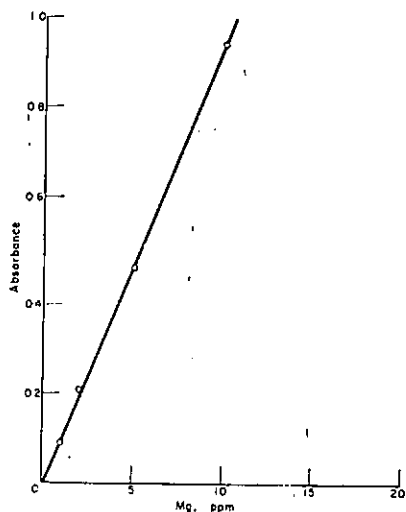


FIG. 10

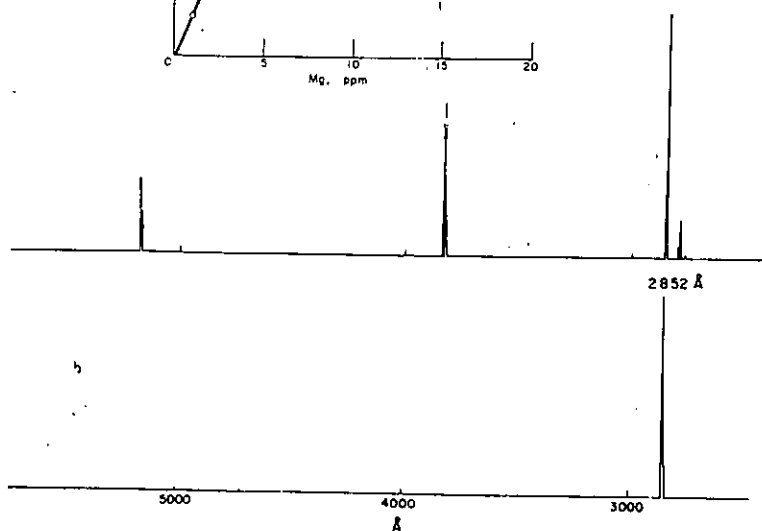


FIG. 11

of only one line at 2852\AA . This situation is expected to be duplicated by other elements in Group II. For copper the sensitivity was slightly less than when using a conventional monochromator and the calibration became curved as shown in Fig. 12, since the resonance radiation consists of the two copper resonance lines 3247\AA , as shown in Fig. 13. The curvature results from the 2 : 1 ratio of the oscillator strengths of the two lines, and will no doubt occur for all the elements in Group I.

Preliminary measurements on other metals such as nickel, chromium, zinc and cadmium indicate that this technique will be applicable to all the elements which can be determined by atomic absorption spectroscopy.

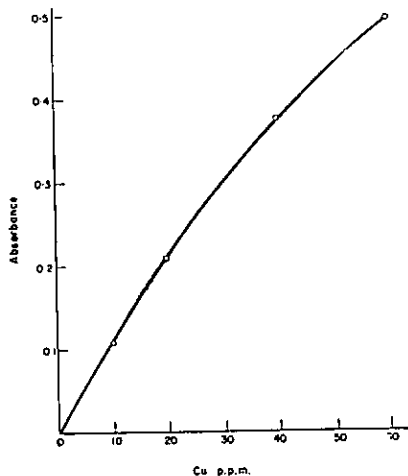


FIG. 12

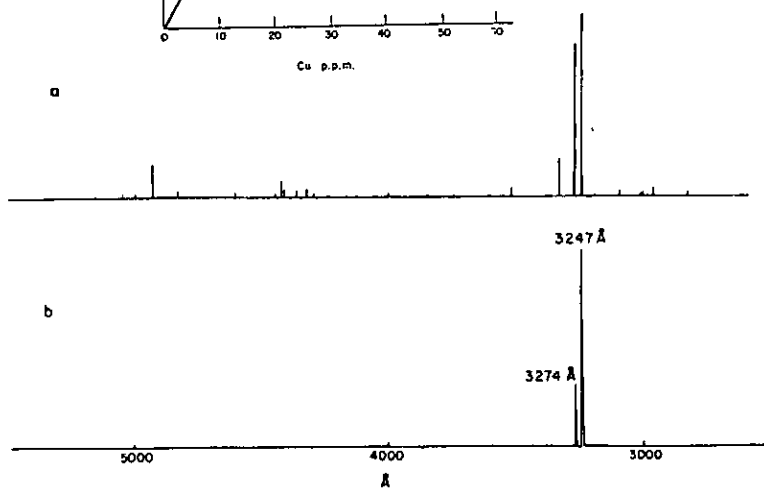


FIG. 13

The performance of such methods depends on the complexity of the absorption spectrum of a particular element, since the resonance radiation is produced by several lines of different intensity, each of which is converted to resonance radiation with an efficiency depending on the absorption of the vapour at the corresponding wavelength.

These results have been so promising that we²² have been encouraged to investigate much simpler systems. In particular we have found that magnesium and calcium can be determined perfectly satisfactorily by using conventional hollow-cathode lamps as light sources and thermally produced vapours as detectors. There now seems little doubt that atomic absorption spectrophotometers incorporating resonance monochromators will be widely used in the near future. They offer particularly interesting possibilities for the construction of simple polychromators for the simultaneous determination of several elements.

Conclusion

After a period of some ten years during which the instrumentation for atomic absorption spectroscopy has remained basically unchanged, there have recently been several major advances in technique which greatly broaden the scope of atomic absorption methods, and which seem likely to result in completely new approaches to the design of atomic absorption spectrophotometers. It seems certain that in the near future these recent advances will result in an even more rapid expansion of the application of atomic absorption methods of chemical analysis. They may also make a useful contribution to other branches of spectroscopy.

Acknowledgement

The advances reported above have been largely due to the work of my colleagues J. V. Sullivan and J. B. Willis, to whom I am grateful for much valuable advice and assistance in the preparation of this paper.

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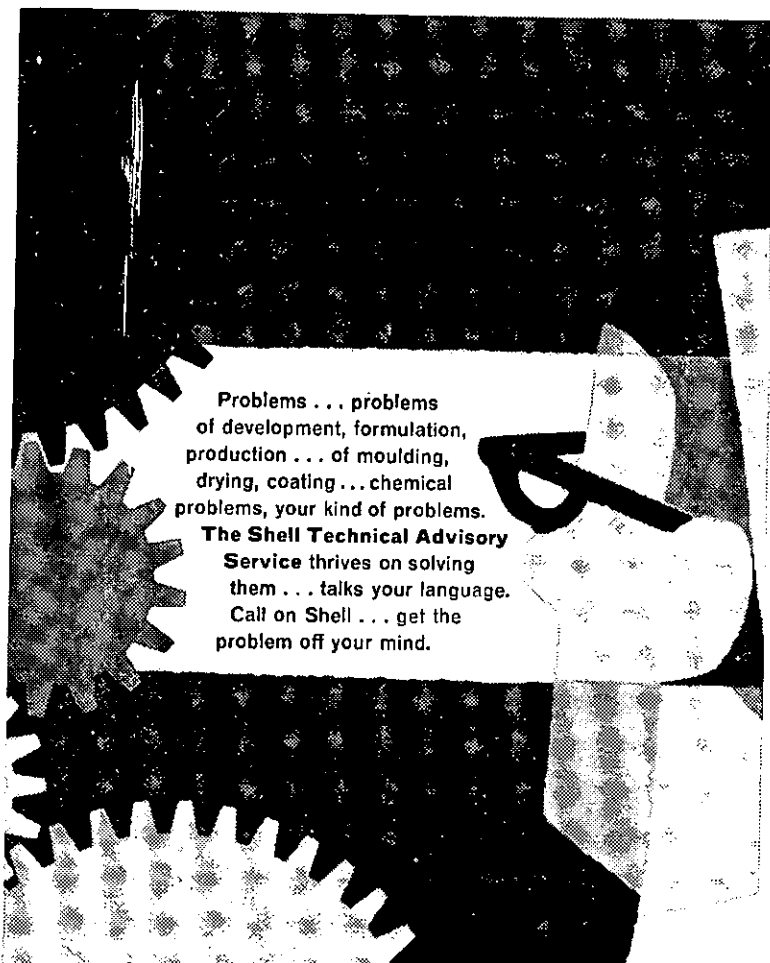
INSTITUTE PRIZES

Members are reminded that the closing date for entries for the three prizes is April 15.

The Chemical Essay Prize; offered for an essay or review paper of not more than 5,000 words, on any aspect of chemical science. The prize is open to all members and local members. The value of the prize in recent years has been £25.

The I.C.I. Prize; this prize of £50 and a medallion has been donated by Imperial Chemical Industries (N.Z.) Ltd. It is awarded for "some major contribution to some branch of chemical science, this contribution to be judged by research work published or accepted for publication during the five years immediately preceding April 15 in the year of the award". Members may apply for the award or they may be nominated by Branch Committees or by individual members.

The Morcam Green, Edwards Prize; this is of the value of £25 and is donated by Messrs. H. H. Edwards and Morcam Green. It is offered "for the encouragement of original work by young chemists in pure and applied chemistry, with emphasis on applied chemistry". Applicants must be below the age of 35 years on June 1 in the year of the award. The candidate is assessed on published work or on a process he has designed or developed, or the product he produces.



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ADVISORY SERVICE

GAS-PHASE KINETICS OF SIMPLE RADICALS AND MOLECULES

Easterfield Address 1965

by

L. F. PHILLIPS

Chemistry Department, University of Canterbury

This paper is concerned essentially with work that has been done at Canterbury University during the past three and a half years. We have been studying gas-phase reactions of simple species, preferably containing not more than three atoms, one of the reactants being usually atomic hydrogen, nitrogen or oxygen. The primary aim of these studies has been to sort out the fine details of such simple reactions, and especially of very fast ones, and to measure the efficiencies of processes by which excess electronic or vibrational energy is transferred from one species to another. This has led in turn to the study of reactions which produce species with excess vibrational or electronic energy, and so to studies of chemiluminescence. There is some hope that this part of kinetics may ultimately become a branch of quantum mechanics, but at present there is a great need for more experimental data. Reactions of this sort have some practical importance in connection with combustion processes, and with the chemistry of the upper atmosphere. They are also relevant to processes occurring in other energy-rich environments, such as plasmas and explosions.

Some typical experimental results are given below, in the form of rate constants for very fast reactions (1-4) and for typical energy transfer processes (5-8).

- (1) $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$; $k = 2.5 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{sec}^{-1}$
- (2) $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$; $k = 2.2 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{sec}^{-1}$
- (3) $\text{N} + \text{NO}_2 \rightarrow \text{products}$; $k = 1.85 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{sec}^{-1}$
- (4) $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$; $k = 4.8 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{sec}^{-1}$
- (5) $\text{N}_2 (v \geq 4) + \text{O}_3 \rightarrow \text{N}_2 + \text{O}_2 + \text{O}$; $k = 5 \times 10^{-13} \text{ cm}^3\text{molecule}^{-1}\text{sec}^{-1}$

FOOTNOTE: This article is based on the address given by Dr. L. F. Phillips at the Institute of Chemistry Conference, Dunedin, 1965, after he had received the Easterfield Medal 1965, awarded by the Royal Institute of Chemistry.

- (6) $N_2(^3\Sigma_u^+) + I_2 \rightarrow N_2(^1\Sigma_g^+) + I_2^*$; $k = 8 \times 10^{-14}$
 $\text{cm}^2\text{molecule}^{-1}\text{sec}^{-1}$
- (7) $T1 + H + Cl \rightarrow T1^* + HCl$; $k = 2 \times 10^{-32}$
 $\text{cm}^6\text{molecule}^{-2}\text{sec}^{-1}$
- (8) $T1I + N + N \rightarrow T1^* + I + N_2$; $k = 4 \times 10^{-29}$
 $\text{cm}^6\text{molecule}^{-2}\text{sec}^{-1}$

In units of molecules per cc per second, the theoretical collision frequency is about 10^{10} , so that the first four reactions above must occur on practically every collision. Reaction (3) is interesting in that it gives rise to a variety of products and will be considered in detail later. The bimolecular energy transfer processes (5) and (6) are slow by comparison, but (5) is nevertheless remarkably efficient for a reaction that involves turning vibrational energy into electronic energy. The rate constant for process (7) is of normal magnitude for a termolecular reaction, but that for process (8) is two orders of magnitude too large for a simple 3-body process. We are therefore led to postulate a mechanism for (8) by which an excited intermediate nitrogen molecule, whose concentration is proportional to $[N]^2$, transfers its energy to the thallos iodide molecule in a secondary process.

Three different methods have been used to study these reactions. In the first, which is to be described by Mr. McEwan in a subsequent paper, $H_2/N_2/O_2$ mixtures are burnt at atmospheric pressure and the progress of reactions involving H, OH and O in the hot gases is followed by observing light emission or absorption at different distances along the flame (Fig. 1). The observed effects are generally produced by reactions of flame radicals with trace additives such as the alkali metals, the halogens, or oxides of nitrogen.

In the second method atoms are produced by partial dissociation of H_2 , N_2 or O_2 in a microwave discharge at a low pressure (ca. 1 torr). This is done in a flow system (Fig. 2), and other reactants are added to the gas stream as it leaves the microwave discharge. The progress of chemiluminescent reactions is then followed by observing the light emission, either with a spectrometer, or with a photomultiplier plus appropriate filters.

The third method (Fig. 3) is similar to the second, except that the reaction mixture is analysed by direct sampling into a mass spectrometer. This is the method which is used for very fast reactions, where the concentration of reactants is kept very low (10^{-4} torr) in order that the reaction may be prolonged for a few milliseconds.

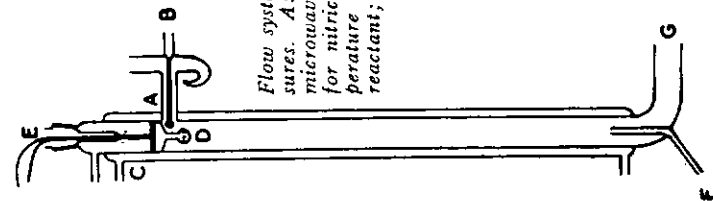


FIG. 1
Flow system for reactions at low pressures. A: Inlet tube for gas from microwave discharge; B: Inlet tube for nitric oxide; C: Jacket for temperature control; D: Inlet jet for reactant; E: Tube leading to vacuum pump.

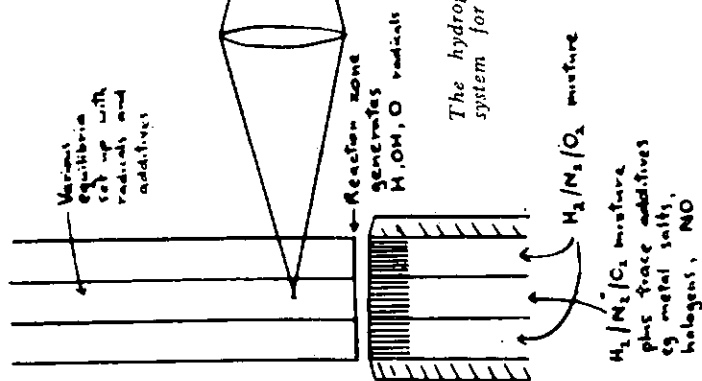


FIG. 2
The hydrogen-air flame as a flow system for studying fast reactions.

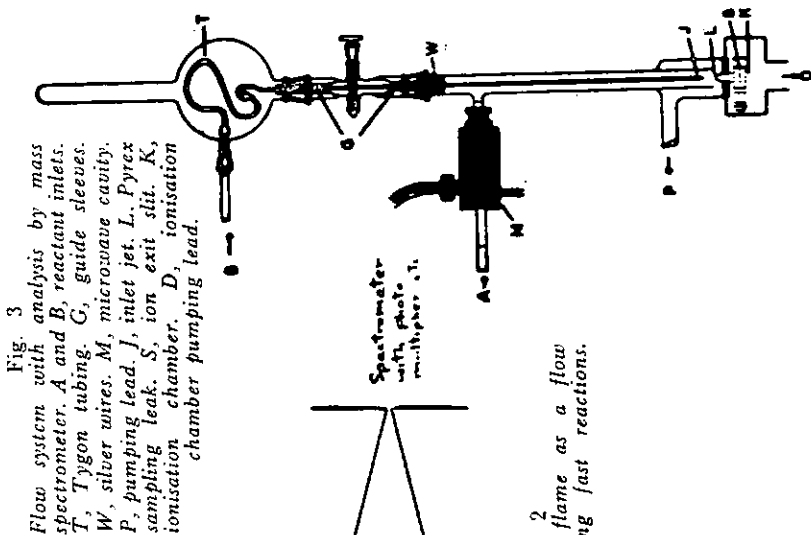
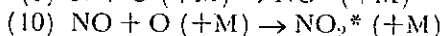
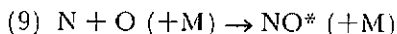


FIG. 3
Flow system with analysis by mass spectrometer. A and B, reactant inlets. T, Tygon tubing. G, guide sleeves. W, silver wires. M, microwave cavity. P, pumping lead. J, inlet jet. L, Pyrex sampling leak. S, ion exit slit. K, ionisation chamber. D, ionisation chamber pumping lead.

To illustrate the second and third methods two typical reactions will be described. The first is the reaction of nitrogen atoms with iodine (a photometric study); the second is the reaction of nitrogen atoms with NO_2 (a mass spectrometric study). For both of these studies it is necessary to be able to measure the amount of atomic nitrogen in a gas stream. Fortunately a convenient and precise measure of nitrogen atom concentration can be obtained by gas-phase titration with nitric oxide. This depends on reaction (2) above, together with the following two chemiluminescent reactions:



If a small amount of nitric oxide is added to a stream of "active", i.e. discharged, nitrogen the nitric oxide is immediately converted by (2) into atomic oxygen and N_2 . Active nitrogen normally glows a bright orange-yellow, but in the presence of atomic oxygen reaction (9) occurs, thereby producing excited nitric oxide which radiates blue light, and the whole tube appears blue. (In this reaction the third body M is written in brackets because it is not established that a third body is required for the light-emitting process, as distinct from ordinary atom recombination). If, however, an excess of nitric oxide is added to the active nitrogen, then all nitrogen atoms are removed by (2) and the gas stream contains only nitric oxide and atomic oxygen. These react according to (10) and the resulting excited NO_2 molecules emit light as a greenish-white continuum. When the nitric oxide flow exactly equals the nitrogen atom flow, both atomic nitrogen and nitric oxide are removed by (2) and the gas stream contains only molecular nitrogen and oxygen atoms, which have no mechanism for emitting visible light. The reaction tube therefore appears dark. The nitrogen atom flow can thus be determined by measuring the amount of nitric oxide which is required to produce the dark "end-point" between the regions of blue and greenish-white emission.

The reaction of iodine with active nitrogen gives rise to an intense blue flame which consists of bands and continua of molecular iodine extending from about 6,000 Å in the red to 2,100 Å in the ultra-violet. The shortest wavelength emissions require an excitation energy of about 140 kcal mole⁻¹. The intensity of the blue emission is proportional to the partial pressure of iodine, but is only slightly dependent on the nitrogen atom pressure.

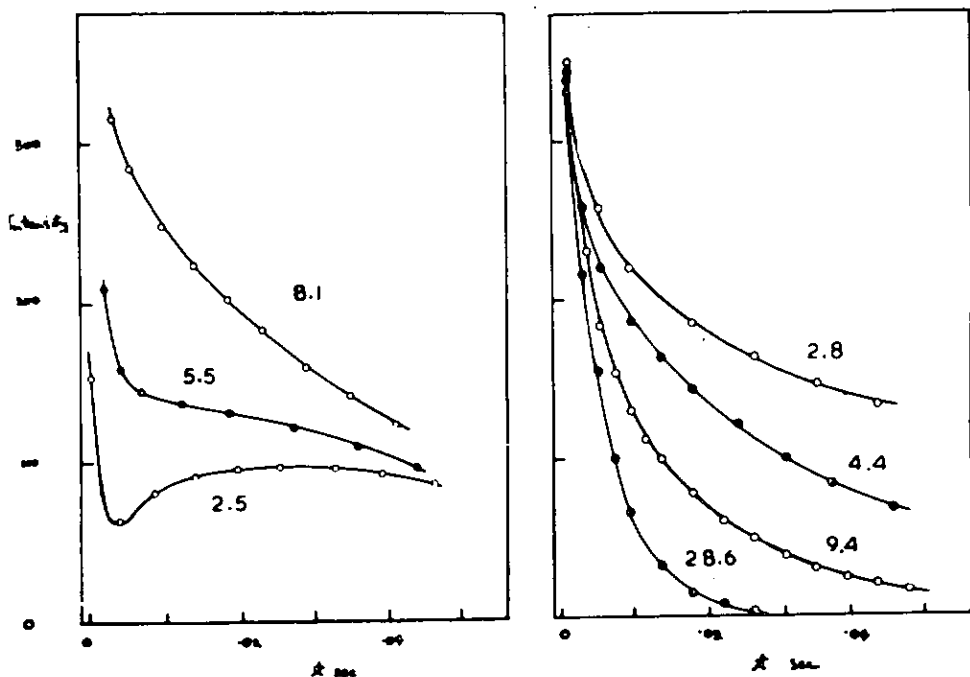
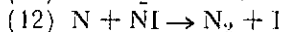
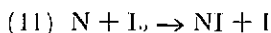


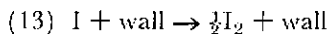
FIG. 4

Decay with time of blue iodine emission and of nitrogen afterglow in presence of iodine. Values of $10^3 \times$ iodine pressure (torr.) marked on curves.

Fig. 4 shows a comparison of the decay of intensity along the reaction tube for the nitrogen afterglow (proportional to $[N]^2$) and the blue iodine emission. It is seen that while the nitrogen atom concentration falls steadily, the iodine emission at low iodine pressures begins at a high value, then passes through a minimum followed by a maximum before falling off again. The high initial intensity can reasonably be attributed to a reaction involving iodine atoms which are produced by the reactions

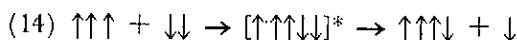


In confirmation of this the iodine emission from near the iodine inlet jet is found to vary as $[\text{I}_2]^2$. Iodine atoms are very short-lived in a glass system, being removed very efficiently by



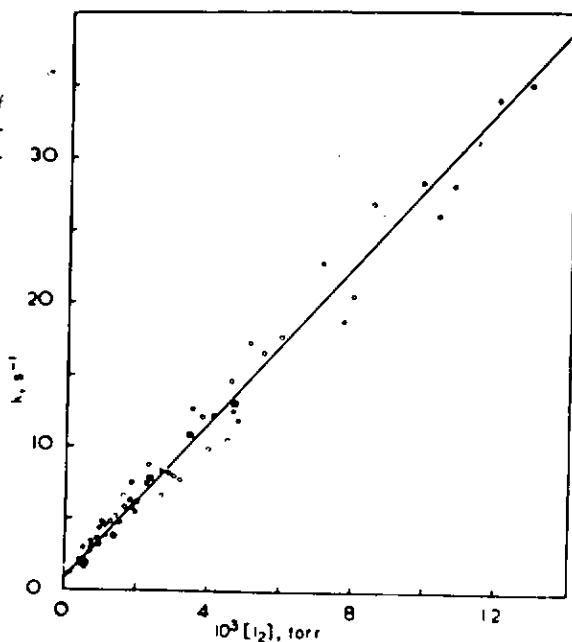
and further down the tube it can be assumed that all of the iodine present is in molecular form. The intensity maximum in this region therefore suggests that some excited species is being produced by the reaction, and that energy transfer from this species to I_2 is responsible for the blue emission in the latter part of the flame.

Now in reaction (12) the nitrogen atom, in the 4S state, has three unpaired electrons, the NI radical in the $^3\Sigma$ state has two unpaired electrons, and the iodine atom in the 2P state has one unpaired electron. This suggests that we can write



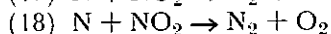
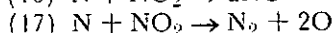
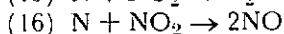
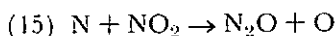
as a representation of reaction (12) in terms of electron spins, and that there is a possibility of the N_2 molecule being formed in a triplet state, i.e. with two unpaired electrons. As it happens there is a metastable triplet state of N_2 , the $A.(^3\Sigma_u^+)$ state, with an energy of 140 kcal/mole and a radiative lifetime of about one second, which neatly fits the observations described so far. The identification of this species as the excited intermediate has been largely confirmed (a) by measuring the lifetime of the blue

FIG. 5
Variation of the rate of decay of the iodine emission with iodine pressure.

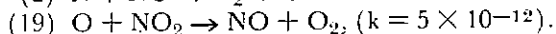
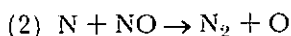


emission when no more N_2 was being formed by reaction (12), and extrapolating the results to zero iodine pressure to obtain a value of 1.1 sec for the radiative lifetime (Fig. 5), and (b) by observing a band due to the A-state in the *absorption* spectrum of the reaction flame. These conclusions have been criticised by Young (in press, Can. J. Chem.), mainly on the grounds that he has failed to observe emission bands characteristic of the $\Lambda.3\Sigma_u^+$ state from the N-I₂ flame. At this stage it appears that his criticism is not justified. We have yet to attempt to observe the emission bands themselves. Similar measurements to those with iodine have been carried out with active nitrogen and chlorine, bromine, ICl, IBr, and methyl iodide. Only ICl and IBr show evidence of the presence of an excited metastable intermediate. With both of these the reaction flame consists mainly of emission from excited I₂, rather than from the interhalogen compound.

The reaction of N with NO₂ is interesting because of the variety of products which can result from the primary reaction, viz.



Reactions (15-18) are all exothermic. Here it is required to measure both the overall rate of the primary process and the relative rates for the different primary reaction paths. The primary reaction is very rapid, and in addition there are two fast secondary reactions to be considered, namely



To measure the overall rate a small amount (ca. 10^{-5} torr) of NO₂ was introduced into a large excess (10^{-3} torr) of atomic nitrogen, and the consumption of NO₂ was monitored with the mass spectrometer. Under these conditions all NO₂ is removed by the primary reaction, and none by (19), while the effect of the other fast secondary reaction (2) is negligible. A further advantage of this method is that the ratio of peak height at mass 46 to partial pressure of NO₂ in the reaction vessel need not be known with great accuracy, because the consumption of NO₂ is essentially exponential. The result is $k_{\text{overall}} = (1.85 \pm .22) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{sec}^{-1}$.

To determine the relative contributions of the individual steps (15-18) a combined photometric and mass spectrometric method was used. When NO_2 is gradually added to active nitrogen the gas first emits blue radiation from excited NO (reaction 9) because of the simultaneous presence of nitrogen and oxygen atoms. If however, enough NO_2 is introduced to just remove all N atoms the reaction tube appears dark. This is "end-point number one". Now if further NO_2 is added, the NO produced by reaction (19) and the atomic oxygen produced in the primary step react together (reaction 10) with the emission of the familiar greenish-white continuum. If still more NO_2 is added there comes a time when all of the oxygen atoms are consumed by (19), and the reaction tube again appears dark. This is "end-point number two". Calling the relative rates of the primary steps a, b, c and d, where

$$(20) \quad a + b + c + d = 1, \text{ we have at end-point one}$$

$$(21) \quad \text{NO}_2 : \text{N} = (a + b + c + d) : (a + 3b + c + d), \text{ while at end-point two}$$

$$(22) \quad \text{NO}_2 : \text{N} = (2a + 3b + 3c + d) : (a + b + c + d)$$

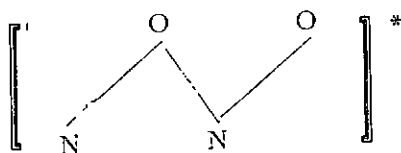
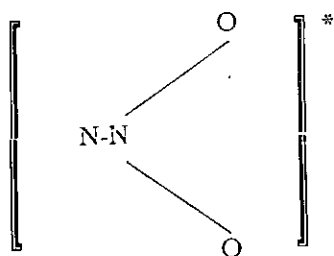
Finally, with the mass spectrometer it is possible to determine the amount of N_2O formed directly from the peak height at mass 44. (This must be done when there are no oxygen atoms about in order to avoid confusion with CO_2^+ at mass 44, which always appears when oxygen atoms are present.) The result is

$$(24) \quad a = 0.43 \pm .04$$

Experimentally it was necessary to use a photomultiplier to detect the two end-points, because at pressures low enough to ensure that the chemical reaction, rather than diffusive mixing, is rate-determining, the light emission is too weak to be monitored visually. The various amounts of NO_2 and N consumed were determined with the mass spectrometer. From the five equations (20-24) in the four unknown a, b, c and d it was possible to determine the set of self-consistent results:

$$(25) \quad a = (0.43 \pm .04), \quad b = (0.33 \pm .07), \quad c = (0.12 \pm .10), \\ d = (0.11 \pm .13).$$

This reaction presents an interesting theoretical problem, because of the need to explain why a variety of products can result from a single bimolecular collision. It seems likely that there may be two different activated complexes possible, namely



The complex I should readily decompose according to (a) or (c), and possibly (d), but it appears necessary to postulate a complex of the form II in order to explain the production of 2NO.

★ ★ ★

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SOIL RESOURCES OF TRACE ELEMENTS

by

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Chairman's Address, Waikato Branch

PART ONE

Introduction

In the long processes of evolution those animal and plant species have survived which are adapted to their environment. In New Zealand we have introduced an alien sward on which we depasture stock, again alien to the environment. There has been no long period of adjustment. The climate has favoured the newcomers. The soil, with respect to its power of supplying the minerals essential to plant and animal life, has not. The development and intensifying of primary production has indeed, and in no small measure, been a struggle against mineral deficiencies.

The Essential Mineral Elements

The essential minerals are for convenience considered in two groups—the major elements needed in relatively large amounts, and the minor, or more precisely micro-nutrient elements, none the less vital but required in “traces”. The former could loosely be described as the building blocks, e.g. bones are largely constructed of calcium and phosphorus, while the latter are concerned more with the life processes in plant and animal.

The relative proportions of the elements in lucerne hay (Rukuhia data), in milk¹ and in meat², are shown in the following tables.

I
MAJOR AND TRACE ELEMENTS IN LUCERNE HAY (ppm)

	N	K	Ca	P	S	Mg
Major	30,000	25,000	20,000	3,000	4,000	3,000
	Fe	Mn	B	Zn	Cu	Mo
Trace	145	67	45	45	11	1.5

II
MAJOR AND TRACE ELEMENTS IN MILK (ppm)

	Ca	Mg	K	Na	P	S		
Major	1300	100	1300	400	900	100		
	Zn	B	Fe	Cu	Mo	l	Mn	Co
Trace	4.00	0.75	0.45	0.10	0.06	0.05	0.025	0.0006

III
MAJOR AND TRACE ELEMENTS IN RAW BEEF RIB
EYE MUSCLE (ppm)

Major	Ca	Mg	K	Na	P		
	26	210	3,000	410	1700		
Trace	Zn	B	Fe	Cu	Mo	Mn	Co
	47	0.05	31	0.45	0.015	0.02	0.002

Note 1. (1) The use of molybdenum, the element present in smallest amount in those listed in lucerne, has had a revolutionary effect on primary production in New Zealand. The amounts previously released in the soil through heavy rates of liming, can be readily applied to hill country by air in molybdenised superphosphate.

(2) The very low trace element content of milk (apart from Zn).

(3) The low Ca level in meat, lower than Zn or Fe.

Those trace elements which have so far been proved essential to plant and/or animal life are listed in Table IV.

IV
ESSENTIAL TRACE ELEMENTS

Plants	Fe	Mn	Zn	Cu	Mo	B	(V, Co)		
Animals	Fe	Mn	Zn	Cu	Mo	I	Co	Se	(F, Br, Ba, Sr)

Skey³, Colonial Analyst, in discussing bush sickness (Tauranga disease) in 1892 wrote ". . . it would be only reasonable to suppose that any soil capable of throwing up a good bite of grass would also be capable of putting into it all those mineral ingredients that are necessary for the healthy growth of animals feeding upon it". He was not quite right. The animal and plant requirements do not exactly correspond, and in fact the answer to Skey's problem lay in a point of difference—cobalt. To meet the needs of the grazing animal, pastures must contain in addition to the elements essential for their own growth, adequate I, Co and Se. More copper is needed by the animal than by the plant. Boron as far as is known, takes no part in the life processes of the animal.

In New Zealand we rely on the legume-rhizobia association to fix atmospheric nitrogen, largely obviating the need for

nitrogenous fertilisers. The N fixation process has its own special requirements—that of Mo in greater amount than demanded by the host plant,⁴ and, a recent discovery, cobalt.^{5, 6, 7} This specific need for cobalt in the legume is paralleled by an equally specific need for it in the ruminant, namely for the synthesis of vitamin B₁₂ by the rumen micro-organisms (1, p. 124).

Vanadium has been shown to be necessary to the alga *Scenedesmus*.⁸ Underwood lists F, Br, Ba and Se as elements which can be classed as probably essential to higher animals on the basis of existing knowledge (1, p. 2).

The Trace Elements

Factors bearing on the adequacy or deficiency of the trace elements in New Zealand soils will be discussed.

(1) Hereditary deficiencies

I am much indebted in this section to Mr. Norman Wells, Soil Bureau, for information concerning total content of elements in New Zealand rocks (also see ref. 16).

The rocks or parent materials from which soils in New Zealand are derived may be considered under the heads:

Plutonic	}	Basic
Volcanic		Acidic
Metamorphic		Schist
		Gneiss
Sedimentary		Greywacke
		Sandstones
		Limestones

Minerals low in silica separate first from the magma. Trace elements, subject to certain conditions of size and valency, can substitute for the major elements in these, the magma thus becoming depleted. Siliceous minerals separating at the final stage are consequently low in most of these elements.

On this concept we would expect soils derived from basalt and andesite to be relatively rich in trace elements, and those from rhyolitic pumice and granites to be poor. In fact this is so, at least as regards total contents. Wells at the recent Science Congress listed various parent rock materials, the associated soils developing on them, and the elements in high and in low concentration in the rocks.

Yellow brown loams and brown granular clays derived from andesite and andesitic ash would be expected to be relatively high in total Co, Mn, V, Cu, Zn, Se, I, Fe but low in Cl and B.

Evidently the elements in high amount are also available, as deficiencies of Co, Cu, Se, well known in other regions, do not occur for example in the volcanic soils of Taranaki. Nor does molybdenum deficiency. Boron deficiencies are common. Red and brown loams from basalt are similarly well provided. Molybdenum responses have been noted however, despite a high level of total molybdenum. Wells suggests that the molybdenum has been trapped in the more mature stages in crystallising iron compounds and rendered unavailable.⁹

In contrast to the yellow brown loams, yellow brown pumice soils from rhyolitic ash would be expected to be low in total Co, V, Cu, Zn, B, Se, I and Fe. They are high in Cl and in some cases in Mo. Turning to agricultural experience, which depends on the availability of the elements, the result of low cobalt in herbage in the central pumice areas is well known. Responses of lucerne to boron are common. So also is a boron deficiency symptom, brown heart, in swedes. Rolt¹⁰ has found copper levels in these soils variable but many in the low-medium, and some in the low brackets. Coup at Ruakura has found low liver copper levels (private communication). The diseases associated with selenium deficiency are common through the pumice region—the main selenium responsive area in the North Island.¹¹ The situation with regard to molybdenum is variable, considerable areas of pumice land being high enough in the element to influence pasture levels and cause molybdenosis in stock.¹² The main such area, associated with exposure of a particular ash shower, is in the neighbourhood of Wairoa. In other areas molybdenum is very low and responses of clovers to the element have been obtained. Curiously enough, depressions through molybdenum application have also been noted and are hard to account for.

Granites, also siliceous and late in crystallising from the magma, are low in all trace elements, e.g. the cobalt deficiency on the Nelson granite-derived soils.

The metamorphic rocks gneiss and schist differ in that the latter has very high amounts of boron, the former very low amounts. I doubt if any land is farmed on gneiss in the remote southwest corner of New Zealand. Much farm land in Otago would be on schist-derived soils, but nevertheless subject to boron deficiency. The boron-containing mineral, tourmaline, is very resistant, and high levels in schist do not necessarily lead to available supplies in the soil. Both rocks are below average in selenium content.

About half the soils in New Zealand are derived from greywacke—"strongly indurated sandstones of different grades and mudstone, the latter represented by thick argillite beds. Conglomerates, equally indurated, are also present".¹³ The term covers a range of materials. You will recall difficulties with the foundation of the motorway in Auckland, and very recently at Whakātane. There are greywackes and greywackes. It is difficult to generalise but the trace element levels are for the most part between the acid and basic rocks, to which reference has been made. Boron is relatively high. Soils of greywacke origin have been associated with molybdenum deficiency.

The trace elements tend to be held more firmly against the leaching processes by soil clay material than the more mobile major elements, and hence parent materials have a strong influence. Nevertheless, interesting studies of the effects of the degree of weathering and leaching on the content of trace elements have been made.

Suites of soils derived from a common source material have been arranged in order of weathering and leaching. Where the parent material is low in an element, e.g. Cu, all members of the suite are low. Where high, a diminution occurs as one progresses from recent to more mature soils, and a deficiency may develop at a certain stage. All older members in the series will then be deficient. Taylor¹⁴ gives several instances with Cu as the illustrative element, while Wells has discussed copper¹⁵ and molybdenum⁹ on similar lines. The concept is held up as an example of the usefulness of soil classification in forecasting deficiencies.

Conversely, the chemical composition of soils can be useful in deciding their degree of weathering, and where they come in the series.

Watkinson¹⁷ considers that selenium as selenite is strongly sorbed on hydrous iron oxides, and that this is its usual mode of occurrence in soils. He reasons that in soil formation under cool climates slow weathering of rocks leads to oxidation of sulphides and associated selenides prior to weathering of iron silicates, and that selenium could be lost by leaching, with little active Fe to retain it. In warmer areas where weathering is more rapid the Se would be trapped by the hydrous iron oxides formed at an early stage. One wonders whether the selenides would not oxidise even faster and be lost all the same. The idea nevertheless, fits in with the known distribution of selenium deficiency, which is far more general in the South Island.

Limestones are low in Se, Co and B but the trace element content is considerably influenced by impurities. For example the particular effectiveness of one Southland limestone, a very low grade one, was traced to its molybdenum content—about 10 times that of purer stones in the region.¹⁸ During soil formation the calcium of limestones is leached away with subsequent concentration of trace elements. The resultant “rendzinas” are high in Se and Co.

Summing up, it is evident that both the parent material and/or the process of soil formation can be responsible for trace element deficiencies—inherited or acquired, as the case may be, before the arrival of man on the scene. This is supported in some cases by early records of animal or plant diseases which later have been attributed to trace element deficiencies. The records are early enough to make it plain that intensive farming was not the basic cause. Cobalt, boron and molybdenum fall into this category.

Skey,³ whose 1892 report I have already quoted in part, at that time examined five soils—two from Katikati where animals were reasonably healthy and three from Tauranga where both sheep and cattle contracted “Tauranga disease” or “bush-sickness” (now known to be due to cobalt deficiency). He reported, “In every case there was found (in the soluble part alone) a sufficient quantity of those fixed ingredients that serve for plant food to supply several successive crops of roots and cereals. No ponderable quantity of arsenic or of any metal likely to exercise a poisonous effect upon animals was found in any case. From the above it appears that there is not any notable chemical, mineralogical or mechanical difference between the healthy soils of Katikati and the unhealthy of Tauranga. . . . These results do not throw any light upon that mysterious and disastrous disease that has for so long infested certain parts of the seaboard of the Tauranga district.” This early evidence fits in well with the inherited nature of Co deficiency, the Katikati soils being derived from andesitic materials, the Tauranga from rhyolitic.

Atkinson states that corky pit of apple, which he later showed to be due to boron deficiency, has been evident in the Nelson district since 1912.¹⁹ Mottle heart of swedes, another boron deficiency complaint, was reported in 1927 “to have been particularly abundant for many years past in Westland”. In the annual report of the Fields Division (excerpt N.Z. J. Agric. 35, 404) 1927, it is said to have been established through experimental work that wood ashes, while not increasing yield,

may decrease or even eliminate the disease. A follow up of that lead might have yielded the answer. As it was, following a report from Canada, borax was successfully used from 1936 on.²⁰

The remarkable responses to liming in Southland from 1890, when a reasonably priced burnt lime first became available (13/- a ton from the Milburn Lime and Cement Co.), are suggestive of the well known molybdenum deficiency having been present even then. Liming has many beneficial effects, but present knowledge points to the regulating effect on trace elements through reduction of soil acidity, as particularly important. Toxic levels of aluminium and manganese are reduced and molybdenum is made more available. The clovers respond to this molybdenum through stimulated nitrogen fixation and there is a general rise in nitrogen status. Other crops, notably brassicas, are also sensitive to molybdenum which is an essential nutrient apart from nitrogen fixation. In 1950 marked responses to molybdenum, paralleling those produced by heavy liming, were demonstrated in Otago and Southland.²¹

Some early reports of benefit from liming in Southland are of interest. Thomas Brydone, Superintendent in New Zealand of the Australia and New Zealand Land Company, in a paper delivered in 1900 said, "We have thoroughly proved in practice that turnips and clovers require lime for their growth, and rape also thrives splendidly after lime". Clovers and rape are particularly molybdenum responsive. W. D. Hunt in the *N.Z. J. of Agriculture* 1916, speaks with unbounded enthusiasm of the effect of lime on southern grasslands. "The growth of all the best grasses and particularly clovers is promoted to an enormous extent." Another quotation, this time from a farmer, "I never sowed clover before I limed because they would not grow; now I never sow them because they seem to be naturally in the land and come up of their own accord". I have seen this miraculous appearance of clover, previously so stunted as to escape notice, following molybdenum application.

A fourth widespread deficiency, that of selenium, has only recently been established. Research leading to its identification is summarised by Underwood (1, p. 308). It is connected with a wide range of syndromes in sheep, cattle, pigs and poultry. Probably the earliest description in New Zealand of a complaint now associated with selenium deficiency was in a report by A. Leslie of research work at Lincoln Agricultural College, 1935. It concerned a scouring and wasting disease of lambed ewes. MacLean

*et alia*²² showed in 1963 that the condition responded to selenium. Outbreaks of another manifestation of selenium deficiency, white muscle or stiff lamb disease (W.M.D.), were described by Hartley²³ as occurring in 1951 on properties at Fairlie and at Tapawera. Heavy losses of chickens in 1951 and 1952, thought at the time to be associated with vitamin E deficiency (Ann. Rept. Animal Ind. Div.), were probably due to a trouble later cured by Se dosing. From 1954 on, incidences of W.M.D. and ill thrift are mentioned in annual reports. Selenium deficiency, though associated with particular soils (usually light textured and for the most part formed under cool climate conditions), yet seems to be a developing, not an inherent, trouble.

(To be continued)



Obituary

LAURENCE FREDERICK ADDIS-SMITH,

M.Sc., D.I.C., F.R.I.C., A.N.Z.I.C.

Laurence Frederick Addis-Smith died at Wellington on December 4th, 1965, following a few days illness. He was educated at Varndean School, Brighton, England, and at Imperial College of Science and Technology, London, where he took a First Class M.Sc. in Chemistry. After service at Lever Bros. Ltd. at Port Sunlight and in the Government Laboratory, he went to Port Elizabeth, South Africa, in 1930, to be Chief Chemist to Lennox Ltd., Pharmaceutical Manufacturers. He later joined Adhesion Chemicals Ltd. in a similar capacity. He was President of the South African Chemical Institute in their Jubilee Year 1951-52.

He left South Africa in 1954 to join the firm of H. W. Lawrence & Son, Analytical and Consulting Chemists, Johnsonville, New Zealand. In this firm Laurence Addis-Smith's wide knowledge of industrial and pharmaceutical chemistry and his connections with chemists in Britain, South Africa, U.S.A. and Canada were used to the full. He became a member of the Association of Official Racing Chemists and published in the Bulletins of this Association several papers on the detection of drugs. He was on the Research Committee of the A.O.R.C. and was for a while a Vice-President of the Association. He was a member of the Wellington Branch of the New Zealand Institute of Chemistry, taking an active part in its meetings. At the time of his death he was Managing Director of H. W. Lawrence & Son Ltd.

SALARY SURVEY — July 1965

by

R. B. MILLER

Soil Bureau, Lower Hutt

This survey was planned for mid-1964, but because of changes taking place in Government salaries at that time it was delayed for a year. Even then some of the changes were still being argued and a final small increase was approved late in 1965. This has been added to the figures used in the analyses.

The questionnaire was similar to those sent out previously except that a question was added asking members in Industry to indicate the type of position they held. This replaced the "administration or bench work" question of 1958 and the "staff controlled" question of 1961.

Returns

Table 1 shows the distribution of returns. The December, 1964, List of Members totalled 765. Of these 136 were not included in the survey, being overseas, retired, students, etc. This left 629 in the seven groups shown in the table. The number of forms returned was 433, or 69 per cent, a slightly lower response than in 1961.

Salary and Age

Table 2 sets out the basic data from the returns in the same form as in previous surveys. Because of the increased spread of salaries the table has become rather large, but the temptation to reduce it has been resisted so that members wishing to make their own calculations may have full and accurate information. The returns from Research Associations, Local Bodies, and Self-employed are too few to allow separate listing, but they are included in the "All Groups" section.

Average Salaries

Table 3 shows average salaries. For comparison the corresponding figures from the 1955 and 1961 surveys are also included. Averages from less than four returns have been omitted.

In calculating averages, scale figures have been used for Government and University members, and the midpoint of the range, i.e. the round hundred, has been taken for other groups.

The average of a few widely scattered figures does not mean much, but there does not seem to be any better simple way than a table of averages for showing the overall pattern.

Since the last survey in 1961 all groups have had salary increases. These have been shown as percentages in Table 4. Overall the increase is about 40 per cent. The University salaries have increased more than the others. Over the last 10 years increases in the younger age groups in Industry, Government and Universities have been very similar. In the older groups there are considerable differences. University salaries have nearly doubled, Government ones have increased by about 75 per cent and Industry by a little over 50 per cent. In these older age groups University salaries are now averaging about £500 more than those in Industry, and Industry about £150 more than those in Government. School Teachers sent in too few returns to allow accurate comparisons but, at least in their early years, they seem to be well below the other groups.

Figure 1 shows the information from Table 3 in graphical form.

Higher Salaries

In the 1948 survey an estimate was made of the proportion of members receiving "higher salaries", a salary of over £1,000 being considered "higher". Since then the £1,000 has been adjusted at each survey using the Government Statistician's Retail Price Index. In Table 5 the proportion of members in each occupational group receiving more than £2,050 a year is shown. Since 1955, when one chemist in seven received a "higher salary", the proportion has increased steadily so that today more than half do so. It seems that chemists are catching up with the cost of living!

Academic Qualifications

Table 6 shows how members with various qualifications are distributed in the different occupational groups. The proportion of doctors in the Universities has increased from 54 per cent to 76 per cent since 1961, mainly at the expense of masters. In Government in 1961 masters made up half the numbers, and bachelors and doctors a quarter each. This year each make up about a third of the total. In Industry there has been a decrease in the proportion of members with higher qualifications in the younger age groups.

Age group	% Masters and Doctors						
21-30	38
31-40	36
41-50	49
> 50	71

The “% replies” column in Table 6 shows the usual low response from members with no degrees. It also shows an exceptionally high return from doctors, a factor which should be considered in interpreting figures.

Table 7 shows the average salaries of members with various qualifications in the main employment groups. Taking all members, masters average £150 more than bachelors and doctors £300 more than masters, but there are big differences in the salary pattern in the various groups. For example in Industry there is little difference between salaries of bachelors and masters. In Government there is over £400 difference between these groups, but only £100 between masters and doctors.

The averages probably illustrate real trends but there is a wide range of salaries in each qualification group and each one has its share of both high and low figures.

Women Chemists

Table 1 shows the number of returns from women, 5 per cent of the total. Numbers are too small to show separately but, as before, most women receive lower salaries than men. The differences average about £100 in Schools and Universities, £250 in Government and over £400 in Industry.

Average Ages

The average ages of chemists in the various employment groups were tabulated in the 1961 report with those found in all previous surveys. The figures below show the trends.

	1955	1965
Industry	38	40
Government	42	44
University	40	38
School Teachers		39
Others		43
All Groups		41

Superannuation

Table 8 shows that the number of members in Industry belonging to subsidised superannuation schemes continues to increase. Over 80 per cent have contributions from employers of 5 per cent or more and, as well, there has been a marked increase since 1961 in contributions of more than 5 per cent, and a decrease in those below 5 per cent.

Occupational Groups Within Industry

In this survey members in Industry were asked to indicate the type of position they held. Results are given in Table 9. Some figures have been omitted where the number of returns is low.

The salary ranges indicate the extent of the overlapping between groups but the averages show some trends. Chief chemists in general average about £300 more than chemists, with technical salesmen coming somewhere between. Works managers average about £400 more than chief chemists, and general managers and managing directors are about £1,000 ahead of works managers.

The age-salary pattern in each group is similar to the pattern when they are all grouped together; with a steady rise to the mid-thirties, then a plateau, and finally a further rise in the fifties.

A comparison of academic qualifications shows that about 40 per cent of chemists and managers are masters or doctors. Over 50 per cent of chief chemists have higher degrees, and this group includes most of the doctors. The technical salesmen have a slightly higher proportion with five masters in nine members. The figures are:

Group	% Masters and Doctors
Technical salesmen	56
Chemist	42
Chief chemist	52
Works manager	39
General manager	41
All groups	45

As noted above there is an increased proportion of members with higher degrees in the higher are groups.

General

The purpose of this paper is to present the facts shown by the survey. Comment is reserved for a later paper in which further comparisons will be made.

It is not, of course, feasible to cover all the relationships between the many variables covered in the survey. If any member would like further information this will be provided if it is reasonably possible.

References

- Salary Survey—June 1955: *J.N.Z. Inst. Chem.* 19: 128-33, 1955.
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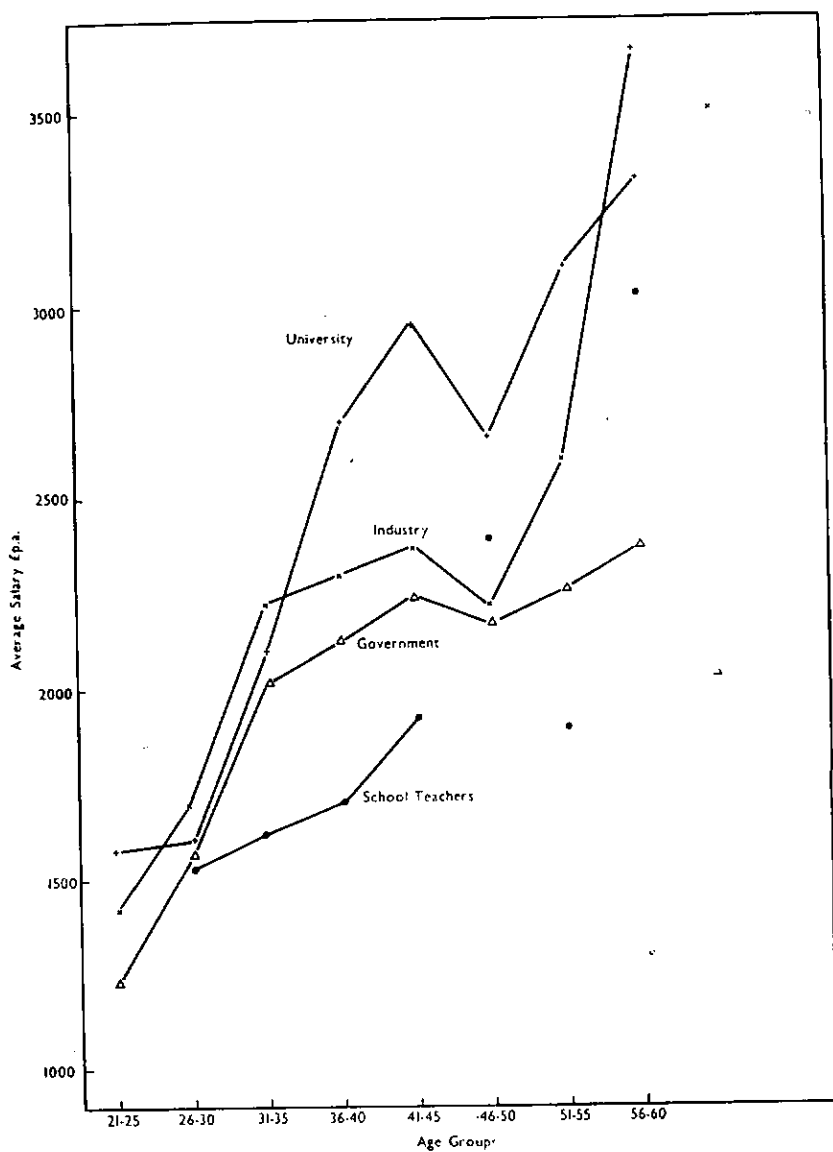


Fig. 1

TABLE 2
DISTRIBUTION OF SALARIES

	Below 1050	1051-1150	1151-1250	1251-1350	1351-1450	1451-1550	1551-1650	1651-1750	1751-1850	1851-1950	1951-2050	2051-2150	2151-2250	2251-2350	2351-2450	2451-2550	2551-2650	ALL
21-25	1	2	2	6	2	5	1				1							1
26-30		1	2	7	9	8	6	7	7	2	1	2	1	1				1
31-35			1	1	5	1	5	8	8	4	5	7	6	6	2			2
36-40				1	1	2	5	3	7	3	4	8	10	4	3	7	3	3
41-45	1	1	1		1	1	2	2	7	6	4	5	3	6	2	10		2
46-50		1			1	1	1	3	4	1	5	3	2	5		7		1
51-55								1	7		5	5	7	5	1	4		2
56-60					1				3		6	2			1	1		1
> 60												2						1
Totals	2	5	7	16	19	18	20	25	43	16	26	34	29	28	9	31	11	
INDUSTRY																		
21-25				4		4	1											
26-30			1		2	3	5	5	2	1	1	1	1			1		1
31-35						1	2	3	3	2	3	2	2					
36-40						2	4	2	4	3	3	3	6	1	1	3	3	
41-45						1	1	1	3	3	2	1		1		3	1	
46-50		1	1			1	1	1	3	3	2	1		1		2	1	
51-55		1				1	1	1	1	1	3	1	2	1		2	1	
56-60								1			3	3	1	2	1	1	2	
> 60												1						
Totals	2	2	5	2	11	14	12	14	10	15	12	12	5	2	10	8		
GOVERNMENT																		
21-25		2	1		1													
26-30		1	1	1		1								1				
31-35						1	1	2			1			3				
36-40			1				1	3			3	3	3					1
41-45	1					1	1	3		1	3	2	5	1				4
46-50								3			1		4					3
51-55								1	4		2	4	3					2
56-60					1			3			1							2
61-65											1			1				
Totals	1	3	3	1	3	2	3	4	18	1	12	9	20	1		12		
UNIVERSITY																		
21-25			1	1	1	1												1
26-30					5	4	1	1	3	1		1						
31-35			1	1		1	1	1			1	3	3	2				
36-40											1	3	3	2				
41-45											1							2
46-50											1							3
51-55					1						1							2
56-60												1						1
Totals		2	1	8	5	2	2	4	1	4	4	4	4	3	4	9		
SCHOOL																		
21-25				1							1							
26-30			2	2			1	2										
31-35			1	3		1	2	1	1	1								
36-40				1														
41-45								1	3			1						
46-50												1						
51-55								2			1	1						
56-60											2							
Totals			4	6		1	3	6	4	5	4	4	1					

TABLE 1
RETURNS

Group	Members in Institute	Total Returns	%	Women	
				No. in Institute	Returns
Industry	249	174	70	6	4
Government	140	107	76	10	8
University	114	81	71	7	4
School Teachers	73	38	52	7	3
Research Assn. ..	27	18	67	2	1
Local Bodies ..	17	9	53	5	1
Self-employed ..	9	6	67	—	—
Total	629	433	69	37	21
Others not in survey, retd., o' seas, stud- ents, etc. ..	136	23	17	17	3

TABLE 5
DISTRIBUTION OF HIGHER SALARIES 1948, 1955 AND 1965

Group	% receiving higher salaries		
	1948 £1000+	1955 £1550+	1965 £2050+
Industry	19	21	50
Government	3	4	64
University	17	22	62
School Teachers	16	0	26
Research Association	..	17	67
Local Body	44
Self-employed	83
All groups	13	14	55

TABLE 8
SUPERANNUATION
(Industry only)

Employers' contribution to superannuation or insurance as percentage of salary (153 replies).

Contribution, %	% of replies
0	9
$\frac{1}{2}$ - $4\frac{1}{2}$	9
5	43
$5\frac{1}{2}$ - 7	20
$7\frac{1}{2}$ - 9	9
> 9	10

TABLE 3
AVERAGE SALARIES (£) FOR AGE GROUPS
WITH A COMPARISON WITH 1955 AND 1961 SALARIES

Age	Industry		Government		University		Teachers	
	1955	1961	1955	1961	1955	1961	1955	1961
21-25	..	1422	758	1230	1050	1580
26-30	..	1400	888	1506	1520	1605	1017	1530
31-35	..	1680	1039	2015	1132	1790	958	1620
36-40	..	1321	1113	1650	1380	1940	1000	1700
41-45	..	2008	1231	1780	1555	2220	1231	1920
46-50	..	2260	1333	1825	1425	2650	1225	1895
51-55	..	2190	1443	1809	1567	3095	1100	..
56-60	..	3030	1350	2180	1550	3225
> 60	1050	..	3030
Totals	..	2230	2370	1880

TABLE 4
PERCENTAGE INCREASES IN AVERAGE SALARIES BY AGE GROUPS

Age	Industry		Government		University		Teaching	
	4 yrs.	10 yrs.	4 yrs.	10 yrs.	4 yrs.	10 yrs.	4 yrs.	10 yrs.
21-25	62
26-30	36	65	27	70	58	67	50	..
31-35	44	90	41	94	58	86	40	69
36-40	33	73	48	91	41	96	19	70
41-45	33	57	44	82	43	90
46-50	58	54	37	62	43	86
51-55	28	51	25	56	..	97	..	55
56-60	62	75	..	108
61-65	93

TABLE 6
NUMBER OF MEMBERS WITH VARIOUS ACADEMIC QUALIFICATIONS IN EMPLOYMENT GROUPS

Qualification	Industry	Government	University	School Teachers	Research Assn.		Total	No. in Institute in Groups Surveyed	% Replies
					Local Body	Self-employed			
No degree ..	2	2	—	—	1	5	28	18	
Bachelor ..	92	33	8	12	3	148	219	68	
Master ..	71	36	11	24	17	159	241	66	
Doctor ..	8	36	62	2	12	120	141	85	
Not stated ..	1	—	—	—	—	1	—	—	
Totals ..	174	107	81	38	33	433	629	69	

TABLE 7
AVERAGE SALARY OF MEMBERS WITH VARIOUS QUALIFICATIONS IN EMPLOYMENT GROUPS (£)

Qualification	Industry	Government	University	Teachers	All Groups
Bachelor ..	2200	1815	1930	1770	2030
Master ..	2260	2240	2100	1940	2170
Doctor ..	2560	2340	2470	—	2460
Totals ..	2230	2135	2370	1880	2220

THE ROYAL SOCIETY OF NEW ZEALAND AND ITS IMPLICATIONS FOR THE NEW ZEALAND INSTITUTE OF CHEMISTRY

by
F. B. SHORLAND

Since its formation in 1934 the New Zealand Institute of Chemistry has existed essentially as a body for the promotion of chemistry without reference to its role in the national and international aspects of New Zealand science. However, there have been in recent times indications of a change in policy as shown by the affiliation of the Institute to the Royal Society of New Zealand as a member body on 25 June 1964. It is true that some of our chemists have become Presidents of the Royal Society of New Zealand but, in general, the members of the Institute have looked upon such an event as of no concern to the Institute.

I believe that in future the Institute of Chemistry must render a greater service to science as a whole in New Zealand and not leave this responsibility mainly to scientists belonging to other disciplines.

Many of the older members of the Institute will recognise that chemistry now covers a very wide field. At one time a lecture given to the Institute would have some meaning to all its members. Attempts are still made to give lectures to the Institute that will appeal but to achieve this objective the specialist has to describe his subject in lay language. This can be beneficial to all concerned but the Institute cannot thereby cater for the specialists who wish to present papers and have them discussed by workers who are leaders in the field. In other words the Institute of Chemistry cannot provide in its present form for all the needs of chemists. The time has come for it to form specialist groups and to become a co-ordinating body. Already there are increasing numbers of chemists giving their attention to societies other than the Institute because these societies cater for their special needs. I refer to the Institute of Food Technology, the Institute of Agricultural Science N.Z. Inc., the Society for Soil Science N.Z. Inc., and so on. There will be a need in New Zealand for a Biochemical Society and a Society of Chemical Industry. The question arises therefore as to whether New Zealand can effectively support these organisations as separate entities or whether they should be formed as branches of the New Zealand Institute of Chemistry.

I believe, therefore, that chemists need for the furtherance of their profession at least three scientific societies. The first need is to belong to a group which deals very specifically with the field they work in. The second is for a society, such as the New Zealand Institute of Chemistry, to further the interests of chemists as a whole, and the third is for an organisation for the purpose of bringing together the various scientific societies. The chemist needs to use his specialised knowledge as a contribution to the solution of problems that he would not otherwise know of. The Royal Society of New Zealand is well able to continue with this task. To these societies may be added the New Zealand Association of Scientists which has a special role in looking after the welfare of the scientist especially in relation to salary questions.

As President of the New Zealand Institute of Chemistry in 1962 I put forward the suggestion that the Institute should realise its responsibilities towards science as a whole and supported the view that there should be closer collaboration with the Royal Society of New Zealand.

The question of the Institute becoming a member body of the Royal Society was debated both at annual meetings of the New Zealand Institute as well as at branches. A series of discussions and negotiations between committees of the Royal Society and the New Zealand Institute of Chemistry followed with the final result that the Institute, despite the earlier apprehension of many of its members, has now become a Member Body. It is perhaps ironical that following this event the new Act of the Royal Society will come into force in January 1966. Under the new Act the Royal Society will be governed by a Council of eight Fellows, together with two representatives from the Member Bodies Committee who may not be Fellows. The Royal Society will now become an Academy in line with the Academies of the United States and of Australia and with the Royal Society of Great Britain, which depend for their representation entirely on distinction in science and not on representation of scientific organisations. There will be now a Member Bodies Committee, however, designed to bring together the member bodies and to form a liaison with scientific societies in general. The Member Bodies Committee will advise Council but, as already pointed out, will not control it. The Institute of Chemistry cannot therefore, now exercise much control over the Royal Society, but the advantages of being affiliated with the Royal Society are nonetheless as great as ever because of recent developments. Professor R. S. Allen, when President of the Royal Society, taking into account the

Rules B14-24, introduced at the half-yearly Council Meeting in November 1959 the concept of four Sectional Committees, viz:

- (1) Mathematics and Physics,
- (2) Chemistry,
- (3) Geology and Physics,
- (4) Biological Sciences.

Each committee was to consist of six representatives, including a Chairman appointed by Council, chosen as far as possible to represent several subdivisions of each branch of science. The committees were to advise Council or its officers and to make suggestions to Council concerning the branch of science that they represented. The first Committee on Chemistry which commenced its duties on 31 May 1960, comprised Professor L. H. Briggs, Chairman, Professor J. K. Dixon, Professor H. Parton, Mr. T. A. Rafter, and Dr. F. B. Shorland. It reported to Council at the half-yearly meeting of 23 November 1960, on the need for a supply of chemists of varied training as the most urgent problem facing the country. The loss of graduates was also referred to.

The reports of the Sectional Committees may be placed before the House. For example, following a resolution of the half-yearly meeting of the Royal Society in 1961 a subcommittee was appointed to produce a comprehensive report based on Sectional Committee's reports for presentation to Parliament.

From time to time it has been suggested that the N.Z.I.C. should act as an advisory body to the Royal Society. At the half-yearly meeting of the Royal Society in 1962 it was agreed that the Sectional Committee should remain but that the N.Z.I.C. should nominate some of the members of the Committee. The suggestion that the Chairman of the Committee should be President of the N.Z.I.C. did not prove acceptable as the term of office of one year is too limited.

The requirement for a National Committee for Chemistry whose function would be to form a channel of communication with corresponding international bodies, especially I.U.P.A.C., became evident.

At the instigation of the Royal Society, it was suggested that the Institute of Chemistry might become a member body of I.U.P.A.C. At this time the Royal Society was taking a renewed interest in the New Zealand I.C.S.U. Committee which was re-constituted in November 1962. It now consists of a member of the Council of the New Zealand Royal Society as its convenor, the President of the Royal Society of New Zealand, and a member of each National Committee, of which 11 are listed in the pro-

ceedings of the Royal Society of New Zealand, 1964 92, 18-20.

The National Committee for Chemistry was set up on 19 March 1964, its members being Professor L. H. Briggs Chairman, Mr. S. G. Brooker, Professor H. N. Parton, Mr. T. A. Rafter, Professor S. R. Siemon, Dr. F. B. Shorland and Professor F. G. Soper. In the meanwhile the Sectional Committee met on 13 August 1964, under the chairmanship of Professor F. G. Soper and recommended that the National Committee should take over the functions of the Sectional Committee. This was acceptable to the Council of the Royal Society at their November meeting. The first National Committee did not meet, but its Chairman very actively investigated the corresponding committees in Great Britain and Australia and drafted the Rules for the National Committee. The present National Committee which met on 18 August 1965 in Dunedin consists of four members, Professor L. H. Briggs, Mr. S. G. Brooker, Professor H. N. Parton and Dr. F. B. Shorland, elected by the Royal Society directly and four members, Mr. M. S. Carric, Professor J. F. Duncan and Dr. A. T. Johns and Professor J. Packer elected by the Royal Society from nominations made by the N.Z.I.C. In consultation with the members of the first National Committee, Dr. Shorland was appointed as the I.C.S.U. delegate, and in addition acted as convenor of the August meeting. As the National Committee in accordance with the Rules of the Royal Society may take over the functions of the Sectional Committee, it was feasible to invoke Rule B15 which reads:

"Each sectional committee shall determine the procedure to be adopted in exercising its functions."

In this way the members of the committee were able to vote on the question of Chairman and Professor Packer was duly elected. Through the National Committees, the Institute of Chemistry can participate fully in the national and international activities relating to chemistry. Following the election of New Zealand to I.U.P.A.C. the Committee will obtain considerable support in the form of publicity and advice regarding the International Conference on Electron Hyperfine Interactions in Spectroscopy which is to take place this year in New Zealand. I consider the steps taken by the Institute in becoming a member body of the Royal Society will have a big impact on the destiny of the Institute and will greatly enlarge its role both nationally and internationally. The value of these steps must not only be judged by what the Institute may gain but also by what the Institute may contribute.

Branch News and Notes

CANTERBURY

Mr. D. J. Stedman, formerly of South Otago High School, has joined the staff of Christchurch Boys' High School.

Mr. K. R. Farnsworth has transferred from Central Hawke's Bay College, Waipukurau, to teach chemistry at Christ's College, Christchurch.

Dr. A. Fischer and Dr. W. S. Metcalf have been promoted to Readerships in the Chemistry Department of the University of Canterbury.

Dr. R. D. Topsom has resigned from the Chemistry Department to take up the foundation chair in chemistry at La Trobe University, Australia. La Trobe is to be the third university in the Melbourne area. Dr. Topsom recently returned from a period of leave spent in fruitful collaboration with Professor A. R. Katritzky at the University of East Anglia, Norwich.

Dr. W. B. Earl, Lecturer in Chemical Engineering, is to spend two years gaining industrial experience with Shawinigan Chemicals Ltd., Montreal, Canada.

Mr. J. O. Kidson, a foundation member of the Canterbury Branch, has retired from his position as head of the Science Department at the Christchurch Boys' High School. He has accepted a teaching appointment for 12 months in the United Kingdom, after which he plans to retire permanently in Nelson.

Mr. A. H. Wooff has been appointed to succeed Mr. Kidson as head of the Science Department at Christchurch Boys' High School.

Mr. T. C. Ralfe, deputy headmaster of the Shirley Boys' High School, left in January to take up a two-year appointment under the Colombo Plan as an inspector of science and mathematics in Sarawak junior high schools.

The second Canadian Wood Chemistry Symposium will be held on June 22-24 1966 in Quebec. The meeting will be devoted to the chemistry and chemical processing of wood and pulp. It is sponsored jointly by the Chemical Institute of Canada and the Technical Section of the Canadian Pulp and Paper Association. Further information is obtainable from the editor, J.N.Z.I.C.



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BOOK REVIEWS

Organic Functional Group Analysis by Micro and Semi-micro Methods. By NICHOLAS D. CHERONIS and T. S. MA. Pp. XXV plus 696. New York, London and Sydney: Interscience Publishers. 1964. Price £9/8/- (U.K.)

The authors of this book, Professor Ma and the late Professor Cheronis, two eminent microchemists, have combined the results of several years intensive and methodical investigation in the field of organic functional group analysis to produce a very useful reference work. Their comprehensive coverage and critical presentation make this book of value not only to the micro-analyst who wishes to keep abreast of recent developments but also to the research worker who wishes to understand the scope and limitations of a particular analytical method.

The book is divided into three sections. The theoretical background of functional group analysis presented in Part I reviews the classification and limitations of analytical methods. Part II, a critical survey comprising 373 pages, reviews more than 2,000 literature references (unfortunately few later than 1960) relating to analytical methods for nearly 100 different functions. Detailed and explicit laboratory instructions for 52 experiments are presented in Part III.

The book is very well written and produced but the cost is unfortunately rather high. It is worthy of a place in organic research and analytical laboratories. It is a fitting memorial to the work of the late Professor Cheronis.

A.L.C.

Particulate Clouds: Dusts, Smokes and Mists, by H. L. GREEN and W. R. LANE. E. & F. N. Spon, London, 2nd Ed. 1964. English price £4/4/-.

The first edition of this book published in 1957 brought together for the first time in one volume the many aspects of this subject. Such has been the demand that a second edition, enlarged by 80 pages and incorporating new knowledge since that date, has appeared after only seven years.

The first part of the book deals with the basic physics and physical chemistry of suspended particulate matter in gases and clouds under the headings of production of particulate clouds, physical characteristics, optical properties, coagulation and filtration, sampling and estimation, and diffusion in the atmosphere. The second part covers industrial and environmental aspects including collection, health hazards, atmospheric pollution, aerosols in nature, and the uses of particulate clouds.

Both authors, members of the staff of the War Department Chemical Defense Experimental Establishment at Porton, are well qualified to write this considerable and important work, which reflects the interests of this establishment in many aspects, both theoretical and practical, of the behaviour of particulates. For all workers in fields involving small particles it forms a valuable book of reference covering a wide range of subjects and reviewing a vast literature.

In the first part, with the exception of the sections on deposition and filtration, sampling and collection, the treatment is substantially fundamental. The topic of atmospheric diffusion has a theoretical rather than a practical approach, and more emphasis on what actually happens in practice would give a better balanced treatment. It was the reviewer's good fortune recently to hear Dr. R. S. Scorer emphasise the importance of observation in the understanding of atmospheric diffusion.

In the second part, where perhaps the authors are least qualified to write, the reviewer finds the coverage of subjects familiar to him, disappointing. For example, a very common method of measuring smoke in the atmosphere is by the optical evaluation of the smoke deposit on filter paper. This method receives only a passing mention, when an adequate theoretical discussion would be most desirable. It is realised that to treat the many topics in the second part more fully would require a greatly enlarged text. Nevertheless the book gives a wealth of information on all aspects of small particles and should be in the library of everyone whose work impinges on this field.

C.F.D.

Would any members elected prior to June 2, 1965, who have not received Associate or Fellowship certificates, please notify the Registrar.

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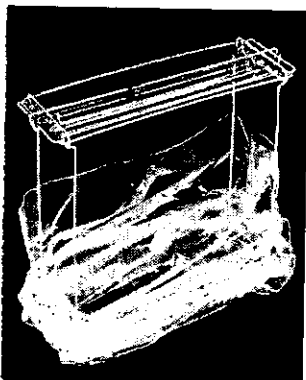
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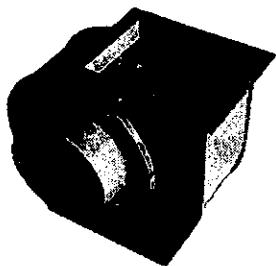
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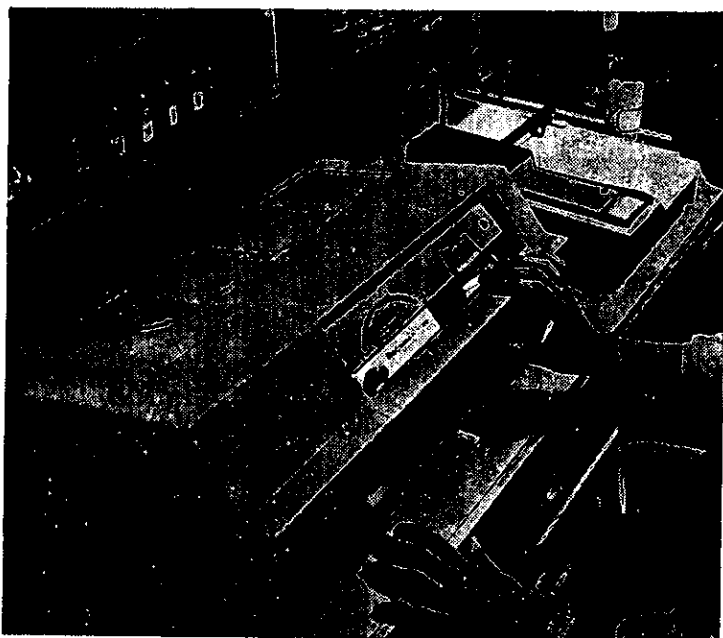
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