

JOURNAL OF THE NEW ZEALAND  
INSTITUTE OF CHEMISTRY

Vol. 25    No. 4  
August, 1961



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# JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

Vol. 25, No. 4

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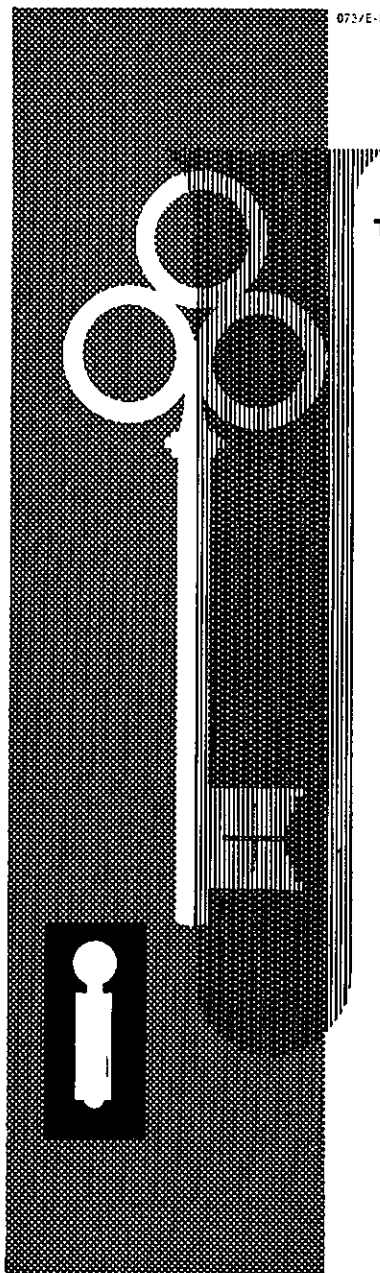
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# JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

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## EDITORIAL

*(Contributed by D.S.M., on behalf of the Conference Committee)*

Once again, for the first time since 1956, members from many parts of New Zealand are to gather in Auckland for the Annual Conference of the New Zealand Institute of Chemistry. But 1961 is far more than the year of another Institute Conference in Auckland; it is the year in which the future of science in this country may be decided.

It would be neither fair nor true to say that all New Zealand Governments have ignored science since the war; but no one could claim that science has been actively encouraged. The continual losses of first-class men overseas—both new graduates and those with long research experience; the inadequacy of salaries and working conditions; and the neglect of inquiry into many problems of national importance have been brought to Government attention by this Institute and many other professional bodies. Platitudes have been spoken, half-promises made; but until this year little positive has been done.

Now a Commission of Inquiry to study New Zealand science has been promised. If it is appointed dozens of submissions will be heard; hundreds of questions asked; and thousands of pages of typescript scanned. Ultimately, a report will be given to the Government, recommending steps to be taken—steps that, without doubt, will be equal in importance to the steps recommended by the Committee on New Zealand Universities.

This is the background against which this year's Conference may be held. It is a background of importance, in one way or another, to everyone attending the Conference. Usually, papers, symposia and the other conference features are of first importance to the members attending; this year, they may take second place to the events outside. If New Zealand science is weighed in the balance, it may well be found wanting.

## WILLIAM SKEY — NEW ZEALAND'S PIONEER GOVERNMENT ANALYST

R. L. ANDREW

*(formerly Director, Dominion Laboratory)*

*30 Fairview Crescent, Wellington.*

When I joined the staff of the Colonial (now Dominion) Laboratory in 1906, William Skey had been dead for only six years but even then his career was becoming legendary. We knew that he was Colonial Analyst for many years, and was practically solely responsible for the work of the laboratory from its inception in 1865 to his death in 1900, and until 1896 the only full-time analyst employed by Government.

The annual reports over that period cover a very wide field, but are mainly concerned with the survey of the mineral resources of the country. Their general accuracy and the completeness of their cover gave us an almost superstitious respect for Skey and the geologists and others associated with him. References in the scientific publications of the day show that Skey was very highly thought of by his contemporaries, and in an obituary notice (*Trans. N.Z. Inst.*, 1900, 33, 554) it is stated that "he attained to such a position as to be recognised as one of the world's famous authorities in certain branches of chemical science". This assessment of Skey has been accepted by those who have simply read the impressive list of titles of his published papers and take the praise of his contemporaries at its face value.

I have systematically examined all the annual reports of the Colonial Laboratory covering Skey's years of service, various records of his work as Analyst to the Geological Survey of Otago from July 1862 to August 1865, and numerous papers published in scientific journals as well as special reports.

This has led me somewhat reluctantly to conclude that Skey's contributions to chemical science are by no means as important as thought by his contemporaries but that the really outstanding contribution to science was his work during thirty-eight years in connection with the survey of the mineral resources of New Zealand. Nevertheless, his contributions to scientific journals are full of interest. They deal with a very wide variety of subjects, but not one of them is the outcome of careful quantitative work, and as a rule they show great haste on his part. Most of them are really more in the nature of notes than full-scale papers. This is not to say that they are of no merit, but one is more impressed with

the indications they give of what Skey might have accomplished had he concentrated on fewer lines of investigation, than with their standing as finished pieces of research.

To me, their main interest is that they reflect conditions so very different from the present, and often pleasantly reveal something of Skey's personality and his outlook on life. This is well illustrated by the following papers and comments "On the Alkalinity of Carbonate of Lime".

The first paper was published in the *Transactions of the New Zealand Institute*, 1868. Skey says:

"Carbonate of lime is described in Chemical Works as neutral to test paper, but this scarcely agreeing with the results of observations I have had to make upon this point in the course of other investigations, I beg to give these results which are as follows:—

(1) Carbonate of lime prepared by igniting pure Oxalate of lime in a closed crucible, at a dull red heat, gives an intense alkaline reaction with reddened litmus paper, after moistening with distilled water, or after re-ignition with pure carbonate of ammonia.

(2) Carbonate of lime, prepared directly from chloride of calcium and bicarbonate of soda by admixture of their aqueous solutions, and washing the ensuing precipitate till all the soda was removed, gave the same reaction with test paper.

(3) Limestone, shells (calcareous), calcspar crystals, are all strongly alkaline to test paper (at least the samples I tried were), the powder of any of these substances, washed with distilled water for many days, does not seem to lose this alkalinity.

(4) Lastly (and I think conclusively) precipitated carbonate of lime, prepared by either of the above processes when agitated with weak hydrochloric acid, in successive quantities, until gradually reduced to a minute proportion of its original bulk, still manifests this reaction to an eminent degree; indeed the solution could not be rendered permanently acid till the whole of the carbonate was dissolved.

It seems impossible, under these circumstances, to attribute this reaction to the accidental presence of free magnesia or lime, sub-carbonate of lime or alkaline carbonates in the precipitate; this reaction may therefore, I think, fairly be attributed to the carbonate of lime".

The paper was published also in *Chemical News*, 1870, 22, 85.

This resulted in a rejoinder in the same volume of *Chemical News*, page 150, entitled "On the so-called alkalinity of carbonate of lime", by Charles R. C. Tichborne of the laboratory of the Apothecaries' Hall of Ireland, Dublin. The writer is somewhat patronising in tone. He says:

"I have been experimenting with lime and its compounds, and as that statement was so contrary to my observations, I think it well to point out wherein, in my opinion, lies Mr Skey's error, (a very natural one.) Such statements creep into our manuals and other works on chemistry without being submitted to sufficient proof, and become accepted as facts."

He then proceeds:

"If Mr Skey will repeat the following experiment, I think he will be persuaded of the neutrality of carbonate of calcium."

The experiment is described and the paper ends in pontifical vein thus:

"Carbonate of calcium is quite neutral, and it is evident that reddened litmus paper is not reliable as a test in such a case as the above."

Skey replied in a paper entitled "Notes in support of the alleged alkalinity of carbonate of lime", *Chemical News* 1872, 25, 147. After a short introduction he says:

"Mr. Tichborne very courteously, and with a considerable amount of plausibility, argues that 'as the reddened litmus which I used has the acid used to colour it only weakly combined with the tinctorial matter of the paper, the carbonate of calcium merely acts by abstracting this acid, and thus the litmus is brought back to its normal colour, blue with a shade of violet, and therefore this is not a reliable test in such a case.'

"In answer to this I would ask, does not the capacity of the lime salt to abstract the acid, argue most forcibly and sufficiently for its alkalinity?"

"If it does not indicate alkalinity in such a case, then reddened litmus, in opposition to all received opinion on this head, is not a proper, nor indeed, a test at all, for ascertaining this character for any substance. I would ask, what other condition or property is required for a substance besides that enabling it to act as an alkali on litmus, wanting which it is neutral?"

Tichborne had argued that as calcium carbonate did not affect turmeric paper it could not be alkaline.

Skey answered: "I take exception to the employment of turmeric paper in such a case as this, as it only shows alkalinity where it exists to a marked extent, and this is not a question of *degree* but one of *condition*, alkalinity or neutrality.

"That turmeric paper cannot indicate alkalinity where this does not reach a certain intensity is manifest from the refusal of the organic base, aniline, to affect it, though it acts both on the juice of red cabbage and of reddened litmus as a body having alkaline characters, which character we uniformly accord it."

There is a delightful touch at the end of the paper—one of the many in his papers and reports which give one some insight into Skey's outlook on life and also of his good manners. Tichborne had "put his neck out" but Skey responded with a true "retort courteous".

"I have to apologize for allowing a length of time to elapse ere noticing these objections of Mr Tichborne, and I waited thus in the hope that some one else might have taken up the question with such authority and potency of argument that would have sufficed to settle it one way or the other, and thus saved me further thought upon it, as it is so much more pleasant and exhilarating—besides being more in accordance with our colonial instincts—to break up fresh ground or to explore new country, than to turn back from this, to tinkering about old work or to protect it from hostile blasts, even though these be ever so courteously blown or kindly tempered."

The paper concludes thus:

"I will only add, I shall be very pleased to have this subject still further discussed, especially as it now appears that some general principle may soon be recognised by the use of which we can easily and certainly classify into three distinctive groups—acidic, basic and neutral—those bodies whose reaction with test paper is difficult to observe by reason of their intense colour or their extreme insolubility in water."

Skey demonstrated that he had a clear grasp of the underlying principles which his critic lacked and in the foregoing para-

graph he of course stated needs which are fully met in a modern laboratory.

Skey's active brain would not permit him to leave the subject until he proposed a method for examining the minerals in rocks by determining their reactions after crushing and applying to test paper.

Skey did not follow the matter further but it appears that here he was thinking on the lines of some specialized modern techniques such as spot testing.

Mellor, in the *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 3, p. 286, says:

"Powdered marble, chalk, Iceland spar, and aragonite were found by Skey [and others named] to be alkaline towards litmus."

One feels that Skey had his due when his work was noted by Mellor.

Since he retired from the position of Dominion Analyst, Mr Andrew has been collecting material for a biography of William Skey. As Mr Andrew's task is still far from completion, he has suggested that some articles extracted from his work so far may be of interest to present readers. It is hoped to publish in a later issue an account of Skey's chemical work in relation to the Geological Survey under Hector.

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### EASTERFIELD MEDAL AWARD

The Committee of the New Zealand Section of the Royal Institute of Chemistry has announced the award of the Easterfield Medal for 1961 to Mr T. A. Turney, Senior Lecturer in Chemistry at Auckland University. The work submitted by Mr Turney for the award consisted of three sets of papers, on nitrous acid and nitrosation, selective organic reactions, and oxidation mechanisms. He is at present writing a book on oxidation mechanisms.

Mr Turney graduated M.Sc. with second class Honours from Victoria University College in 1949 and was a junior lecturer there until appointed lecturer at Auckland in 1955. He was promoted to Senior Lecturer this year.

The title of Mr Turney's proposed Easterfield Address is "Nitrous Acid and Nitrosation".

## ABSTRACTS OF PAPERS CONFERENCE, 1961

### THE STRUCTURE OF TETRAMERIC HYDROGEN CYANIDE

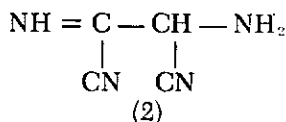
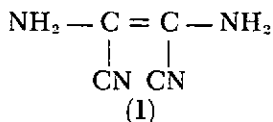
M. P. HARTSHORN and J. VAUGHAN

*Chemistry Department, University of Canterbury.*

Amongst the polymerization products of hydrogen cyanide is a crystalline solid of molecular weight<sup>1</sup> 108 consistent with a tetrameric formulation.

Recent X-ray diffraction studies<sup>2</sup> have corrected earlier X-ray work<sup>3</sup> which supported a dimeric formulation, and have demonstrated that in the solid state the compound has the tetrameric form (1) proposed by Grischkevitch-Trochimovsky<sup>4</sup>. Structure (1) is consistent with the chemical reactions<sup>4</sup>, dipole moment<sup>3</sup>, ultra-violet<sup>5</sup>, infra-red<sup>3,6</sup>, and Raman spectra<sup>3</sup> of the compound.

Hinkel *et al.*<sup>8</sup>, however, proposed formula (2) for the tetramer and denied any possibility of tautomerism, in spite of the fact that they were forced to assume hydrogen migration and double bond rearrangement in formulating some of their reaction schemes. There remains one piece of evidence which points to the real existence of structure (2).



Hinkel and Watkins<sup>9</sup> apparently established the existence of an asymmetric carbon atom in the molecule when they claimed to have achieved a resolution of the racemate, in obtaining a laevorotatory diastereoisomeride. The resolving agent used was *d*-camphor-10-sulphonic acid. The *d*-camphor-10-sulphonate of the tetramer was prepared by mixing hot, ethyl acetate solutions of the components; the salt was immediately precipitated. This salt, after prolonged heating under reflux in ethyl acetate, yielded a compound (A), which was regarded as the product of a gradual conversion of the more soluble *d*-diastereoisomeride into the less soluble *l*-compound.

When this work was repeated it became obvious that no resolution had taken place; the differences in optical rotation and properties between the salt and compound (A) noted by Hinkel *et al.* (*loc. cit.*) being the manifestation of a chemical rather than a stereochemical change. Evidence has now been obtained which indicates that compound (A) is formed from the salt by condensation of the second amino group of the tetramer with the carbonyl group of the resolving agent resulting in azomethine formation.

Thus all evidence now points to structure (1) for tetrameric hydrogen cyanide, even though the possibility of tautomerism may not be excluded.

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### A COMPARISON BETWEEN THE COMPLEX OXALATES OF IRON III AND RUTHENIUM III

A. L. ODELL and R. W. OLLIFF

*Chemistry Department, University of Auckland.*

It is well-known that there is a marked change in the "bond-type" of co-ordination compounds formed by successive metals descending a group of the periodic table. Such changes can be described in many ways, *e.g.*:

- (1) The "ionic"—"covalent" discontinuous transition of Pauling.
- (2) Increased "crystal-field" or "ligand-field" splitting of the *d*-level.
- (3) Partial breakdown of the Russell-Saunders coupling, and increased contributions from other types of coupling.

Evidence for such a phenomenon is of a number of different kinds:

- (1) Change in magnetic moment.
- (2) Considerable increase in the ligand-field splitting parameter *Dq* as found from absorption spectra.
- (3) Increased change from the free ion of the Racah electron interaction parameter *B*, also obtained from absorption spectra.

- (4) In many cases there are considerable changes in rates of reaction—*e.g.*, exchange reactions, aquatization, etc.
- (5) Changes in the spin-orbit coupling constant,  $\chi$ , as obtained from paramagnetic resonance.
- (6) Variation in the spectroscopic splitting factor,  $g$ , also from paramagnetic resonance studies.

An investigation has been made of the trisoxalato complexes of iron III and ruthenium III and comparisons have been made along the lines of the first four methods indicated above.

## IODIDES OF TRANSITION METALS RHENIUM AND OSMIUM

J. E. FERGUSSON, B. H. ROBINSON and W. R. ROPER

*Chemistry Department, University of Canterbury.*

The chemistry of the simple halides of rhenium and osmium will be reviewed briefly and in particular the iodides. The iodides provide an interesting series in that, first, they are quite often converted into one another by removal of iodine under controlled heating or by heating with excess iodine; and, secondly, the transition metal iodides generally contain the metal in a low valency state. These two factors make the iodides useful as starting materials for producing complexes of transition metals in low oxidation levels.

For this reason the iodides of rhenium and osmium have been studied and evidence has been obtained for the following:

<i>Rhenium</i>	<i>Osmium</i>
ReI <sub>4</sub>	OsI <sub>4</sub>
ReI <sub>3</sub>	
ReI <sub>2</sub> <sup>°</sup>	(OsI <sub>2</sub> ) <sup>?</sup>
ReI	OsI <sup>°</sup>

<sup>°</sup>Obtained for the first time in this work.

The interrelationships of these iodides and their properties will be discussed in detail. The results indicate that the weak oxidizing power of free iodine has a part to play in stabilizing ReI<sub>2</sub>. All the compounds are black and generally insoluble in most organic solvents. Magnetic moment measurements have been carried out and the results indicate the absence of simple ReI<sub>x</sub> structures where  $x$  is 1-4. The various iodides have been characterized by powder photography.

The insoluble nature of most of the iodides reduces their potential as starting materials for new low valency complexes. However, a few preliminary investigations will be discussed.

## A CALORIMETRIC STUDY OF THE FORMATION OF SOME SULPHATE-CATION COMPLEXES IN WATER

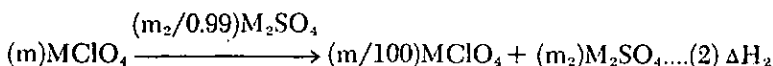
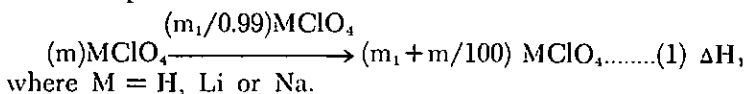
J. M. AUSTIN and A. D. MAIR

*Chemistry Department, Canterbury University.*

The little information available on the enthalpy and entropy changes associated with complex-ion formation by sulphate ions has been derived from temperature coefficient studies of equilibrium constant data found from absorption spectra, electromotive force, conductance and solubility observations. The accuracy of the thermodynamic properties so derived has often been questioned and many reviewers have stressed the desirability of direct calorimetric determination of enthalpy changes. We wish to present the result of a calorimetric determination of the enthalpy of formation of the complex ions,  $\text{HSO}_4^-$ ,  $\text{NaSO}_4^-$ ,  $\text{LiSO}_4^-$ ,  $\text{MgSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CdSO}_4$ ,  $\text{CuSO}_4$ ,  $\text{CoSO}_4$  in aqueous solution.

The calorimetric observations involve finding the enthalpy change accompanying the one-hundred-fold dilution of the cation concerned in complex formation, both in the presence or absence of sulphate ions.

For example:



The enthalpy change for complex-ion formation has been calculated from the difference between these two heat effects and the amount of complex formed according to known equilibrium constants.

## SORPTION ON POROUS MATERIALS AND THE USE OF DIELECTRIC MEASUREMENTS IN ITS INVESTIGATION

J. M. THORP

*Chemistry Department, University of Auckland.*

The sorption of gases and vapours in porous materials has important applications in an increasing number of industries and in a wide variety of fields, a few of which are outlined.

The phenomenon of sorption is discussed in general terms of layers of adsorbed molecules and capillary condensation. By

means of isotherms, information such as the surface area, mean pore radius and saturation volume, can be estimated.

Further information as to the state of the adsorbed molecules has recently been obtained by the determination of the changes in the apparent dielectric constant of a powdered adsorbent when known amounts of gas or vapour are added. If a plot is made of the change in capacitance (or dielectric constant) against the amount adsorbed per g of adsorbent, a definite change in slope is found to occur at the completion of a uni-molecular layer. This method is being used at present to examine the phenomenon of capillary condensation in silica gel and alumina, using both polar and non-polar vapours.

#### REFERENCE

THORP, J. M. (1959): *Trans. Far. Soc.*, 55: 442.

### COMPOUNDS OF BIOCHEMICAL INTEREST PRESERVED IN GEOLOGICAL MATERIALS

MICHAEL H. BRIGGS

*Department of Chemistry, Victoria University of Wellington.*

Extracts of six different types of fossil-bearing rocks of widely differing ages were shown by paper chromatography to contain amino acids. The presence of peptides in a lower Pleistocene siltstone was demonstrated by the biuret reaction. Similar extracts from seven rock types devoid of fossils contained neither amino acids nor peptides. A water extract of the Mokoia carbonaceous chondrite contained a complex mixture of organic substances. No amino acids or peptides were present, but analysis by paper chromatography and spectroscopy indicated nitrogenous compounds that may be purines or degradation products of purines.

### THE APPLICATION OF ANION EXCHANGE AND SOLVENT EXTRACTION ENRICHMENT TECHNIQUES TO THE SPECTROCHEMICAL DETERMINATION OF TRACE ELEMENTS IN GEOLOGICAL MATERIALS

R. R. BROOKS

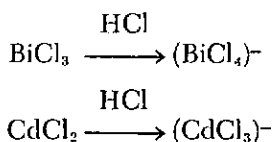
*Biochemistry Department, Massey College, Palmerston North.*

The spectrograph is ideally suited for trace element analysis in geological materials since not only does it enable many elements to be determined simultaneously but it is also highly sensitive for many of these.

Some ten elements (O, Si, Al, Fe, Mg, Ca, Na, K, Ti and Mn) comprise over 99% of the earth's crust but many of the remainder can be determined directly with the spectrograph although present at very low concentrations. There are certain elements such as Cd, Bi, Tl, etc., which usually have such low abundances that some form of enrichment is necessary before they can be determined satisfactorily.

In devising a procedure for enriching trace elements to the threshold of spectral sensitivity care must be taken that the volume of added reagents should be kept to a minimum to avoid contamination and that these reagents should be easily purifiable.

An enrichment procedure has been developed which is based on the fact that certain elements are able to form negatively charged chloro-complexes in the presence of hydrochloric acid, Namely:



By a most fortunate chance, none of the major constituents of the earth's crust (with the exception of iron which forms a very weak complex) are able to form chloro-complexes in 2*N* hydrochloric acid solutions whereas many of the trace elements form strong complexes at this normality.

The experimental procedure consists of dissolving the rock samples, adjusting the acid concentration to 2*N* with hydrochloric acid, passing the solution through an anion exchange column containing the strongly basic exchanger Amberlite IR 400 and washing the column with 2*N* acid. The major constituents of the rock are thereby washed out of the column and the absorbed trace elements can be eluted with a small quantity of *n*/4 nitric acid. The eluates are taken to dryness, collected in a sodium chloride carrier and determined spectrochemically.

Enrichment factors of up to 10,000 have been achieved by this method and the distribution of many trace elements (Zn, Cd, Bi, Tl, Sn, Au and the Pt metals) in silicate rocks has been studied. A modified procedure has been applied to the determination of Au, Cd and Bi in seawater where enrichment factors of up to 10<sup>7</sup> were achieved.

A solvent extraction enrichment technique has been developed in which Tl and In have been extracted as the iodo-complexes into ethyl ether and the extract determined spectrographically.

## QUANTITATIVE FLUORESCENCE ANALYSIS

W. S. METCALF

*Chemistry Department, University of Canterbury.*

A number of questions arise when one is devising a new method of fluorimetric analysis, or modifying an old one. The measurement of fluorescence and our understanding of the mechanism of fluorescence emission have both been advanced in recent years. This new knowledge contains answers or partial answers to some of the practical questions that follow.

What kinds of substance fluoresce? How can a reagent be converted into a fluorescent derivative?

Fluorescence and light absorption are always associated— which is the better property to use as a measure of concentration?

How does fluorescence depend on concentration, and how is this dependence modified by temperature, solvent, pH, ionic strength, and impurities?

What limits the accuracy and the sensitivity of a fluorimetric method?

What is the scope of a simple fluorimeter and how is this scope widened by increasing the complexity and expense of the source of exciting light and the detector of the fluorescence?

## THE REACTIVITY OF CO-ORDINATED ACETYLACETONE

F. J. B. ACGETT, D. R. LLEWELLYN and A. L. ODELL

*Chemistry Department, University of Auckland.*

There is much evidence that, when the tris-oxalato chromium-III anion is dissolved in water, its ligands undergo rapid "one-ended" dissociation and re-association reactions. Such ring openings account for the observed  $^{18}\text{O}$  exchange of the complex with solvent water at essentially the same rate as oxalic acid exchanges with water, and also account for the very much slower exchange rate of the  $^{14}\text{C}$ -labelled ligand with the complex.

Re-activities of tris-acetylacetonates of Fe-III, Cr-III and Co-III in aqueous media have now been studied but no trace of "one-ended" dissociation has been observed, the re-activity being dominated by aquation reactions.

## SOME METHODS OF PREPARATION OF STABLE ISOTOPE SAMPLES FOR MASS SPECTROMETRIC ANALYSIS

F. J. B. ACGETT, MISS C. J. BISHOP, D. R. LLEWELLYN  
and A. L. ODELL

*Chemistry Department, University of Auckland.*

Although radioactive isotopes have been used extensively in investigating chemical reactions the use of stable isotopes

has been somewhat restricted. One reason for this is the difficulty of obtaining the relevant atom in a suitable compound for isotopic abundance measurements in a mass spectrometer.

It is undesirable to introduce condensible organic compounds into a mass spectrometer and hence the experimenter is presented with the problem of converting the labelled atom of the starting material into a suitable gas without altering its isotopic abundance. This severely restricts the type of reaction which may be used and, for example, with  $^{18}\text{O}$  this precludes oxidation procedures.

Most workers in the  $^{18}\text{O}$  field have used pyrolytic procedures to crack organic compounds containing oxygen to form a mixture consisting mainly of carbon monoxide and low molecular weight hydrocarbons. This method suffers from the disadvantage that ethane, mass 30, is indistinguishable by mass spectrometry from  $\text{C}^{18}\text{O}$ , so that rigorous purification of the carbon monoxide is necessary if this gas is to be used directly for mass spectrometry. Lauder and co-worker (1) have overcome this difficulty by using bromine as a hydrocarbon scavenger. The present paper describes an improved cracker and an alternative method of eliminating ethane.

Carbon monoxide produced in the cracker is disproportionated into carbon dioxide and carbon by utilization of the reaction

$$2\text{CO} \longleftrightarrow \text{CO}_2 + \text{C}$$

A 2,500 volt a.c. discharge between parallel copper plates promotes this reaction, and the carbon dioxide which is quenched out on a liquid-air cooled surface is readily purified by pumping off non-condensable gases.

Preparations of  $^{13}\text{C}$  and  $^{15}\text{N}$  samples do not present the same difficulties, as oxidation methods are permissible—*e.g.*, in studies on the isotopic fractionation of HCN by distillation the  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopic abundances were determined on single samples of  $\text{H}^{13}\text{C}^{15}\text{N}$  after conversion to  $\text{CO}_2$  and  $\text{N}_2$ . The sample was first passed over hot  $\text{CuO}$  to produce  $\text{CO}_2$ , which was condensed out with liquid air, and then over hot copper to reduce the  $\text{NO}$  formed to  $\text{N}_2$ .

#### REFERENCE

- (1) LAUDER, I., ZERNER, B. (1959): *Aust. J. Chem.*, 12: 621.  
LAUDER, I., WILSON, I. R. (1959): *Aust. J. Chem.*, 12: 613.

### AMINE EXCHANGE AND THE TRANS EFFECT IN PLATINUM II COMPLEXES

T. P. CHEESEMAN, D. R. LLEWELLYN and A. L. ODELL  
*Chemistry Department, University of Auckland.*

Directing influences in substitution reactions of 4 coordinate platinum II "square" complexes have been known for a

long time. Present theories recognize two factors which determine the steric course and speed of such reactions:

- (a) An Inductive effect, arising from electrostatic phenomena within the molecule.
- (b) A Mesomeric effect arising from  $\pi$  orbital interactions.

The former effect is always present and accounts for some small observed changes in rate, but the latter occurs only in the case of strongly trans directing ligands and is responsible for large changes in rate.

Chat (1) has measured N-H stretching frequencies (by infra-red methods) of secondary amines co-ordinated trans to various other ligands in Pt II complexes. He has shown that, if these measurements can be taken as a measure of Pt-N bond strengths, the latter depend mainly on inductive phenomena but in strongly trans directed cases are also dependent upon the mesomeric redistribution of electrons in the vicinity of the directing ligand. Other minor effects may also be contributing.

The present paper discusses variations in the rate of exchange of  $^{14}\text{C}$ -labelled diethylamine with platinum complexes containing this ligand as a measure of the lability of the group when it lies trans to a variety of reference groups. Correlations with N-H stretching frequencies are considered.

#### REFERENCE

- (1) CHATT, J. (1958): *J. Inorg. Nuc. Chem.*, 8: 67.

## A NEW TECHNIQUE OF TRITIUM EXCHANGE KINETICS

A. T. WILSON

*Chemistry Department, Victoria University of Wellington.*

A new technique of tritium exchange kinetics will be presented. Examples will be given of its use to study weak chemical bonding, for example, the properties of water adsorbed on to wool, nylon, clay, minerals, etc. Its use to study the environment of a keto group in an organic compound will also be discussed.

## RADIOCHEMICAL METHODS IN WATER AND SEWAGE TREATMENT RESEARCH

J. K. JOHANNESSON

*Wellington City Corporation Laboratory.*

The use of isotopes for tracer and radiochemical methods of analysis here found a very useful place in the field of water and sewage treatment, along with such techniques as polarography and spectrophotometry.

During investigation in the author's laboratory, of sewage treatment by electrolysis of sea water and sewage mixtures, the use of  $^{36}\text{Cl}$  has provided a means of determining perchlorate ion by means of isotopic dilution with labelled perchlorate, the preparation and use of which will be described. Further the combination of free chlorine labelled with  $^{30}\text{Cl}$  enables the measurement of the uptake of this element in both the reduced as well as the N-chlorinated form in the bacterial cells.

The use of  $^{32}\text{P}$  with liquid cell counting has proved a very simple method of following the formation of  $\text{Mg}(\text{OH})_2$  and its subsequent removal together with flocculated sewage by the cathodically produced hydrogen. This is due to the adsorption of the phosphate on the floc.

The fertility of the reservoirs and the action of chlorine and of copper upon algae have been studied in the W.C.C. Laboratory by following the photosynthetic uptake of carbon dioxide labelled with  $^{14}\text{C}$ , and these are now routine methods for observing the action of chlorination. Prior to this there was no ready method for assessing the viability of algae since observation and measurement were visual using the microscope, and did not distinguish between viable and moribund forms.

At present a method of estimating small quantities of sulphate in water is being examined. A sample of water is ion exchanged and a known amount of sodium sulphate  $^{35}\text{S}$  is added, the solution evaporated to dryness and counted.

The measurement of river flow may be carried out by addition of an isotope and integrating the amount found downstream. The application of this method to the Manawatu River where 10 mc of  $^{131}\text{I}$  was used will be described.

## ISOFLAVONES FROM RED CLOVER

E. WONG

*Plant Chemistry Division, D.S.I.R., Palmerston North.*

Red clover (*Trifolium pratense*) is known to contain the isoflavones biochanin-A, genistein and formononetin. The oestrogenic activity of red clover is presumably associated with the occurrence of these compounds. Two more isoflavones have now been found to occur in red clover. Daidzein (4', 7-dihydroxyisoflavone) was identified on chromatographic and spectral evidence. The second compound, present only as a very minor constituent, has been isolated. The chemistry of this isoflavone and its probable identity will be discussed. The oestrogenic activity of the isoflavones and their individual contributions to the total activity of the plant material will also be discussed.

## EXTRACTIVES FROM THE BARK OF LEPTOSPERMUM SCOPARIUM

R. E. CORBETT, M. A. McDOWALL and S. G. WYLLIE  
*Chemistry Department, University of Otago.*

Hexane extraction of the outer bark of *Leptospermum scoparium* gave a waxy solid (7.5%). This has been separated into acid and neutral fractions by treatment with alkali.

The acid fraction has given three triterpene acids, acetyl ursolic acid, betulic acid, and oleanolic acid, by chromatography on silica gel.

The neutral fraction was chromatographed on alumina. Elution with appropriate solvents has given the following seven fractions: aliphatic esters, aliphatic alcohols, a phenolic ester, a sterol fraction, a triterpenoid hydroxylactone, a triterpenoid diol, and a triterpenoid ester.

The saponification products of the aliphatic esters have been identified by gas chromatography as have been the alcohols combined with p-coumaric acid to form the phenolic ester.

## INTERACTION BETWEEN AMINO COMPOUNDS AND SUGARS

E. L. RICHARDS

*Biochemistry Department, Massey Agricultural College, Palmerston North.*

The interaction between amino acids or protein and reducing sugars has been shown to be the cause of much of the browning that occurs during the manufacture and storage of dried foods. It is assumed that the first step in the reaction is the formation of glycosylamines which undergo the Amadori rearrangement to form 1-amino-1-deoxyketose derivatives. These compounds can then be dehydrated and cyclized to form furan derivatives and eventually brown polymers.

Recently diketose amines have been isolated from further reaction of the sugar with the 1-amino-1-deoxyketose derivatives and these compounds possibly have an important role in non-enzymic browning reaction.

Browning of dried skim milk or a synthetic lactose-casein mixture at 40° C, 70% RH and pH 6.4 produces degradation of the lactose similar to the alkaline degradation of the sugar and a theory is proposed to explain this.

## CARBOXYLIC ACIDS OF HYDROCARBONS RELATED TO NAPHTHALENE

J. MITCHELL, R. D. TOPSOM and J. VAUGHAN  
*Chemistry Department, University of Canterbury.*

Carboxylic acid derivatives of the following compounds have been prepared, (a) naphthalene, (b) 1-methylnaphthalene,

(c) acenaphthene, (d) 1,8-dimethylnaphthalene and their  $pK_a$  values determined.

In the series of acids with the carboxyl group "para" to an alkyl substituent, only 1,8-dimethyl-4-naphthoic acid is of particular synthetic interest. The important step in this synthesis was a much improved preparation of the parent hydrocarbon. The  $pK_a$  sequence for the series indicates unambiguously that interference between the two methyl groups in 1,8-dimethyl-4-naphthoic acid results in a loss of coplanarity.

The acids with the carboxyl group "ortho" to an alkyl substituent were of greater general synthetic interest. The Hauser rearrangement was the basis of the synthesis of 1-methyl-2-naphthoic and 1,8-dimethyl-2-naphthoic acids but, as might be expected from spacial considerations, 3-acenaphthoic acid could not be prepared in this way. Several alternative synthetic methods are available, however, for this acid. The sequence of acidity constants in this "ortho" series may be related to the degree of steric interference in each compound and the ultraviolet spectra generally support this.

## THE EFFECT OF PREHYDROLYSIS ON THE KRAFT PULPING OF *PINUS RADIATA*

D. J. BRASCH and K. W. FREE

*Dominion Laboratory, D.S.I.R., Wellington.*

Run-of-the-mill chips of *Pinus radiata* have been hydrolysed with hot (140-180° C) water under a wide range of conditions, and then pulped using a conventional kraft cooking process. The chemical properties of both the hydrolysed chips and the kraft pulps have been determined. It has been found that prehydrolysis conditions can be chosen to yield a kraft pulp with an alpha cellulose content of 96%, which is low in pentosans, and which has good bleaching characteristics. If the prehydrolysis conditions used are mild, the resulting kraft pulp is lower in alpha cellulose and high in pentosan. However, a hydrolysis carried out at either too high a temperature or for too long a time is also undesirable, since in this case kraft pulps with high lignin content are obtained in low yield. Little increase in alpha cellulose is achieved by a too severe prehydrolysis.

An attempt has been made to define the main effects of prehydrolysis on the chemical properties of a prehydrolysed kraft pulp by extending the concept of "reactivity factor" to the hydrolysis stage. This factor is derived by considering the following: (1) Maximum temperature of prehydrolysis, (2) time taken to reach the maximum temperature, (3) time of hydrolysis

at the maximum temperature. By calculating the reactivity factor for any given set of prehydrolysis conditions, some of the chemical properties of a prehydrolysed kraft pulp can be predicted.

## FERTILIZERS FOR AERIAL TOPDRESSING OF NEW ZEALAND SULPHUR-DEFICIENT SOILS

H. P. ROTHBAUM

*Dominion Laboratory, D.S.I.R., Wellington.*

Plants contain approximately twice as much sulphur as phosphorus, and Bogdanov first suggested 60 years ago that sulphur-deficiency might develop in grasslands. In New Zealand, Doak demonstrated a response of lucerne to sulphur addition in 1929, but farmers became concerned only when, in 1953, Lobb publicized the beneficial effects of sulphur on clover; since then, large quantities of sulphur-containing fertilizers have been used. Sulphur-deficiency was noticed so late because superphosphate and ammonium sulphate both happen to contain sulphur, and industrial smoke also deposits large quantities of sulphur. This last factor confines sulphur-deficiency to thinly-industrialized countries like Australia and New Zealand. In addition, both these countries apply much of their fertilizer by aerial topdressing, so that fertilizers specially formulated to suit our conditions are needed.

It is found that inorganic sulphur acts quicker than organic sulphur, and small particle sizes more rapidly than large particles. Leaching, cost of materials, and inflammability of elemental sulphur must also be taken into consideration and gypsum and elemental sulphur appear to be the only practical alternatives for fertilizers specifically designed for sulphur-deficiency. Gypsum is quick-acting, but fairly expensive in New Zealand, while elemental sulphur is relatively cheap, but slow-acting if in the form of coarse particles. Finely divided sulphur, however, forms dust-clouds with serious explosion hazards, and must therefore be diluted before spreading.

The relation between particle size of sulphur and effect of diluent on explosion, inflammability, and electrostatic discharge risk was examined. It was found that the limiting safe sulphur content is inversely proportional to the specific surface of sulphur in fertilizer mixtures. Superphosphate and gypsum were found to be better explosion-dampers than limestone, possibly because limestone contains no water of crystallization. Taking all factors into consideration, it is considered that 23% commercial screened

sulphur is the maximum safe constitution. In highly sulphur-deficient areas, gypsum is a suitable diluent. For general use, superphosphate is the best diluent, as, although more expensive, it simultaneously supplies essential phosphate. Limestone is not a suitable diluent.

## FORMS OF SOIL PHOSPHATE AND THEIR SOLUBILITY IN VARIOUS SIMPLE EXTRACTANTS

J. L. GRIGG

*South Island Soil Testing Station, Taieri.*

Soil phosphate occurs in many forms of combination, those of most importance being:

- (1) Primary minerals such as hydroxyapatite.
- (2) Secondary forms—*e.g.*, variscite, strengite, phosphate adsorbed on hydrous oxides of aluminium and iron and on aluminosilicates; phosphate adsorbed on calcium carbonate, mono-, di- and octo-calcium phosphates.
- (3) Organically bound phosphate.

Recent fundamental work has enabled a number of the inorganic forms to be separated by a sequence of extractions giving a broad classification of the phosphate into several fractions:

- (1)  $\text{NH}_4\text{F}$  soluble: Aluminium bound phosphate, mono- and di-calcium phosphates.
- (2)  $\text{NaOH}$  soluble: Iron bound phosphates.
- (3)  $\text{H}_2\text{SO}_4$  soluble: Apatite phosphate.
- (4) Citrate-dithionite soluble: Phosphate occluded in crystals of iron oxide.

The first three fractions include most forms likely to be available in greater or less degree to plants.

Four groups of South Island soils have been examined for the relative proportions of these fractions. Results have been compared with the amounts extracted by several widely used procedures for measuring "available" phosphate, the Truog, Bray No. 1 and No. 2 and Olsen methods, and a method of extraction using an ion exchange resin.

Since it was not possible to determine the 3 fractions before and after extraction with these solutions owing to changes in distribution of the phosphorus (*e.g.*, re-adsorption by ferric oxides of dissolved apatite phosphorus), multiple regression techniques have been used to measure the correlation with the forms extracted.

Results indicate the following significant regression coefficients:

- (1) The Truog and Bray No. 2 methods correlate significantly with the  $\text{NH}_4\text{F}$  and  $\text{H}_2\text{SO}_4$  soluble forms.
- (2) The Bray No. 1 and Olsen methods and the resin extraction correlate only with the  $\text{NH}_4\text{F}$  soluble form.

A practical consequence of this is that the method at present used by the Soil Testing Service (Truog) is likely to give erroneous results on soils high in apatite phosphorus which is of little availability to plants or on soils to which ground rock phosphate has been applied, especially on soils low in iron and aluminium oxide. Such soils include the recent alluvial soils derived from greywacke of the east coast of the South Island, and some Brown-grey earths of the dry upland regions. These soils give high Truog tests yet respond to phosphate applications. On these soils the Bray No. 1 or Olsen methods give results more in line with phosphate fertility level.

## THE USE OF TWO-DIMENSIONAL NUCLEOTIDE MAPS IN THE STUDY OF NUCLEIC ACIDS

G. B. PETERSEN

*Plant Chemistry Division, D.S.I.R., Palmerston North.*

The separation of large oligonucleotide fragments obtained through the chemical or enzymic degradation of deoxyribonucleic acid (DNA) or ribonucleic acid (RNA) has until now proved to be difficult. Our observation that the removal of terminal monoesterified phosphate groups from pyrimidine polydeoxynucleotides greatly enhances their mobility on paper electrophoresis has led to a method of separating virtually all the pyrimidine poly-nucleotide sequences in DNA.

DNA is degraded with diphenylamine in acid solution to products in which the pyrimidine nucleotide sequences of the original DNA molecules are represented as pyrimidine oligonucleotides of varying length, each of which bears two terminal monoesterified phosphate groups.

After terminal dephosphorylation with phosphomonoesterase this mixture of products was submitted to paper electrophoresis in one dimension followed by chromatography in the direction at right angles to the electrophoresis. The oligonucleotide fragments were found to be well-separated by this procedure and in this way a two-dimensional "map" of the pyrimidine oligonucleotide sequences of the DNA was obtained. Sequences of up to eight nucleotides have been separated and identified. This

procedure promises to be of value in the study of DNA obtained from various sources.

The application of the method to enzymic digests of DNA and RNA is being examined and results will be reported at the meeting.

## **RIBONUCLEIC ACID FRACTIONS FROM WHEAT GERM**

J. W. LYTTLETON

*Plant Chemistry Division, D.S.I.R., Palmerston North.*

Two main classes of ribonucleic acid (RNA) are now recognized as occurring in most living cells. These are (1) a high molecular weight RNA (*c.* 800,000-2,000,000) which is associated with protein in nucleoprotein particles (ribosomes), and (2) a lower molecular weight RNA (soluble RNA, 20,000-50,000) which exists free in the supernatant of the centrifuged cell extract. Both these classes of RNA have been isolated from wheat germ, and characterized in terms of their sedimentation behaviour in the ultracentrifuge and their base composition.

The isolation methods and the probable significance of these fractions in protein synthesis will be discussed.

## **THE ROLE OF PROLINE IN PLANT REPRODUCTION**

R. M. ALLISON

*Crop Research Division, D.S.I.R., Christchurch.*

The high solubility and neutrality of proline make it an admirable storage compound for nitrogen and carbon. Its formation from glutamic acid is well established in a number of organisms, and the reversal of these enzymatic steps would enable it to be utilized by plant tissues, for transamination and oxidation via the Krebs cycle. Evidence implicating proline in plant reproduction processes will be presented.

## **STRUCTURAL STUDIES ON SPORIDESMIN**

E. P. WHITE

*Ruakura Animal Research Station, Hamilton.*

The formula  $C_{15}H_{20-22}ClN_3O_6S_2$  has been established by analysis of four crystalline solvates ( $CCl_4$ , benzene,  $CH_2Br_2$ ,  $CH_3I$ ), and of the diacetate.

Analysis for groups and identification of products formed, and techniques of U.V., I.R., N.M.R. establish the following: (1) Two  $-OCH_3$  groups on an aromatic nucleus ( $-SCH_3$  is ruled out).

- (2) Two  $-NCH_3$  groups, one associated with  $C=O$  as hydrolysis gives one equivalent of methylamine. The other is likely to be similar in a cyclic system.
- (3) One  $-CCH_3$  probably associated with a double bond or  $-NH-$ ; Kuhn-Roth determination gives 0.3 groups.
- (4) No  $-CH_2$  groups. One  $-CH$  is aromatic.
- (5) One  $-OH$  is an enol, titratable with  $NaOH$ ; in water it is in enol form as the U.V. spectrum does not alter on adding  $NaOH$ . The other  $-OH$  is alcoholic. In the diacetate the  $6.00 \mu$   $C=O$  band disappears, and no  $-OH/-NH$  stretching remains. Diazomethane gives no methylation and preparation of other acyl derivatives failed.
- (6) Two likely  $C=O$  bands in the I.R. one giving the enol, the other at  $5.86 \mu$  typical of a ketone but probably  $C=O$  of a cyclic methylimide.
- (7) Sulphur may be as  $-S-S-$  on analogy with gliotoxin and  $-S-S-$  compounds particularly when associated with  $C=O$ .
- (8) N.M.R. shows at least 20 protons—3 peaks cannot be assigned with certainty.

Degradations produced a variety of products each in low yield. Catalytic hydrogenation worked only with Adams' catalyst giving  $H_2S$  and a complex mixture. Techniques expected to give a *des-thio* compound removed sulphur, giving mixtures. Acid reductions usually gave  $H_2S$ .  $LiAlH_4$  gave a mixture of basic products. Acid degradation gave products soon becoming coloured. A product of "natural breakdown" of impure sporidesmin is probably  $C_{12}H_{12}ClNO_4$  and is a red isatin or quinolinedione-like compound. This was identified from at least 5 degradation techniques. This suggests a  $C_{12}$  unit containing two  $-OCH_3$ , one  $-NCH_3$ , and  $C=O$ , and another part containing  $-NCH_3$ ,  $-OH$  and  $C=O$ . Possibly  $-S-S-$  holds these together.

Sporidesmin-B has been obtained from cultures. This has similar I.R. and U.V. spectra and O- and N-methyl contents to sporidesmin.

## INSECT DEHYDROGENASES

G. B. KITTO

Department of Chemistry, Victoria University of Wellington.

A study has been conducted on the dehydrogenase enzyme systems of some New Zealand insects. The tissue levels of some dehydrogenases have been determined and the significance of their variation is discussed. Insects used were: katydid, *Caedicia simplex*; mantis, *Othodra ministralis*; weta, *Hemideina thoracica*; stick-insect, *Argosarchus horridus*.

**CONFERENCE PROGRAMME****Tuesday Evening, August 29**

8.00 p.m. Informal Gathering.

**Wednesday Morning, August 30**

- 9.00 a.m. Registration.  
 10.30 a.m. Morning Tea.  
 11.00 a.m. Opening of Conference.  
 11.30 a.m. Presidential Address.

**Wednesday Afternoon****A Series** **Pages 123-7**

- 2.00 p.m. The Structure of Tetrameric Hydrogen Cyanide (M. P. Hartshorn and J. Vaughan).  
 2.18 p.m. A Comparison between the Complex Oxalates of Iron (III) and Ruthenium (III) (A. L. Odell and R. W. Olliff).  
 2.36 p.m. Iodides of Transition Metals Rhenium and Osmium (J. E. Fergusson, B. H. Robinson and W. R. Roper).  
 2.54 p.m. A Calorimetric Study of the Formation of some Sulphate-Cation Complexes in Water (J. M. Austin and A. D. Mair).  
 3.12 p.m. Sorption on Porous Materials and the Use of Dielectric Measurements in its Investigation (J. M. Thorp).

**B Series** **Pages 127-9**

- 2.00 p.m. Compounds of Biochemical Interest Preserved in Geological Materials (M. H. Briggs).  
 2.18 p.m. The Application of Anion Exchange and Solvent Extraction Enrichment Techniques to the Spectrochemical Determination of Trace Elements in Geological Materials (R. R. Brooks).  
 2.36 p.m. Quantitative Fluorescence Analysis (W. S. Metcalf).  
 3.30 p.m. Afternoon Tea.

**A Series** **Pages 129-32**

- 4.00 p.m. The Reactivity of Co-ordinated Acetylacetonone (F. J. B. Aggett, D. R. Llewellyn and A. L. Odell).  
 4.18 p.m. Some Methods of Preparation of Stable Isotope Samples for Mass Spectrometric Analysis (F. J. B. Aggett, Miss C. J. Bishop, D. R. Llewellyn and A. L. Odell).  
 4.36 p.m. Amine Exchange and the Trans Effect in Platinum II Complexes (T. P. Cheeseman, D. R. Llewellyn and A. L. Odell).  
 4.54 p.m. A New Technique of Tritium Exchange Kinetics (A. T. Wilson).  
 5.12 p.m. Radiochemical Methods in Water and Sewage Treatment Research (J. K. Johannesson).

**B Series****Pages 132-4**

- 4.00 p.m. Isoflavones from Red Clover (E. Wong).  
 4.18 p.m. Extractives from the Bark of *Leptospermum scoparium* (R. E. Corbett, M. A. McDowall, S. G. Wyllie).  
 4.36 p.m. Interaction between Amino Compounds and Sugars (E. L. Richards).  
 4.54 p.m. Carboxylic Acids of Hydrocarbons Related to Naphthalene (J. Mitchell, R. D. Topsom and J. Vaughan).  
 5.12 p.m. The Effect of Prehydrolysis on the Kraft Pulping of *Pinus radiata* (D. J. Brasch and K. W. Free).

**Wednesday Evening**

- 8.00 p.m. Public Lecture by Professor R. C. L. Bosworth entitled "Energy and the Limits of the Earth's Resources."

**Thursday Morning, August 31**

Visits (See Conference Notice Board).

**Thursday Afternoon**

- 2.00 p.m. Developments in Macro Kinetics (Professor R. C. L. Bosworth—Guest Lecturer).  
 3.15 p.m. Afternoon Tea.

**A Series****Pages 135-7**

- 3.45 p.m. Fertilizers for Aerial Topdressing of New Zealand Sulphur-Deficient Soils (H. P. Rothbaum).  
 4.03 p.m. Forms of Soil Phosphate and their Solubility in Various Simple Extractants (J. L. Crigg).

**B Series****Pages 137-9**

- 3.45 p.m. The Use of Two-Dimensional Nucleotide 'Maps' in the Study of Nucleic Acids (G. B. Petersen).  
 4.03 p.m. Ribonucleic Acid Fractions from Wheat Germ (I. W. Lyttleton).  
 4.21 p.m. The Role of Proline in Plant Reproduction (R. M. Allison).  
 4.39 p.m. Structural Studies on Sporidesmin (E. P. White).  
 4.57 p.m. Insect Dehydrogenases (G. B. Kitto).

**Thursday Evening**

- 8.00 p.m. Social Function.

**Friday Morning, September 1****A Series****Pages 143-4**

- 9.00 a.m. The Distribution of Magnesium in N.Z. Soils (A. I. Metson and R. B. Miller).  
 9.18 a.m. The Effect of Fertilizer Applications on Soil Magnesium (D. E. Hogg).  
 9.36 a.m. Magnesium Deficiency in Pastures (K. J. McNaught).  
 9.54 a.m. The Determination of Magnesium by Atomic Absorption Spectroscopy (J. E. Allan).

**B Series****Pages 144-51**

- 9.00 a.m. Studies on the Lipids of the Common Pea (*Pisum sativum* L.) with Special Reference to the Occurrence of Galactolipids (S. Adhikari and F. B. Shorland).
- 9.18 a.m. The Effect of Butylated Hydroxytoluene on the Incorporation of Acetate  $1^{14}\text{C}$  into the Lipids of the Rat (A. R. Johnson).
- 9.36 a.m. Composition of Fat from Various Parts of Polled Angus Steer (S. Adhikari, J. G. Colebrook and S. G. Brooker).
- 9.54 a.m. The Preparation and Properties of Isomeric Octadecadienoates and Octadecatrienoates (D. R. Body).
- 10.12 a.m. Studies on the Composition of Milk Phospholipids (L. M. Smith).
- 10.30 a.m. Morning Tea.
- 11.00 a.m. Theory and Application of Nuclear Magnetic Resonance (I. K. Walker).
- 11.18 a.m. Recent Advances in Atomic Absorption Spectroscopy (J. E. Allan).
- 11.36 a.m. Electronic Spectra of Co-ordination Compounds (N. F. Curtis).
- 11.54 a.m. Applications of Differential Infra-red Spectroscopy (B. Cleverley).

**Friday Afternoon**

- 2.00 p.m. Easterfield Lecture (T. A. Turney).
- 3.00 p.m. Afternoon Tea.
- 3.30 p.m. Annual General Meeting, N.Z.I.C.
- 5.00 p.m. Annual General Meeting of the N.Z. Section of the R.I.C.

**CONFERENCE COMMITTEE**

Professor D. R. Llewellyn (Chairman), *Programme*; Mr R. C. Selkirk (Deputy Chairman), *Accommodation*; Miss M. P. Bartrum, *Ladies' Entertainment*; Mr C. W. Harland, *Visits and Excursion*; Mr D. G. Howard, *Films*; Mr L. W. Jagger, *Social Function*; Mr R. S. Jebson, *Visits and Excursion*; Mr H. S. Maslen, *Registration*; Mr D. S. Milne, *Public Relations*; Mr D. A. Morrison, *Exhibition*; Mr R. W. Oliff, *Registration*; Mr T. H. Wilson, *Teas and Exhibition*; Mrs J. M. Waters (Secretary-Treasurer), *Programme*.

**OFFICIAL NOTICE**

A General Meeting of members of the New Zealand Institute of Chemistry (Inc.) will be held in the Chemistry Department, University of Auckland, on Friday, September 1, 1961, at 3.30 p.m.

**AGENDA**

1. Apologies, welcome, etc.
2. Confirmation of Minutes of the last General Meeting held at Victoria University of Wellington on Thursday, August 25, 1960.
3. Institute Prizes for 1961.
4. Officers for the coming year.
5. Annual Report for the year ending July 31, 1961.
6. Balance Sheet for the year ending April 30, 1961.
7. General.

W. E. HARVEY,  
Hon. General Secretary.

## THE DISTRIBUTION OF MAGNESIUM IN N.Z. SOILS

A. J. METSON and R. B. MILLER  
*Soil Bureau, D.S.I.R., Wellington.*

## EFFECT OF FERTILIZER APPLICATIONS ON SOIL MAGNESIUM

D. E. HOGG  
*Rukuhia Soil Research Station, Hamilton.*

The effect of various fertilizers, particularly potassium chloride, on accelerating losses of magnesium, has been studied through successive leachings of columns of soil 2 in. in diameter. Fertilizers were applied to the surface and mixed in the top  $\frac{1}{2}$  in. of soil. Following each leaching with water, the columns were partially dried in a draught of air at 25° C. A study on Horotiu sandy loam showed an immediate loss of magnesium following the application of potassium chloride.

That these magnesium losses were also occurring in the field was shown by soil sampling a rates of potassium trial, exchangeable Mg decreasing with increasing rates of K.

The laboratory technique described has been applied to other representative soils. Comparative losses of magnesium following KCl applications are presented.

The role played by nitrogenous fertilizers in accelerating magnesium losses is shown both by laboratory studies and by declining exchangeable Mg levels in long-term field trials.

The effect of additions of serpentine superphosphate on exchangeable magnesium levels in the soil has been studied in the laboratory by comparing additions of serpentine superphosphate with straight superphosphate. In the soils examined, the increase in exchangeable magnesium approximated the water-soluble Mg content of the serpentine super. applied.

Figures are presented showing the range of exchangeable magnesium levels found in a recent survey on pumice soils.

## MAGNESIUM DEFICIENCY IN PASTURES

K. J. McNAUGHT  
*Rukuhia Soil Research Station, Hamilton.*

Pasture responses to magnesium nutrient are relatively uncommon. Last year responses were obtained in a field trial at the Forestry Nursery at Kaingaroa on Te Rere sand and early

this year responses appeared in a similar trial at Whakarewarewa on Whakarewarewa sandy loam after re-topdressing. The soil at Kaingaroa contained only 0.07 m.e.% exchangeable magnesium, that at Whakarewarewa 0.12 m.e.%.

Plant magnesium levels in the control plots have been of the order of 0.10 to 0.15% of the dry matter in both trials. White clover leaves showing deficiency symptoms have magnesium levels below 0.1%.

The magnesium requirement for optimum growth of white clover may be about 0.13 to 0.15%; for red clover possibly slightly higher. In these trials, levels in associated grasses were similar to those in the white clover, but on soils of higher magnesium status, the concentration in clovers is normally 25 to 50% higher than in associated grasses.

## THE DETERMINATION OF MAGNESIUM BY ATOMIC ABSORPTION SPECTROSCOPY

J. E. ALLAN

*Rukuhia Soil Research Station, Hamilton.*

Atomic absorption spectroscopy provides a simple and reliable method for the determination of magnesium. The sensitivity limit is about 0.01 ppm, and concentrations greater than about 0.1 ppm can be determined with a reproducibility of 1-2%. Interference effects are few. The equipment required and the application of the method to the determination of magnesium in materials of agricultural interest will be described.

## STUDIES ON THE LIPIDS OF THE COMMON PEA, WITH SPECIAL REFERENCE TO THE OCCURRENCE OF GALACTOLIPIDS

S. ADHIKARI and F. B. SHORLAND

*Fats Research Laboratory, D.S.I.R., Wellington.*

Although galactose is well known in the field of lipid chemistry as part of the cerebroside molecule in the fatty matter of the brain the occurrence of galactose or of other sugars in plant lipids has only recently become known. Following the identification in wheat flour of galactosyl-*l*-glycerol esters of fatty acids by Carter and co-workers in 1956 investigations in the Fats Research Laboratory by Weenink and others have established that galactolipids and not triglycerides, as previously supposed, are the main lipid constituents of grasses, clovers and of leaves generally. Simultaneously Benson and co-workers found that

galactolipids comprise an appreciable portion of the first formed products of photosynthesis by the organism *Chlorella*.

As an extension of the work on the occurrence and formation of galactolipids in plants we have examined the seeds, pods, stalks and leaves of the common pea (*Pisum sativum* L.). It has been found that the leaves contain, as expected, galactolipids as the main lipid constituent but galactolipids also occur in minor amounts in all the tissues examined. Most seed oils which have been examined are from seeds with a high yield of oil suitable for commercial utilization and their properties indicate that they are almost entirely triglycerides. Pea seeds, on the other hand, yield only about 4% of oil which is mainly non-glyceridic and contains definite amounts of galactolipid. The investigation has so far not established a relationship between the occurrence of chlorophyll and galactolipid but the presence of galactolipid in a green seed is perhaps suggestive in this regard.

## THE EFFECT OF BUTYLATED HYDROXYTOLUENE ON THE INCORPORATION OF ACETATE $1^{14}\text{C}$ INTO THE LIPIDS OF THE RAT

A. R. JOHNSON

*Fats Research Laboratory, D.S.I.R., Wellington.*

It has been previously established (1) that an increase in the fat level of the diet of the rat enhances the chronic toxicity of the antioxidant butylated hydroxytoluene (BHT). BHT promotes a linear increase in serum cholesterol levels (2). These effects were not observed with two other antioxidants, butylated hydroxy anisole and propyl gallate.

In the present investigations (3) the previous findings on the effect of 0.5% dietary BHT on growth and cholesterol levels were confirmed. In addition it has been shown that the effects of BHT on the incorporation of  $^{14}\text{C}$  labelled acetate into the lipids of the animal were in the main dependent upon the presence of dietary lard.

Irrespective of the presence or absence of lard, BHT produced increases in the basal metabolic rate, in the concentration of carcass and blood cholesterol and of liver and blood phospholipid and in the rate of synthesis of carcass cholesterol and liver free cholesterol.

In the absence of lard, BHT generally increased the rate of lipid synthesis as shown by an increased rate of turnover of carcass fatty acids, and in the rate of synthesis of liver ester cholesterol, total liver lipid, fatty acid and phospholipid. There

was also an increase in the recovery of  $^{14}\text{C}$  labelled expired  $\text{CO}_2$  after 1 hour but a reduction after 3 hours owing to increased incorporation into the depot fatty acids. All these effects can be explained by an increase in the availability of acetyl co-enzyme A.

In the presence of lard BHT decreased the incorporation of  $^{14}\text{C}$  into the carcass and liver fatty acids and reduced the rate of synthesis of liver ester cholesterol and phospholipid. It is recognized that the tissue fatty acids and the fatty acid moiety of the cholesterol esters and phospholipids can be derived either from acetyl coenzyme A or exogenous fat. It is suggested that the presence of large amounts of exogenous fat depresses the endogenous synthesis of fatty acids and the animal is unable to utilize for fatty acid synthesis the increased amounts of acetyl co-enzyme A induced by BHT.

#### REFERENCES

- (1) DAY, A. J., JOHNSON, A. R., O'HALLORAN, M. W., SCHWARTZ, C. J. (1959): *Austral. J. exp. Biol.*, 37: 295.
- (2) BROWN, W. D., JOHNSON, A. R., O'HALLORAN, M. W. (1959): *Ibid.*, 37: 533.
- (3) JOHNSON, A. R., HOLDSWORTH, E. S.: *In preparation.*

### COMPOSITION OF FAT FROM VARIOUS PARTS OF POLLED ANGUS STEER

S. ADHIKARI

*D.S.I.R., Dacca, East Pakistan\**

J. G. COLEBROOK and S. G. BROOKER

*Abels Limited, Auckland.*

Fatty tissues were obtained from a prime Polled Angus steer aged two years. The tissues were digested in a domestic pressure cooker to give five types of fats—kidney, caul, anus, back and cod. These have been analysed for the usual constants with the results given in Table 1.

TABLE 1

Type of Fat	Iodine Value	Saponification Equivalent	Unsaponifiable Matter	Melting Point (Capillary Tube)
Kidney	36.9	285	—	48.0° C.
Back	54.3	283.5	0.44%	36.5° C.
Caul	38.4	285	0.51%	48.5° C.
Anal	38.1	284	0.49%	46.0° C.
Cod	48.2	283	0.57%	41.0° C.

\*Temporarily attached to Fats Research Laboratory, D.S.I.R., Wellington, under the Colombo Plan.

The fats are also being examined for fatty acid composition by gas chromatography and the glyceride composition investigated (1) by permanganate oxidation followed by magnesium salt separation of oxidation products to give the relative proportions of mono-, di- and tri-unsaturated glycerides, (2) by lipase hydrolysis to decide the proportion of unsaturated fatty acids in the 1- and 2- positions in the glyceride molecules, and (3) by crystallization of fully saturated glycerides from acetone according to Kartha. Results of these investigations will be communicated.

## THE PREPARATION AND PROPERTIES OF ISOMERIC OCTADECADIENOATES AND OCTADECATRIENOATES

D. R. BODY

*Fats Research Laboratory, D.S.I.R., Wellington.*

Geometrical isomers of conjugated octadecadienoates have been prepared by the dehydration of ricinoleic acid (12-hydroxy-9-octadecenoic acid), which is the major fatty acid of castor oil.

The non-conjugated isomers were fractionally distilled under reduced pressure from their conjugated analogues as methyl esters. During this process it was found that a certain amount of separation between various conjugated octadecadienoates occurred as well.

Low temperature crystallizations of fractions rich in one or the other conjugated isomers yielded nearly pure *cis-trans* and *trans-trans* methyl esters. The configurations about the double bonds were determined by ultra-violet and infra-red spectroscopy.

During the course of investigations, a third isomer was found. It has been isolated as 80% pure by the application of successive urea complex fractionations and low temperature crystallizations. All the experimental and theoretical evidence obtained so far is consistent with the view that it is a *cis-cis* conjugated octadecadienoate.

These products from the dehydration of methyl ricinoleate have been compared with those obtained from the alkali isomerization of pure methyl linoleate. It has been shown that all three types of geometrical conjugated diene isomers are formed during the isomerization process.

The work on the conjugated isomers of methyl octadecatrienoate is only in the initial stages. A concentrate of methyl linolenate has been alkali isomerized and subjected to a series of low temperature crystallizations and urea fractionations. These fractions have been analysed by gas-liquid chromatography and

ultra-violet spectroscopy. The results indicated quite a complex composition. When pure methyl linolenate was isomerized, only 13.1% of conjugated triene was formed, the remainder being conjugated dienes and perhaps unchanged material. These conjugated dienes must still retain the third double bond, but in a position of at least two methylenic groups from the conjugated centre.

Throughout the work, gas-liquid chromatography has been used to follow the various preparative steps. Conjugated diene isomers could be analysed, the three main types of geometric isomers being clearly distinguishable; however, the conjugated trienes could not be estimated exactly because they partially isomerized while on the column.

## STUDIES ON THE COMPOSITION OF MILK PHOSPHOLIPIDS

PROFESSOR LLOYD M. SMITH

*Department of Food Science Technology, University of California, Davis, California.*

## THEORY AND APPLICATION OF NUCLEAR MAGNETIC RESONANCE

I. K. WALKER

*Dominion Laboratory, D.S.I.R., Wellington.*

The nuclear magnetic resonance phenomenon has progressed rapidly from its initial discovery in 1946 to become an essential tool of organic chemistry. This progress has resulted from the discovery that the magnetic field in a molecule is modified at any particular atomic nucleus by the immediate molecular environment. Chemists can thus use the nucleus as a probe to explore molecular structure. Commercial spectrometers are now available capable of resolution better than  $10^{-6}$ .

Any nucleus possessing spin will behave like a small bar magnet by virtue of its rotating positive charge, and to this magnetic effect will be coupled a gyroscopic effect caused by the rotating mass. If placed in a magnetic field, this gyromagnetic ratio will cause it to precess at a characteristic frequency if it be displaced from a position of rest. Since the magnetic field is modified by the molecular structure, the precession frequency will be similarly modified, and can be measured. The nuclei of particular interest to chemists are H, F, B, P and C, since these have a sufficient abundance of isotopes possessing spin. Of these by far the major chemical interest is in hydrogen. N.M.R. is of particular use here, since there is no other physical

tool available that can so easily sense the molecular environment in the proximity of hydrogen in organic molecules.

For the chemist's purpose, instruments using electromagnets are better than permanent magnets, since they provide a stronger field. This gives more distinct spectra, and better resolution. Wavelength calibration is carried out by comparing the resonance with that from a standard compound (such as water or benzene or cyclohexane in the case of protons).

There are seven major purposes for which the chemist can use N.M.R.:

- (1) Elucidation of structural formulae.
- (2) Detection of intermolecular interactions.
- (3) Investigation of tautomerism.
- (4) Measurement of interatomic distances in solids.
- (5) Detection of internal motions in crystals.
- (6) Analysis of water in organic materials.
- (7) Investigation of conduction electrons in metals.

As yet the major emphasis is on qualitative aspects rather than quantitative, but many laboratories are hopeful of putting the effect on a more quantitative basis in future.

## RECENT ADVANCES IN ATOMIC ABSORPTION SPECTROSCOPY

J. E. ALLAN

*Rukuhia Soil Research Station.*

Work at Rukuhia and published work from overseas laboratories over the last two years will be reviewed. The strongest absorption lines and the analytical sensitivity have been determined for all the elements which exist as atoms in flames. The use of organic solvents to increase sensitivity has been investigated and the mechanism established. Analytical procedures for the determination of a variety of elements in metallic and non-metallic materials have been described, and various interference effects investigated.

## ELECTRONIC SPECTRA OF CO-ORDINATION COMPOUNDS

N. F. CURTIS

*Chemistry Department, Victoria University of Wellington.*

The fundamental concept underlying modern treatments of the spectra of transition-metal co-ordination compounds is the removal of the degeneracy of the five *d* orbitals of the penultimate electron shell. The relative energies of these orbitals are changed in a manner which depends upon the symmetry of the system, and by an extent which depends upon the "co-

ordinating ability" of the ligands. The visible spectra of these compounds usually arise from electron transitions between these various  $d$  levels, the transitions being forbidden by the usual selection rules, and hence of low intensity ( $\epsilon \sim 10-100$ ). Each spectral band represents the energy difference between two electron configurations, and from these the energy differences between the various  $d$  levels can usually be calculated.

The nickel (II) ion,  $d^8$ , forms octahedral co-ordination compounds, with a triplet ground state (two unpaired electrons). If two trans ligands are imagined to be gradually withdrawn, the energy levels are altered, and a singlet state (diamagnetic) becomes relatively lower in energy, and will eventually "cross-over" to become the ground state. The compound will normally exist in whichever of these two forms (octahedral, or square-planar) has the lower energy. This depends largely upon the "co-ordinating ability" of the ligand, "weak" co-ordinating agents, such as water, ammonia, etc., form octahedral co-ordination compounds, "strong" co-ordinating agents, such as cyanide ion, form square planar compounds. The spectra of solutions of tris-butylendiamine-nickel(II) complexes have peaks characteristic of both the octahedral, and planar, Ni(II) ions, although from the formation constants, and other data, it appears that dissociation to the bis-diamine is negligible. The singlet form must therefore be derived from the triplet form by the withdrawal of two trans amine groups, leaving a system in which the field experienced by the nickel ion is dominated by the four "equatorial" groups, although the "polar" groups probably remain co-ordinated, at greater distance.

With butylenediamine complexes (*iso*, *dl*, and *meso*), the energy of the two forms are very similar, and a study of the spectra gives information about the "cross-over" point, where octahedral co-ordination gives way to square-planar co-ordination.

## APPLICATIONS OF DIFFERENTIAL INFRA-RED SPECTROSCOPY

B. CLEVERLEY

*Dominion Laboratory, D.S.I.R., Wellington.*

Double-beam infra-red spectrometers are widely used in chemical research and analysis. By means of the double-beam principle, the troublesome atmospheric water vapour absorption is eliminated as the two beams of the instrument pass through air paths of the same length, so that their light absorptions, being equal, cancel out at the detector. The spectrum of a solvent can

be compensated in the same way, by placing an equal thickness of the solvent in the reference beam so that the instrument records only the spectrum of the solute.

This same principle has still wider applications, which allow the solution of problems in analysis that would be difficult to solve by other means. A strong background absorption can be eliminated by placing in the reference beam some material which also absorbs in the same region of the spectrum as the background. Where the absorption spectra of the components of a sample interfere so that the components cannot be estimated from the optical densities of suitable absorption bands, the spectrum of one of these interfering components can be eliminated using the differential method. In the same way, an absorption band which is characteristic of one group of atoms in a molecule can be eliminated from the spectrum if necessary. The technique is applicable to samples in all three phases, and in solution, and special applications and refinements have been devised for the analysis of insecticides, fats, oils and greases, textiles, and other materials.

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## CONFERENCE

### GUEST LECTURER

**Professor R. C. L. Bosworth,**  
D.Sc.(Adelaide), Ph.D.(Cantab.)



Professor Bosworth graduated from Adelaide University where he was a research student under Professor Sir Kerr Grant on an overseas scholarship to study under Sir Eric K. Rideal in the Department of Colloid Science. Returning to Australia, he joined the Colonial Sugar Refining Company in 1938, holding the positions of Research Officer and Research Manager. In 1957 he was appointed to the staff of the University of New South Wales as Associate Professor in Physical Chemistry.

Distinguished positions which Professor Bosworth has held include: Chairman, N.S.W. Branch Institute of Physics; President, Royal Society of N.S.W.; President, Chemical Society of University of N.S.W. He is at present President of the N.S.W. Branch of the British Society of Rheology. Professor Bosworth has published about 60 papers and is the author of three books, *Physics in Chemical Industry*, *Heat Transfer Phenomena*, and *Transport Processes in Applied Chemistry*. He is also part author of Honig's *Principles of Sugar Technology*.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)  
BALANCE SHEET AS AT 30th APRIL, 1961

1960				1960			
	<b>Current Liabilities:</b>				<b>Current Assets:</b>		
70	Sundry Creditors .....	52 14 8		28	Petty Cash Funds .....	32 14 4	
14	Provision for Taxation .....	15 6 0		375	Bank of New Zealand .....	447 3 8	
118	Subscriptions Received in Advance .....	62 19 0	130 19 8	681	National Savings Account .....	704 17 3	
202				252	Post Office Savings Bank .....	—	
				25	Sundry Debtors .....	8 11 6	
	<b>Provisions and Special Funds:</b>				Subscriptions in Arrears .....	104 0 0	
125	Provision for Overseas Visi- tors' Travelling .....	302 8 1			less Provision for Overdue Subscriptions	50 0 0	
150	Provision for Printing .....	150 0 0		94		54 0 0	
75	Education Fund .....	75 0 0		20	Advance, Conference .....	20 0 0	1267 6 9
29	Compounded Subscriptions ..	37 15 6		1475			
30	Provision for Essay Prize .....	30 0 0	595 3 7		<b>Trust Fund Investments, at Cost:</b>		
409				633	Post Office Savings Bank .....	199 9 0	
	<b>Trust Fund:</b>			500	Hutt County Council De- bentures .....	500 0 0	
	As per statement attached ..	1224 6 6		—	Lytelton Harbour Board De- bentures .....	500 0 0	
	<b>Accumulated Funds:</b>			50	Cash in General Account .....	24 17 6	1224 6 6
	Balance as at 30/4/60 .....	919 19 2		1183			
	less Transfer to Overseas Visi- tors' Travel- ling Expenses Provision .....	300 0 0			<b>Fixed Assets, at Cost:</b>		
	less Excess of Expenditure over Income for Year .....	29 15 8	329 15 8	54	Office Equipment .....	66 3 0	
					less Depreciation	18 3 0	48 0 0
920			590 3 6		Addressograph Plates .....	31 3 6	
				2	less Depreciation	30 3 6	1 0 0
				56			49 0 0
2714			£2,540 13 3	2714			£2,540 13 3

## INCOME AND EXPENDITURE FOR YEAR ENDED 30th APRIL, 1961

1960		1960		1960	
303	Administration Expenses:	241	9	6	
231	Travelling Expenses .....	239	1	8	
	Printing, Stationery and Postages .....	200	0	0	
200	Salary, Registrar .....	130	0	0	
150	Branch Expense Allowances .....	50	0	0	
50	Honorarium to Secretary .....	24	8	11	
19	General Expenses .....	21	0	0	
16	Audit Fee .....	19	16	4	
—	Conference Expenses .....	7	0	0	
9	Depreciation .....	—	—	—	
20	Registrar's Transfer Expenses .....	221	9	1	
998	Cost of Journal .....	35	0	0	
231	Honoraria to Editors .....	932	16	5	
35	Membership List .....	256	9	1	
266	Chemistry Essay Prize .....	75	0	2	
25	Chemistry in Action — Net Cost .....	25	0	0	
57	Expenses of Questionnaire .....	23	19	3	
—	Provision for Taxation .....	21	2	9	
7	Examination Committee Expenses .....	15	6	0	
	Honorarium to Examination Secretary .....	43	11	6	
	less Receipts .....	36	7	6	
	Cost of Salary Survey .....	7	4	0	
18		—	—	—	
1371		£1,356	17	8	
911	Subscriptions:	1270	9	11	
4	Proportion Compounded Subscriptions .....	9	1	6	
915	Interest Received:	1279	11	5	
25	National Savings Account .....	23	16	1	
9	Bank of New Zealand .....	6	15	11	
8	Post Office Savings Bank .....	4	7	11	
42	Commissions on Journal Subscriptions .....	34	19	11	
14	Monographs — Net Surplus .....	8	14	9	
—	Examination Committee — Net Surplus .....	3	15	11	
9	Conference Surplus .....	—	—	—	
1005	Excess of Expenditure over Income for Year Transferred to Accumulated Funds .....	1,327	2	0	
366		29	15	8	
1371		£1,356	17	8	



## BRANCH NEWS AND NOTES

### AUCKLAND BRANCH

Mr I. S. Hunt has left New Zealand Wallboards Ltd., to take up a position in charge of timber preservation research at Merida, Venezuela.

Dr D. Hall and Dr R. C. Cambie have resigned their posts at Auckland University to take up positions at Pittsburgh and Oxford Universities, respectively.

### MANAWATU BRANCH

Dr J. C. Hawke recently attended the A.N.Z.U.S. Conference in Brisbane and also visited biochemistry laboratories in various parts of Australia.

Dr G. W. Butler has been awarded a U.S. Department of Health Postdoctoral Research Fellowship, and will be leaving in August for one year at the Plant Biochemistry Department, Davis, University of California. He will also attend en route the Eighth Pacific Science Congress to be held in Honolulu in August.

Mr Graeme Latimer is at present touring dry milk factories in various parts of North America, Europe and Asia.

Dr R. M. Dolby is visiting the U.S.A. to inspect casein factories and to investigate possible market potentialities for New Zealand casein.

Dr K. Perry has resigned from his position at The Dairy Research Institute (N.Z.) and has returned to Britain.

Drs H. Whitehead and F. H. McDowall have been invited to South Africa in August to be the principal speakers at the Conference of the South African Dairy Products Manufacturers' Association.

### WELLINGTON BRANCH

We regret to record that the Hon. W. H. Gillespie, M.P., Minister of Agriculture, died on April 23. His successor in office, the Hon. T. L. Hayman, has been elected an Honorary Local Member of the Institute.

Mr W. E. Childs of B.A.L.M. Lower Hutt is now an Overseas Member with the same firm in Australia.

Mr R. J. Monk has transferred from the Biochemistry Department of the Cawthron Institute to be Chemist with the Nelson City Council.

Dr J. K. Martin, formerly with Tasman Vaccine Laboratory Ltd., Upper Hutt, is now with the D.S.I.R. Soil Bureau, Taita.

Mr J. J. S. Cornes, who retired from the Dominion Laboratory a few years ago, is now Chemist to the Waitomo Portland Cement Co., Box 274, Te Kuiti.

Mr H. McD. Rankin, of N.Z. Breweries, Wellington, is now with the same Company in Auckland.

### CANTERBURY BRANCH

The second meeting for this year of the Junior Chemical Society was addressed by Mr A. W. Mayne of Lever Bros. Ltd. on the production of glycerol. At this meeting the four winners of the Lever Bros. Awards were announced. They were: J. Longbottom and M. Elder, Christchurch Boys' High School; B. S. Weir, Shirley Boys' High School; and M. Saunders, Linwood High School.

Dr P. Meredith of the Wheat Research Institute has been awarded a post-doctoral fellowship by the National Research Council of Canada. He will take up this fellowship at the Grain Research Laboratory, Winnipeg.

## OTAGO BRANCH

Dr J. C. Dacre of the Medical School left in July for a year's refresher leave in London. He will be working with Professor R. Tecwyn Williams in the Department of Biochemistry at St. Mary's Hospital Medical School.

Dr Dacre has been invited to give a lecture to the 1962 Gordon Research Conference on Toxicology and Safety Evaluations to be held at Kimball Union Academy, Meridan, New Hampshire.

Congratulations are extended to Mr G. Beath, Principal of the Dunedin Teachers' Training College, on his recent election to the Council of the University of Otago by teachers in Primary Schools.

Mr G. A. Holmes, Superintendent of the Invermay Agricultural Research Station, gave an interesting account at the May meeting of some insecticides, weed killers, and soil deficiency problems.

The Otago Branch committee has been gratified with the pleasing attendances at monthly meetings. Much interest is being shown by both undergraduate and research students, and this augurs well for the future.

## THE REGISTRY

## Resignations

CARADUS, J. N.

MARTIN, W. E. B.

## Leave of Absence

CAMBIE, R. C. For two years. WERRY, C.C. For two years.

## CONFERENCE CLAREYHUES

All visitors should first observe  
Our Rangitoto's complex curve.  
Interpretation of the latter  
Shows R. absorbs much Waitemata.

•                    •                    •

Members allotted to O'Rorke—  
Remember *linen* when you leave for Auck.  
(Note—this request quite clearly shows  
Chemists, like cows, use cellulose).

•                    •                    •

Something around the Manakau  
Makes  $H_2S$ —no one knows how.  
Don't think "manure", don't mention "sewer"—  
Let's say it's a newer Rotorua.

## COUNCIL MINUTES

ABRIDGED MINUTES OF A MEETING OF THE COUNCIL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.) HELD IN THE CONFERENCE ROOM, D.S.I.R., WELLINGTON, ON FRIDAY, MAY 12, 1961, AT 10.00 A.M.

### PRESENT

Professor H. N. Parton (President, in the Chair), Prof D. R. Llewellyn (Auckland), Dr E. P. White (Waikato), G. M. Wallace (Manawatu), W. E. Dasant (Wellington), D. J. Hogan (Canterbury, Registrar), Dr W. G. Hanger (Otago), and Dr W. E. Harvey (Hon. Gen. Secretary).

### WELCOME ETC.

The Chairman welcomed Dr Harvey who has resumed the office of Hon. General Secretary.

*Resolved:* That a letter be sent to Mr A. P. Oliver thanking him for his services as Acting Hon. General Secretary.

### CONFERENCE 1961

Professor Llewellyn reported that the Prime Minister had agreed to open the Conference.

Professor R. C. L. Bosworth of Sydney University will be the Guest Lecturer at Conference. Professor Bosworth is coming to New Zealand to give a course of lectures in the Department of Chemical Engineering, University of Canterbury. It was agreed that if possible we should arrange for Professor Bosworth to visit other centres and Professor Llewellyn undertook to handle these arrangements. It was agreed that Professor Bosworth's expenses would be a charge on the Overseas Visitors Fund.

### EXAMINATIONS COMMITTEE

The Auckland Delegate reported that Mr O. H. Keys had been approached but had not agreed to form an Examinations Committee. It was agreed that it was essential to make immediate arrangements for conducting the L.A.C. examinations and that the Otago Committee should not be asked to undertake this task.

*Resolved:* That the Hon. General Secretary and the Wellington Delegate be asked to form an *ad hoc* committee to conduct the examinations for this year only.

The nature of the duties performed by the Examinations Committee is expected to change now that the Education Department courses for Chemical Technicians are running and it was agreed that it was desirable to form a new Committee as soon as possible, so that these matters could be considered in detail. Professor Llewellyn will continue his enquiries among possible members of the Auckland Branch.

*Resolved:* That the Secretary write to the Otago Examinations Committee expressing Council's thanks for the way they had served the Institute for a number of years.

### STANDARDS INSTITUTE REPRESENTATIVE

Council approved the action taken by the Hon. General Secretary in re-nominating Mr G. A. Lawrence to the Standards Council.

### SALARY SURVEY

*Resolved:* That the Professional Status Committee be asked to proceed with a Salary Survey forthwith.

### PROFESSIONAL STATUS

The Hon. General Secretary reported that, at the request of the Professional Status Committee, he had written to the Nelson City Council about an advertisement for a "Laboratory Assistant" which had appeared in daily papers. A reply from the Nelson City Council expressed general agreement with the Institute's criticism.

### CHEMISTRY IN ACTION

*Resolved:* That 2,000 copies of the new *Chemistry in Action* be printed and offered for sale on the same basis as in earlier years.

### MEMBERSHIP APPLICATIONS

*Resolved:* That all documents (e.g., University Certificates) must be retained with Associate and Fellowship application form for perusal by the Membership Committee, unless sighted by the Hon. General Secretary or the Registrar.

### OVERSEAS VISITORS, 1960

The Hon. General Secretary reported that to date those bodies that contributed to the cost of the overseas visitors in 1960, with the exception of the D.S.I.R., had agreed to leave the amount contributed in excess of that required, in the Institute's Overseas Visitors Fund. The University of Auckland had yet to decide what it would do.

The General Secretary reported that, following a discussion with Prof L. H. Briggs, and after conversation with the Wellington Delegate, he authorized the expenditure of £10 from the Overseas Visitors Fund, this sum, together with £5 made available by the Chemical Society through its local representative, to go to Professor N. A. Soerenson of Norway, who paid a short visit to New Zealand.

*Resolved:* That the action taken by the Hon. General Secretary be approved.

### "ROYAL" TITLE

The majority of Branches reported that they did not support the suggestion that the Institute seek to get approval for the addition of the word "Royal" to the title of the Institute.

*Resolved:* That no action be taken.

### PUBLIC SERVICE ACT

*Resolved:* That the Hon. General Secretary write to Mr Ray Hannan of the N.Z.P.S.A. stating that the Institute considered that the Public Service Act should contain a provision that any person accused of "political unreliability" should have an unconditional right of appeal to a Reviewing Authority.

### COMMITTEE ON NEW ZEALAND SCIENCE

Council agreed with the suggestion made by the Wellington Branch that any committee to investigate science in N.Z. should include (a) a majority of overseas people, (b) an overseas chairman, (c) as one member a N.Z. scientist of standing such as Dr F. J. Llewellyn or Dr F. G. Soper.

#### ADDRESSOGRAPH PLATES

Council approved the application from a commercial organization to use the Institute addressograph plates to circulate to members details of a senior position vacant.

*Resolved:* That the fee for use of the addressograph plates be £10.0.0.

#### EMPLOYMENT COMMITTEE REPORT

*Resolved:* That the Committee be asked to consider up-dating the report prior to its circulation to Vocational Guidance Officers, the Technicians Certification Authority, etc.

#### ADVERTISING PHOTOGRAPHS

*Resolved:* That the Professional Status Committee be asked to comment on certain advertising matter which includes photographs of members of the Institute who are named.

W. E. HARVEY,  
*Hon. General Secretary.*

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### A NEW APPROACH TO PROTEIN RESEARCH

A new approach to the study of the sequence of amino acids in protein was reported at the second Annual Medical Symposium sponsored by International Business Machines Corporation in Endicott, New York, in October, 1960. How the proteins can be broken down into sub-units for study is determined by "questions of strategy" answered by an electronic computer.

The project was reported by Dr Sidney A. Bernhard, Chief of the Section on Physical Chemistry, National Institute of Mental Health, Dr Dan F. Bradley, also of the National Institute, and Dr William L. Duda of IBM Research, in a paper, "Sequence of Amino Acids in Protein".

This paper suggests a new approach to sequencing, involving the use of a computer to help to make time-saving logical decisions. Difficult tasks of computation can then be shifted from the scientists to the computer. Conceivably, future tasks of sequencing amino acids may be dramatically shortened, possibly to as little as 10 per cent. of the time taken by present procedures that often run for years.

The amino acid chains must be broken down into subchains of various sizes in order to yield information that will be useful in the sequencing or reconstruction of each chemical segment. The role of the electronic computer is principally that of performing logical operations rather than simply calculating arithmetic.

Drs Bernhard, Bradley and Duda faced three fundamental problems in their work: (1) Determining how much of a given type of information was required for the solution of a problem; (2) Solving logical problems involving the breaking up of different combinatorial mathematics problems; (3) Programming the computer, an IBM 7090.

In 1958 Dr Frederick Sanger was awarded a Nobel Prize for determining the sequence of 64 amino acids in insulin, a feat which took between eight and ten years by conventional biochemical techniques. Since then the sequence of amino acids in other protein chains has been accomplished.

The paper, announcing the success so far achieved in using computers to determine the sequence of amino acids, promises a greatly reduced time factor for future research accomplishments in biochemistry and genetics.

**BOOK REVIEWS**

*INTRODUCTION TO CERAMICS*, by W. D. Kingery. Published by John Wiley & Sons, Inc., New York, 1960. 781 pages. Price 12 dollars.

This is an interesting book with admirable objectives. It is not, however, an introduction to ceramics. The author in his preface says that the last 300 pages are intended as a textbook for graduate students in ceramic engineering, who should hardly need to be introduced to their subject at this stage. The general reader interested in making pottery, or the scientist wishing to learn details of ceramic processes and materials, had best seek elsewhere for his information. The ceramic scientist engaged in research and development will find much to interest him in this large, attractively produced and expensive book.

The book is written particularly for the use of senior and graduate students in ceramic engineering at the Massachusetts Institute of Technology where the author is Associate Professor of Ceramics. Its aim is to familiarize these students with the physics and chemistry which are basic to ceramics science and the physical properties of ceramic materials.

The first two sections of the book comprise 78 pages and are entitled "Introduction and "Ceramic Processes". They describe ceramics and their history, raw materials and methods of processing. They constitute what would normally be considered the subject matter of an introduction to ceramics. In this book they are intended only as introductory material to later sections for students who are expected to know already a great deal about ceramics. They give, therefore, only the sketchiest outlines of the subject matter. The 40-page section on forming processes is quite informative, but the other chapters are brief, inaccurate, and mention only American sources of raw materials.

Sections 3 and 4 comprise 380 pages and are entitled "Characteristics of Ceramic Solids" and "Development of Microstructure in Ceramics". They deal with the physics and chemistry basic to ceramics, and include chapters on atomic and crystal structure, structural imperfections, surfaces, phase diagrams, crystal growth and microstructure of ceramics. In general, the material is well prepared but the chapters tend to be uneven in standard. A first-year knowledge of chemistry will be sufficient to follow some arguments but an Honours knowledge will be required to follow others. The chapters draw heavily on textbooks on the physics and chemistry of solids. The advantage to the ceramicist is that only those aspects of these subjects of pertinence to ceramics are dealt with in this book.

Section 5 comprises 301 pages and is entitled "Properties of Ceramics". It deals with the physical properties of ceramic materials and includes chapters on thermal, optical, plastic, strength, electrical and magnetic properties. It contains much information which is otherwise accessible only in scientific journals. The chapters tend to emphasize properties of the newer ceramic materials such as ferroelectric ceramics, magnetic ceramics, nuclear fuels and metal-ceramic composites.

The success of the book should properly be judged by the success it achieves in providing American ceramic engineers with a physical and chemical background to their subject. The strong emphasis given in the book to fundamental knowledge is to be commended. This is undoubtedly

the only approach which can ensure that developments in ceramics will keep pace with an increasingly technological age.

The book is of limited interest in New Zealand. Ceramic scientists will find it valuable, and other workers in materials will find the chapters on solid state physics and chemistry and the properties of ceramic materials of interest. Professors of physics and chemistry would be well advised to obtain copies so that they will know what subjects will require-emphasis if New Zealand is to provide its own materials scientists for its future industries.

—L.D.S.

## BOOKS RECEIVED

*LIST OF MEMBERS AND CLASSIFIED LIST OF PRODUCTS, 1960.*  
The Stainless Steel Fabricators' Association of Great Britain.

This 41-page booklet lists alphabetically over 500 types of product and British firms which produce them. There is also a list of trade names and specifications of stainless steel. Interested readers may obtain a copy by application to the Secretary of the Association, P.O. Box 360, Edgbaston, Birmingham 15.

*SEMICONDUCTOR ABSTRACTS, Vol. 1, 1958 Issue.* Compiled by Batelle Memorial Inst., under auspices of the Electrochemical Society, Inc. John Wiley and Sons, Inc., N.Y., 1961. 528 pp. Price, \$14.00.

This volume contains over 1,900 abstracts on semiconducting and luminescent materials and their applications, with author and subject indexes.

*LABORATORY HANDBOOK OF TOXIC AGENTS.* C. H. Gray, Editor-in-Chief, Royal Institute of Chemistry, London. 170 pp. Price, £1 (15/- to R.I.C. members).

This book has resulted from the work of the R.I.C. Committee set up in 1958 to consider hazards in the use of common laboratory chemicals. The early chapters deal succinctly with the general nature of these hazards and principles which determine the consequences of exposure to them; with measures which should be taken in the ordinary laboratory to reduce the risk of exposure; and with laboratory first aid. The last chapter covers, in 17 pages, precautions against radiation. The bulk of the book, 113 pages, lists alphabetically the poisonous and corrosive gases, reagents and solvents commonly present in laboratories. For each substance relevant properties are given together with toxic effects and first aid measures. To facilitate reference these pages are on blue paper. This book should not only be held in all laboratories where chemicals are commonly used; it should also be scanned by both chemists and technicians to ensure that their procedures are free from available hazard.

*THE PROTON IN CHEMISTRY,* by R. P. Bell. Methuen and Co. Ltd., London, 1959. 223 pp. Price, £2 2s. 0d.

Based on the author's George Fisher Baker lectures given at Cornell in 1958, this book discusses the nature of acids and bases and theoretical aspects of reactions involving them. Recent work on concentrated solutions of acids and the hydrogen isotope effect are especially considered. The treatment provides a synthesis of these and related topics in relation to modern concepts of acids and bases and their properties.

**STERIC ASPECTS OF THE CHEMISTRY AND BIOCHEMISTRY OF NATURAL PRODUCTS.** Biochemical Society Symposia No. 19, Cambridge University Press, 1960. 138 pp. Price, 20s. (paper), 30s. (cloth).

Seven papers, with condensed discussions, deal with recent developments in the knowledge of stereochemical influences on biosynthesis, the mechanisms of the action of drugs, the specificity of enzymes, and similar chemical processes of living matter.

**THE BIOCHEMISTRY OF MUCOPOLYSACCHARIDES OF CONNECTIVE TISSUE.** Biochemical Society Symposia No. 20, Cambridge University Press, 1961. 125 pp. Price, 15s. (paper).

These seven reviews consider aspects of the nature of the acid mucopolysaccharides, their histological demonstration in connective tissue, their analysis, functions, and degradation by enzymes.

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### **A CORRECTION**

We regret a series of errors in a note in the June issue (Otago Branch Notes, page 114), concerning establishment of a soil testing service. The South Island Soil Testing Station at Taieri is under the control of the Department of Agriculture and continues a service previously operated by Mr Grigg for the Agriculture Department from Winchmore.

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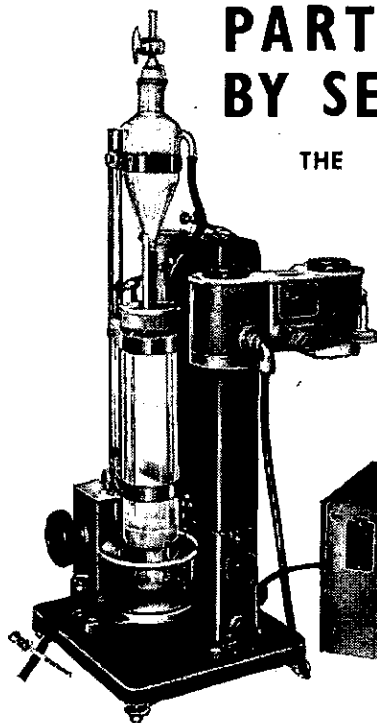
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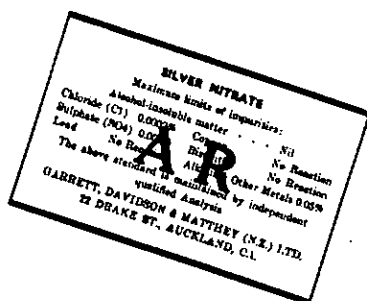
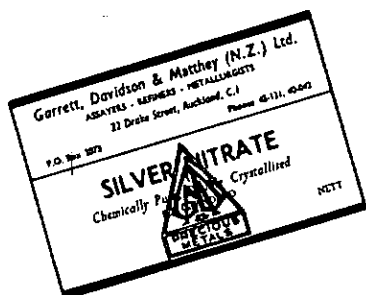
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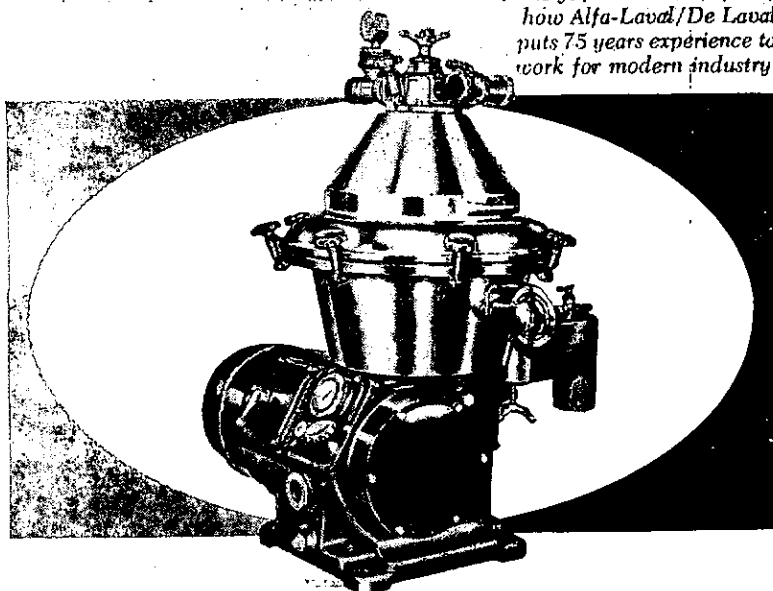
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