

chemistry

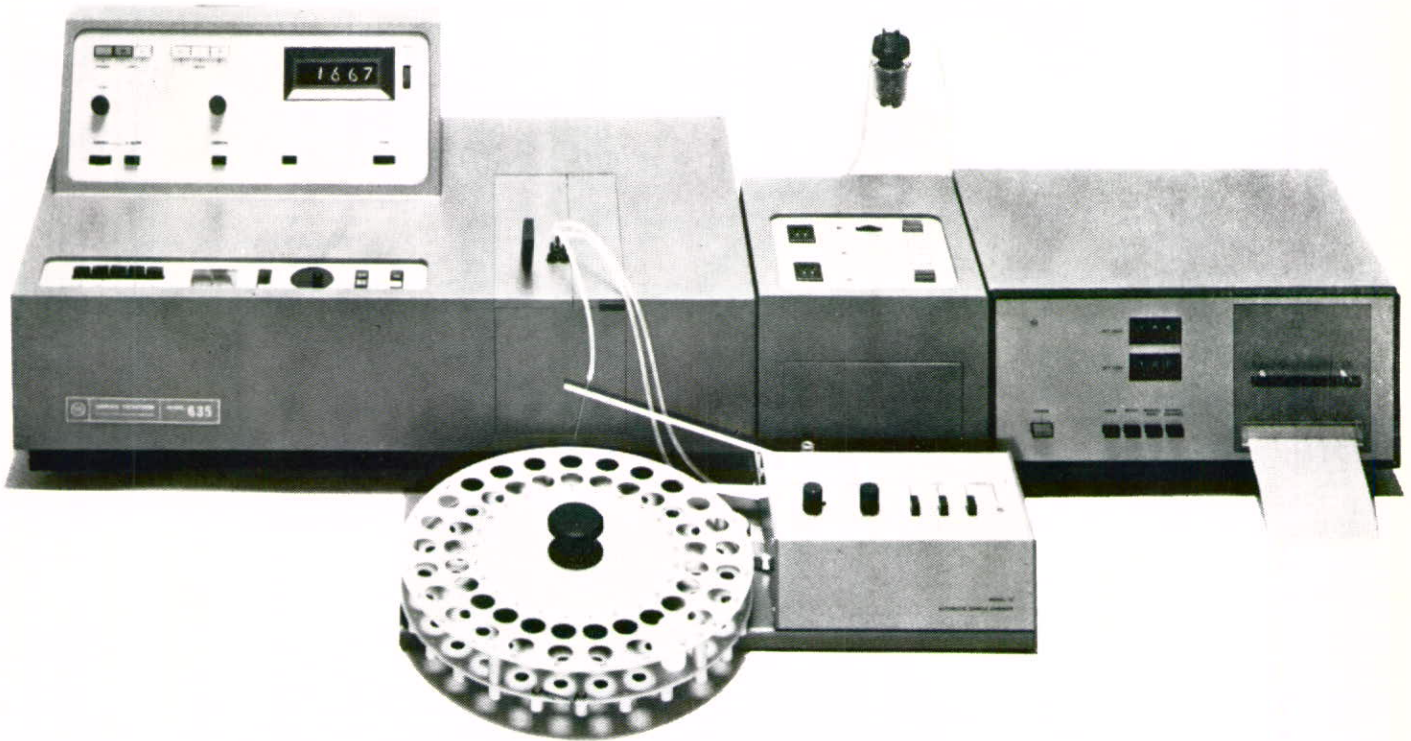
in new zealand



conference issue

august 1974

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ANZA **AUDITED CIRCULATION**
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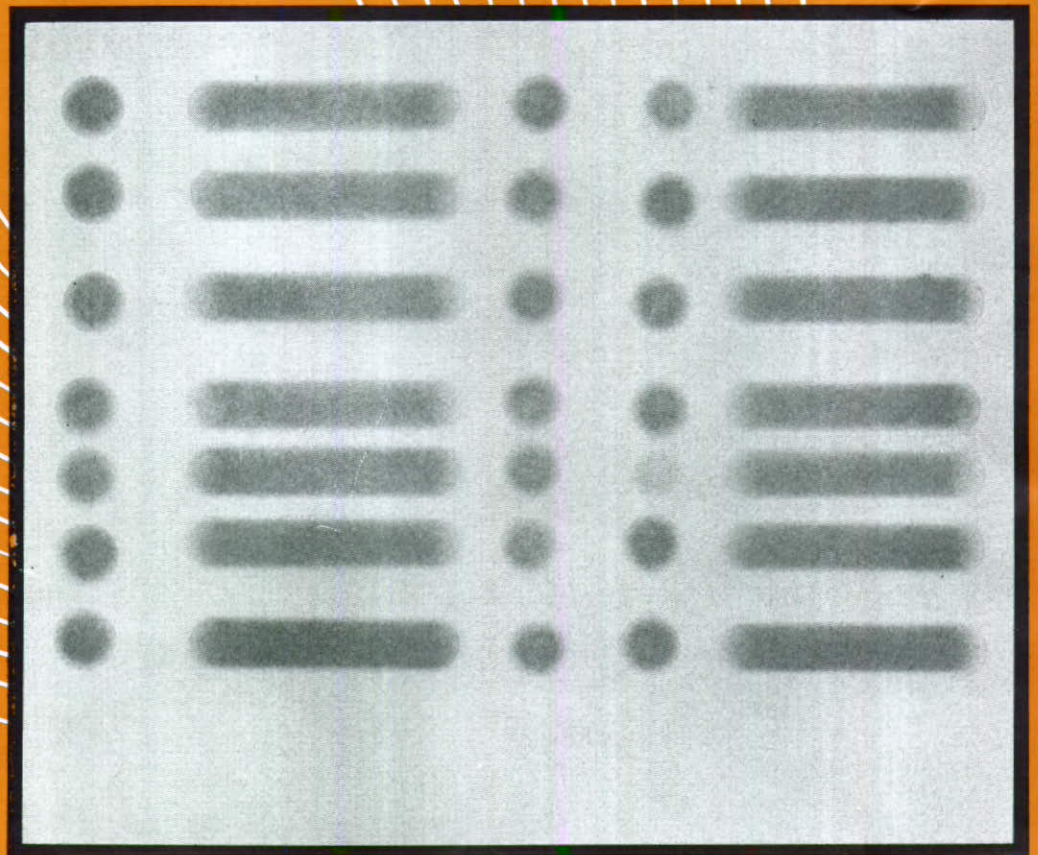
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Auckland University Chemistry Department.
Venue for Conference 1974.

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Conference 1974

Welcome to Auckland

In recent years the Institute Conference has tended to get bigger and better. Whether or not getting bigger is a good thing is debatable, but one thing is for sure, in terms of the papers to be presented (157), the 1974 Conference in Auckland will be bigger than any of its predecessors. Moreover, your Organising Committee sincerely hopes that this Conference will be better than any yet held in Auckland. We have incorporated a number of changes into the programme. Three one-day symposia, two focussing on the varied roles and responsibilities accepted by chemists today and one of a more technical nature, will be the main feature. However, the specialist sessions have been given greater emphasis and they now cover the whole Conference period. This will lead to the inevitable conflict of interest but we believe that to give more prominence to the specialist sessions is a step forward. On the social side we have retained the buffet dinner which so successfully highlighted the 1973 Conference in Christchurch, and for added measure we have included a visit to the local Mercury Theatre. Such is the attractiveness of the programme for the wives of visiting delegates that at least one member of the Organising Committee thought seriously about foregoing the technical sessions in favour of the Ladies' programme.

The theme of this year's Conference is "Chemistry Serves Society", and all of the invited symposium lectures have been selected with this theme in mind. It is somewhat appropriate that one of the symposia will be concerned with "Professionalism and the Chemist" since some 49 years ago concerted efforts were being made on the Auckland scene to form a society "wherein chemists might gather together to discuss matters of a professional nature". The outcome was the formation of the Auckland Chemical Society, the forerunner of our

present New Zealand Institute of Chemistry. Again, where better than Auckland to feature a symposium on "The Social Responsibility of the Chemist". As its largest city there can be few other places in New Zealand where chemists have a greater opportunity to be aware of the part chemists can play in modern society. As for the symposium on "The Science and Technology of Fats" — we can but hope that "it's not positively thickening."

1974 could well be the year of the visitor. In addition to our official guest lecturers Dr A. Walsh and Professor W. H. Elliot from Australia and special guest lecturer Dr J. W. Moore from Scotland, no fewer than ten other overseas visitors will be delivering papers at the Conference. We welcome this participation by our overseas colleagues since they give an international flavour to our Conference.

1974 also saw the XI Commonwealth Games in Christchurch described by some commentators as the "friendly Games". We would like to borrow the catchphrase and make the 1974 Conference the "friendly Conference". To this end we would urge all delegates to partake in the social gatherings which we have arranged and to make full use of the social facilities which have been provided. We would also urge the more senior members of the Institute to make a deliberate effort to introduce themselves and talk to the younger delegates. Too often we have seen the fresh graduate standing alone at a Conference because he has a natural reluctance to approach his older colleagues.

The Conference Committee warmly welcomes you to Auckland and hopes that you have a most enjoyable Conference. And if you do find yourself with time on your hands the Conference Chairman has been allocated a special fund for the entertainment of the lonely visitor.

R. C. CAMBIE,
Conference Chairman.

Guest Lecturers



DR A. WALSH, D.Sc., F.A.A., F.R.S.

Dr Walsh was educated at Manchester University where he graduated B.Sc. with Honours in physics and with an M.Sc.Tech. He was awarded an honorary D.Sc. from Monash University, Melbourne in 1970. From 1939-46 he was a spectroscopist for the British Non-ferrous Metals Research Association in England and he then moved to Australia to take up the position of leader of the Spectroscopy Section of the Division of Chemical Physics of C.S.I.R.O. in Melbourne. Since 1958 he has been the Chief Research Scientist and Assistant Chief of the Division.

Numerous medals and awards have been received by Dr Walsh. He was elected a Fellow of the Australian Academy of Science in 1958 and a Fellow of the Royal Society in 1969. His honours include the Britannica Australia Science Award for 1966, the Royal Society of Victoria Research Medal for 1969, the Talanta Medal for 1969, and the Maurice Hasler Award by the Society of Applied Spectroscopy, U.S.A. for 1972. He was President of the Australian Institute of Physics from 1967-68, President of the Physics Section of ANZAAS in 1972 and was a member of the Council of the Australian Academy of Science from 1966-69. He was the Einstein Memorial Lecturer of the Australian Institute of Physics in 1967, and his other distinctions include Honorary membership of the Society of Analytical Chemistry, London, and Foreign Membership of the Royal Academy of Sciences, Stockholm.

Dr Walsh is acknowledged as a world authority on atomic emission, absorption, and fluorescence spectroscopy and has published extensively in these fields and in those of infra-red and Raman spectroscopy. His expertise in the field of spectroscopy has been

recognised by his appointment to the Editorial Advisory Board of *Spectrochimica Acta*, *Analytica Chimica Acta*, *Spectroscopy Letters*, and *The Analyst*.

DR J. H. MOORE, D.Sc., F.R.I.C.

Dr Moore studied chemistry under the late Professor E. D. Hughes, F.R.S. and the late Professor G. W. Robinson, F.R.S. in the University of Wales. After graduating in 1948, he joined the teaching staff of the Physiological Chemistry Department in the University of Reading. In 1959 Dr Moore was appointed to the staff of the National Institute for Research in Dairying where he worked in the Nutrition Department in collaboration with Professor S. K. Kon. Since 1966 he has been a member of the staff of the Hannah Research Institute, Ayr, Scotland where he is Deputy Director and Head of the Biochemistry Department. In addition, Dr Moore is an honorary lecturer in the Department of Biochemistry at the University of Glasgow.



Dr Moore's main research activities have been concerned with various aspects of lipid biochemistry and nutrition. These have included investigations into the relationships between diet, blood lipids and cardiovascular degeneration, aspects of lipid mobilisation, transport and metabolism by the chick embryo and the relationship between triglyceride structure and the physical properties of milk and adipose tissue fat. More recently, research work at the Hannah Institute has involved studies on the biohydrogenation of polyunsaturated fatty acids by rumen micro-organisms, the metabolism of essential fatty acids by the young ruminant and aspects of fatty acid and triglyceride synthesis in the mammary gland.



PROFESSOR W. H. ELLIOT, F.A.A.

Professor Elliot, the Biochemistry Guest Lecturer for 1974, obtained his first degree and Ph.D. from Cambridge University, U.K. As a Fellow of Trinity College he carried out post-doctoral work at Cambridge University and then moved to Harvard University, U.S.A., as a Rockefeller Fellow. Following appointment to the staff of the Biochemistry Department at Oxford University he moved to the Biochemistry Department of the Australian National University, Canberra, where he was awarded a Personal Chair. Since 1972 he has been Professor of Biochemistry and Head of Department at the University of Adelaide.

Professor Elliot's current research activity is concerned with the mechanism of protein secretion through membranes and with the control of the synthesis of a specific enzyme in liver cells.

GUEST LECTURES:

Dr A. Walsh, from C.S.I.R.O., Melbourne will deliver the Conference Guest Lecture on Monday evening at 8 p.m. He will speak on "Atomic Absorption Spectroscopy". Dr Walsh's lecture will be preceded by a presentation to Dr Wallace, Director of the Ruakura Soil Research Station, of a framed photograph of the late Eric Allan as a tribute from the latter's many Australian friends.

Professor W. H. Elliot from the University of Adelaide will deliver the Biochemistry Guest Lecture at 9 a.m. on Wednesday morning. His address is entitled "The Vectorial Transport of Proteins Across Cell Membranes".

Dr J. H. Moore from the Hannah Institute, Ayr, Scotland will deliver a special Guest Lecture entitled "Aspects of Lipid Metabolism in the Ruminant Animal" on Thursday morning at 9 a.m. Dr Moore's visit to the Conference has been sponsored by the Conference Committee, Abels Limited, and Alta Lipids Ltd.

VISITING SPECIALIST GROUP

PLENARY LECTURERS



PROFESSOR R. N. GRIMES

(INORGANIC)

Professor Grimes is Professor of Chemistry at the University of Virginia, U.S.A., and a 1974 Fulbright Research Scholar. A graduate of the University of Minnesota, Professor Grimes carried out post-doctoral work at Harvard University and the University of California and was Plenary Lecturer at an International Conference on Boron Chemistry at Leeds in 1974.

The research interests of Professor Grimes include inorganic and organo-metallic cage and cluster compounds, especially metalloboranes, metallocarboranes, and related systems and synthesis, structural characterisation, and reaction chemistry. He is author of the book "Carboranes".

DR R. BOLTON (ORGANIC)

Dr Bolton is a Lecturer in Chemistry at Bedford College, University of London and is currently Visiting Lecturer at the University of Auckland. He is no stranger to New Zealand, having been a visiting Lecturer to the Victoria University of Wellington in 1967.

Dr Bolton's research interests include both heterolytic and homolytic aromatic substitution, aromatic fluorocarbon chemistry, and the effect of planarity upon resonance stabilisation in solvolytic reactions. In addition to publishing widely on the above topics he is the author of two books "Electrophilic Additions to Unsaturated Systems" (with P. B. D. de la Mare) and "Organic Mechanisms".



PROFESSOR W. D. LOMIS

(BIOCHEMISTRY-ORGANIC)

Professor Loomis, Professor of Biochemistry at Oregon State University, is visiting New Zealand as an NRAC Senior Research Fellow in the Applied Biochemistry Division, DSIR, Palmerston North. He is a graduate of the University of California, Berkeley, and a member of the American Society of Plant Physiologists, the American Society of Biological Chemists, Sigma Xi, and other professional societies. During 1965-66 he was visiting scientist at the University College of Wales, Aberystwyth.

Professor Loomis' research interests include the biochemistry and physiology of terpenes in plants, and the investigation of protein-phenol and protein-quinone interactions as related to plant enzymology and to other uses of plant proteins.

OTHER HIGHLIGHTS

Plenary lectures of 1 hour have been arranged by a number of the Specialist Groups. These will be given by Dr. R. Bolton (Organic, Monday at 3.30 p.m.), Professor W. D. Loomis (Biochemistry—Organic, Tuesday at 2 p.m.), Professor J. W. Tomlinson (Physical—Electrochemistry, Wednesday at 9 a.m.), Mr G. R. White (Chemical Education, Wednesday at 2.30 p.m.), and Professor R. N. Grimes (Inorganic, Wednesday at 4 p.m.).

The Easterfield Address will be delivered on Tuesday morning at 9 a.m. following presentation of the Easterfield Medal to the 1974 recipient.

The Presidential Address will be delivered by Dr P. K. Foster on Wednesday evening at 8 p.m.

Conference Symposia

Abstracts of Papers

SCIENCE AND TECHNOLOGY OF FATS

Tuesday, 27th August

The Chemistry of Fats (Symposium Plenary)

S. G. Brooker

Abels Limited, Auckland

A review of more recent developments particularly in the following areas:

- (1) The major and minor constituents of fats.
- (2) Glycerides as the major constituent of fats: their physical and chemical nature.
- (3) Chemistry of fatty acids.
- (4) Positional analysis of fatty acids in glycerides.
- (5) Chemical reactions of glycerides and fatty acids.

Some reference will be made to the significance of these developments in the edible fat industry.

The Biochemistry of Fats

(Symposium Plenary)

J. C. Hawke

Massey University, Palmerston North

The following aspects of the biosynthesis of fats will be reviewed:

- (1) pathways in the biosynthesis of saturated, monoenoic and polyenoic fatty acids;
- (2) unity and diversity in the enzymology of fatty acid biosynthesis;
- (3) pathways in the biosynthesis of triacylglycerols.

Some emphasis will be given to the comparative biochemistry of triacylglycerols and their constituent fatty acids.

Modification of the Physical Properties of Butter

R. S. Jebson

N.Z. Dairy Research Institute, Palmerston North

Early methods of improving the spreadability of butter at lower temperatures, concentrated on cream cooling techniques. It was found that if cream was cooled slowly a smaller proportion of liquid fat was incorporated in the crystals, leaving a higher proportion as free liquid fat and consequently a softer butter. In particular if a modified Alnarp process, in which the cream was cooled quickly to 5°C, held for 10 sec, quickly heated to 20°C, held at this temperature for 4 to 6 hours, then slowly cooled to churning temperature, a maximum of free liquid fat was available and an appreciable softening of butter occurred.

After butter is made there is at first a rapid increase in hardness, followed by slower increases to an asymptotic limit, the period of increase being approximately 30 days. If after the setting, the butter is subjected to a mixing or reworking process the butter is softened considerably and although setting takes place again the limit hardness is much lower. The softening effect of reworking is proportionately much greater for harder than for softer butters.

More recently, fractional crystallisation of milkfat into hard and soft fractions has been investigated. A greater degree of softening can be achieved by incorporating the soft fraction derived by this technique but softening occurs at all temperatures and such butters are too soft at summer ambient temperatures while still not being sufficiently soft to be completely spreadable immediately after removal from the refrigerator. The most recent development is a solvent crystallisation process by which milkfat is crystallised from solvent at a number of successive temperatures. The middle

melting point fats can therefore be removed and the hard and soft fractions combined to give a butter which is soft but essentially viscostatic over the temperature range 5-20°C.

The essential steps in this process are, addition of the solvent to anhydrous milkfat, crystallisations, removal of the crystals by filtration or centrifugation, and recovery of the solvent from the crystals by first evaporation, and second, steam distillation.

Physical Properties of Edible Fats

R. Norris

N.Z. Dairy Research Institute, Palmerston North

Apart from flavour and nutritional aspects, fats are important food constituents because of the way their physical properties influence the texture of food. Thus, foods containing liquid fats (mayonnaise), solid fat (chocolate) or a mixture of solid and liquid phases (margarine, butter) all have distinctive characteristics. A major part of the technology of edible fats is therefore concerned with the production of glyceride mixtures which will either soften and melt or remain plastic and workable within a given temperature range.

Because of the absence of polar groups, the hydrocarbon chains (which account for greater than or equal to 85% of total weight of fats) dominate the physical properties of fats. For example, they are responsible for the sensation of "oiliness" associated with liquid fats. In the solid state the packing modes of hydrocarbon chains give rise to the phenomena of polymorphism and solid solution formation. The changes in packing caused by changes in the arrangement and composition of hydrocarbon chains explain the importance of chemical structures in determining the physical properties of a fat.

Technically, the two most important groups of physical properties of fats are those associated with (1) phase changes, for example, solid-liquid equilibrium, solid solution formation and polymorphism; (2) the rheology of mixtures of solid and liquid fats.

Extraction of Oil Seeds Using the Expeller Process

A. J. D. Robb

Fletcher Industries, Dunedin

The history of oil seed extraction processes is briefly described followed by a detailed description of the modern expeller process. The construction of the typical expeller is described, and the mechanical processing of the oil seed and its prior preparation. The efficiency of the process as this relates to the rolling and cooking of the raw material and the maintenance of wearing parts is discussed along with the technical and laboratory control for processing and finished product quality.

Post-Prandial Thoughts on Fats

Marion F. Robinson

Nutrition Department, University of Otago

To what extent fats are nutritionally important is very much a matter of controversy. Man gets his fats from both animal and plant foods. Just as for other nutrients, man can consume too much or too little fat, the latter a very rare happening in New Zealand. We can estimate what man ingests but cannot predict with certainty the subsequent handling of the dietary fats. People vary in their metabolic response to food, such as in their absorption of fats; and each man does not always follow the same pattern from day to day. Variations in response to one nutrient affect the responses to other nutrients, a malabsorption of fats is associated with malabsorption of minerals, e.g. Ca, Mg, Fe, Cu, Zn, Mn, Cr, and the fat soluble vitamins A, D, E, K. But man fortunately can often adapt to such changes.

Some dietary manipulation of the fat intake by New Zealanders is considered "prudent," but how much, for whom and for how long is open to debate.

Fats and the Physician

P. J. Scott

Department of Medicine, University of Auckland

Amongst large populations, several factors are related to the incidence of arterial disease. It is still not known whether these epidemiological factors merely represent associations, rather than cause and effect relationships. There is a relationship between the nature of fat in the diet and mean blood lipid levels of particular human populations. *Individual* people with high blood lipid levels have a high incidence of arterial disease. We still lack evidence to support, in a satisfactory manner, the thesis that the diet of the *individual* "normal" person who exhibits none of the other known associations of arterial disease, will act as a major determinant in deciding that person's medical future in terms of arterial disease. This unsatisfactory situation arises from lack of knowledge concerning the true relationships between dietary fat, transport, synthesis, catabolism of fats, and the relationship of these processes to deposition of lipids in arteries. There is further uncertainty concerning the relationship of artery wall changes to events immediately preceding strokes or coronary heart attacks. As always, incomplete information and unproven hypotheses excite controversy. Nevertheless, the physician faced with a patient or family, and medical scientists guiding policies on national health, have either to act on the evidence as they see it, or else stand aside completely.

PROFESSIONALISM

Wednesday, 28th August

Factors Influencing Scientific Policy Making in Government (Symposium Plenary)

A. T. Johns

Director General, Ministry of Agriculture and Fisheries, Wellington

The procedures for policy formation in Government in New Zealand are described and the place of science indicated. The organisational structure for science administration varies considerably from country to country and appears to be in a state of evolution everywhere. The changing roles and image of science in the national scene are discussed particularly from the point of view of agriculture.

Professionalism in Chemistry (Symposium Plenary)

A. M. Kennedy

The University of Canterbury

Chemistry: Tubs, Test Tubes and Theory—A Professional Mix?

J. G. Fletcher

Auckland Technical Institute

The dropping of the first atomic bomb over Japan in 1945 heralded a hitherto unknown awareness of science by society and the beginning of the postwar chemical knowledge explosion. One of the side effects of this growth is the emergence of so many subdisciplines of chemistry.

Only now, are the chemical professional associations catching up with these changes and the effects they have had on their members' attitudes towards professionalism.

Following a survey of how overseas chemical bodies are re-examining their functions, suggestions for future activities, relationships and attitudes within the N.Z.I.C. are forwarded.

These proposals support the hypothesis that it might become increasingly more difficult for chemists to be proud of their profession in the questioning, environment-conscious society of tomorrow.

Thoughts on the Organisation of Science in New Zealand

F. B. Shorland

Department of Biochemistry, Victoria University

The organisation of government science in New Zealand has developed in response to immediate needs, beginning in 1865 with the Geological Survey and Colonial Laboratory and extending later to the Departments of Agriculture, SIR, Marine, Internal Affairs, Forest Service, Health, each with their scientific units giving rise at times to conflicting and overlapping interests.

The relationship of government science to university science concerning salaries, equipment and subject matter is a continuing concern of government scientists. Dr Robertson, Director General, DSIR, recently maintained* *inter alia*, that the University is most suited to creativity; 'mission' oriented research requires more support by relevant post-graduate university research, and that more liaison with the university should be secured by further encouragement of joint symposia, vacation employment and by siting of government laboratories on the university campus.

It is considered by the present author that the problems outlined by Dr Robertson would be largely overcome by redesignating the DSIR divisions as Institutes of the University and according the staff academic designations. Recruiting would be facilitated and the choice of Director, now limited by PSC regulations would be widened. Library facilities would be greatly improved as would the range of equipment. In this way not only would economies be effected, but the prospects for the development of centres of excellence would be enhanced.

**Proceedings of the Royal Society of New Zealand*, 1973, 101, 89-92.

Chemistry and Food Production in the Future

D. J. Higgins

Kemphorne Prosser & Co. Ltd., Dunedin

The speaker outlines predicted world food requirements in the future and comments on the levels of fertiliser and agricultural chemicals which will be necessary in their production.

He indicates some areas where new chemical developments could assist both internationally and in New Zealand, and suggests some areas where research should take place.

He goes on to discuss the extent to which environmental factors will influence the production of the required quantities of chemical materials and queries whether it will be possible or desirable to sustain some commonly held views in this area.

Solidarity in a Science-Based Profession

G. A. Wright

Departments of Chemistry, University of Auckland

Chemistry graduates find employment in a wide variety of occupations ranging through research, development, analysis, quality control and production, to administration, management and teaching. It is customary for chemists to owe their main professional loyalties to their employing organisations, and only a few chemists deal directly with members of the public as clients. This appears to be the reason why the profession of chemistry has less impact on community affairs than do other professions (law, medicine, architecture, engineering) in spite of the fact that we live in a scientific age.

A good case can be made for more active participation by members of the Institute of Chemistry in debate on public issues. Chemists have much to contribute: they are trained in scientific method as a technique of solving problems, and they have a considerable knowledge of chemical substances and the underlying principles which explain their behaviour. Several current issues will be discussed from the point of view of the professional chemist, including nomenclature and classification of hazardous chemicals, recognised standards for testing and analysis, and the design of comprehensive scientific surveys such as the Waitemata Harbour Project.

SOCIAL RESPONSIBILITY

Thursday, 29th August

The Option's of Mankind's Future

A. T. Wilson,
University of Waikato (Symposium Plenary)

During the last century man has modified his environment on a massive scale — alas not always for the better. It is for the scientist to warn his community of the changes inherent in its actions and to devise economical methods whereby his society can preserve and improve the "quality of life".

During the next century man will at least have the capabilities to modify man. This development will open a Pandora's box which will make the present environmental problems faced by society look like child's play.

The options open to mankind in the next millennium depend basically on whether or not he wishes to control his rate of increase. If he can, a steady state will be attained. If he continues to increase his numbers, the result will be interesting but not necessarily catastrophic.

Where the Buck Stops (Symposium Plenary)

L. R. B. Mann
Department of Biochemistry, University of Auckland

That science has given the human race immense benefits is virtually universally believed. Almost as widely accepted is the need for regulation of science to prevent immense harm (including, literally, destruction of the human race) resulting from applications of science. Who is to be responsible for this regulation?

1. The limits to growth must be understood and acted on by governments within the next few years if we are to survive with anything like an orderly, decent world. Scientists must play a greater role in providing politicians and the public with reliable information and policy option analyses on matters where mistaken or unwise scientific advice taken in secret by politicians could cause great damage.

2. Not only what scientists say, but also what they do, should now come under careful ethical scrutiny by their professional associations. Of particular relevance to chemists are recent proposals that prevention of chemical and biological warfare can be achieved in no other way than through scientists' own professional societies.

Where, then, does the buck stop? Our answer will depend on whether we acknowledge that we are always more than scientists: citizens as well.

The Quality of Scientific Evidence

T. J. Sprott
T. J. Sprott and Associates, Auckland

Chemical Information

W. S. Metcalf
Department of Chemistry, University of Canterbury

What kind of information can those outside the profession use to their advantage, and how will they be given it?

Chemical information can be entertaining, spectacular, and mind stretching. We can share these pleasures.

Consumer protection could be improved by the development of plain, memorable, and sufficiently unambiguous nomenclature for consumer products. It would remove some confusions that are used in advertising for commercial advantage. Some clear way of costing components would serve a similar purpose.

Chemical information suitably injected should increase the efficiency of manufacturing, farming, engineering, and the service trades, not only on the major problems which appear in the Research Association and DSIR reports, but also in a multitude of small ways.

We will not be consulted because those whom we might benefit have no notion of what we have to offer. An exception must be made for research workers in related disciplines who have studied elementary chemistry as part of their training.

If chemists are jobless the fault lies with chemists, not with farmers, nor manufacturers, nor the public, nor administration, nor politicians, but just with chemists who have insufficient imagination to see applications of their knowledge, or who, having such imagination, take no for an answer.

Chemistry and Conservation

A. F. Wilson
New Zealand Forest Products, Tokoroa

This paper will examine the responsibility of chemists in managing the resources of the human environment. The role includes:

- Conserving energy in industrial processes.
- Ensuring that there is no unnecessary wastage of raw materials.
- Protecting industrial workers from toxic materials, exposure to loud noises, fire and explosions.
- Ensuring that industrial products and effluents have no harmful effects on the people who use the products or who may be exposed to the effluents.

The Disposal of Industrial Wastes

M. E. U. Taylor
Auckland Regional Authority

The growing social and economic cost of disposal of industrial wastes is causing this aspect of the manufacturing process to assume an importance far greater than it was ever accorded in the past. The nature of some of these wastes can cause considerable disposal problems although industrial chemists could sometimes reduce these by a more thoughtful approach to process design. Ways of minimising both the direct and indirect costs to industry are also becoming more urgently needed, and the paper explores some approaches to this.

SPECIALIST GROUPS

Abstracts of Papers

Analytical

Recent Developments in X-Ray Fluorescence

N. E. Whitehead*, D. C. Robinson, and G. E. Coote
Institute of Nuclear Sciences, DSIR, Lower Hutt

Excitation by X-rays, radioisotope sources, charged particles, and non-dispersive detection, are reviewed, and it is shown that X-ray excitation is more sensitive for individual elements (less than 0.1 mg/kg is possible), whereas charged particle excitation (about 5 mg/kg) preserves a much more uniform sensitivity and is more sensitive for the light elements. Using the latter technique, ion exchange resins were analysed for elements Na to Cl (concentrations 200 mg/kg to 60 g/kg); hair from archaeological specimens contained large amounts of lead and arsenic; air filters were analysed for lead and bromine (and showed a very high correlation); metallic impurities in plate glass were shown to be mainly tin, with 0.1% lead; bromine levels in soils were determined to be 20-50 mg/kg.

The Rapid Determination of Tungsten in Ores and Concentrates by Atomic Absorption Spectrophotometry

B. F. Quin

Department of Chemistry, Biochemistry, and Biophysics, Massey University, Palmerston North

The intensifying search for tungsten ore deposits has led to an increasing need for rapid and accurate methods for the analysis of tungsten ores and concentrates.

Despite the suitability of atomic absorption spectrophotometry for rapid analysis, there have been very few attempts to apply this method to the analysis of tungsten. This can be largely attributed to the tendency of tungsten to form a wide range of polymeric and heteropolymeric anions in acid solution. The type of tungsten species formed is dependent on the type of compounds used for dissolution, and on the presence or absence of other elements in the sample. As the various anions produced differ in the ability with which they can be dissociated into free tungsten atoms, reliable results could not be obtained.

To surmount this problem, a method was developed which involves dissolution of the ore sample with a mixture of nitric and hydrofluoric acids, followed by evaporation to dryness. The acid-free residue in which tungsten is now present as hydrated tungsten oxide, is then redissolved in dilute alkali, in which tungsten exists solely as the discrete tungstate anion. Tungsten is then determined rapidly and accurately by conventional atomic absorption spectrophotometry, using a nitrous oxide-acetylene flame.

Direct-Reading Emission Spectrometry for Geochemical Surveys

M. H. Timperley

Chemistry Division, DSIR, Petone

An analytical system using a direct-reading emission spectrometer interfaced to a mini-computer and developed specifically for silicate analyses will be described.

Samples are mixed with buffer and burned in a specially designed chamber using a d.c. arc. The mini-computer interfaced to the spectrometer controls all spectrometer functions after arc initiation and calculates and prints the results in parts per million or percent. A natural sediment serves as a standard and a technique is used which permits background corrections to be derived from this same standard. Adequate sensitivity is achieved for both "volatile" and "involatile" metals in one burn by controlling the integration time of each individual line emission to ensure optimum line to background ratios.

The capabilities of the system in terms of accuracy, precision and speed of analysis will be discussed.

Emission Spectroscopy with Mini-Computer Processing in the Process Control of an Aluminium Smelter

I. E. Norrish* and G. French

N.Z. Aluminium Smelters Ltd., Invercargill

An application of Optical Emission spectroscopy as used by the N.Z.A.S. Bluff Smelter.

The calibration process is discussed along with problems associated with matrix effects on differing aluminium alloys and how these are overcome by the use of a mini-computer.

Application of the mini-computer to indicate out of specification elements and customer certification, the significance of sampling and instrument errors, their relationship to the aluminium production process, and the stability, laboratory environment and day to day operations are also considered.

Equipment in use includes an A.R.L. 29000B Direct reading Spectrograph with High Precision Source Unit and P.D.P.-11 mini-computer.

Observations on the Atomization Process for B, Al, Si, Ti, V, Zr, Mo, and Ba in Nitrous Oxide-Acetylene Flames

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An investigation has been carried out to determine the way in which atomic absorbance readings for B, Al, Si, Ti, V, Zr, Mo, and Ba in nitrous oxide-acetylene flames on a slot burner are influenced by HClO_4 , HCl, HF and H_2SO_4 . Lateral profiles of absorbance in flames with and without an argon shield were determined using a narrow aperture optical system and the flame gas temperatures at the position of maximum absorbance were measured using the iron 'two-line' method. The maximum atomic absorbance reading for each element in aqueous solution has been related to the corresponding flame gas temperature and intensity of C_2 emission in flames which were diluted and cooled with added nitrogen. A study of these results has thrown new light on some of the factors controlling atom production and analytical sensitivity for refractory elements in nitrous oxide-acetylene flames.

Design and Performance of a Flameless Atomiser for Atomic Absorption Spectroscopy

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A flameless atomiser for use in atomic absorption spectroscopy has been developed. This atomiser has been designed to utilise either graphite rods or tantalum strips in an unenclosed system. The design concept will be discussed and comparison made between graphite and tantalum as element material in flameless atomisers. Sensitivity and interference data will also be presented.

The Development of Referee Methods for Trace Metals in Clinical Chemistry by Atomic Absorption Spectroscopy

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Referee methods are methods of known accuracy based on the use of Standard Reference Materials certified by the National Bureau of Standards (N.B.S.) Washington. The method for calcium in serum has been completed and methods for serum magnesium, serum lithium and blood lead are being produced. The first step is the preparation of the protocol, or candidate for the reference method, in which all variables, sources of interference are identified, a suitable diluent evaluated, and optimisation of instrumental parameters described. In the validation procedure eight laboratories following the detailed protocol analysed the samples by atomic absorption. Their results were compared to Isotope Dilution Mass Spectroscopy (I.D.M.S.) accurate to within $\pm 0.2\%$ as a reference method. The utility of the methods lies in establishing the absolute value of these metals in control sera, in calibration materials for automated equipment and in evaluation of the accuracy of many field methods in use. Details of the validation exercise for calcium in serum will be given.

The Determination of Chloride Ion Concentration in Nanolitre Samples of Biological Fluids

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In the investigation of ionic regulations and active transport of ions by animal tissues, it is often necessary to measure the ionic concentrations in small volumes of fluid.

From many invertebrate excretory organs it is only possible to collect samples of a few nanolitres. Using the method described it is possible to measure chloride ion concentration with high accuracy from samples of this size.

A known volume of sample (0.5-5 nanolitres) is placed on the tip of a fine silver wire under paraffin, and contact established with it through a blunt glass microelectrode filled with sodium nitrate in agar. The other end of this salt bridge is in contact with a silver nitrate solution in which is inserted a silver wire. Chloride ions are precipitated from the sample by silver ions electrolytically released by the passage of current from an external source. The end point is determined potentiometrically, and the amount of silver released is measured by the total charge on a condenser placed in series with the cell.

Examples are given of the use of this method in the investigation of the uptake of chloride ions by freshwater insects, and of the functioning of the insect excretory system.

The Isolation of Uranium and Thorium from Calcareous Material for Analysis by α -SPECTROSCOPY

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For alpha spectroscopy purposes uranium and thorium must be purified by a factor of about 10^8 . The material is dissolved in acid and the uranium and thorium precipitated with iron carrier. The precipitated material is redissolved and reduced with sulphur dioxide. It is loaded on a column of Bio-rad AG 50W X-12 and most elements, except uranium and thorium, are eluted with 3.5M HCl. The uranium and iron are then eluted with 8M HCl and saturated oxalic acid respectively, and are finally purified by extracting them into thenoyltrifluoroacetone in toluene at pH 4 and 1.9 respectively. Yields are 70-80% compared with less than 50% in the literature. To achieve this, phosphate, fluoride, and sulphate ions must be avoided and/or eliminated.

The Accuracy and Precision of Chemical Analysis of Cement

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The compound composition of cement can be analysed in three ways:

- (i) From chemical analysis a potential compound composition is calculated.
- (ii) From the intensities of X-ray diffraction peaks the amount of each compound present is calculated.
- (iii) From unground cement clinker it is possible to use microscopic point counting techniques to estimate the compound composition.

Chemistry Division, DSIR, has assembled six samples of cement and cement clinker and these samples have been circulated to 40 laboratories throughout the world. In this paper the current results from the chemical analyses will be reported. The cements have been analysed for SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , CaO , MgO , SO_3 , Na_2O , K_2O , Mn_2O_3 , P_2O_5 , as well as the insoluble residue and uncombined CaO .

Using techniques developed by Youden the between-laboratory and within-laboratory values for the standard deviations have been calculated. Methods of dealing with outliers will be described and the results obtained by different analytical procedures will be described.

Biochemistry

Regulatory Properties of the Lactate Dehydrogenase from *LACTOBACILLUS CASEI*

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The L(+) lactate dehydrogenase from *Lactobacillus casei* differs from that in other species of *Lactobacillus* in requiring fructose diphosphate for activity. In this respect it more closely resembles the lactate dehydrogenase from streptococci. However, the *L.casei* and streptococcal enzymes differ markedly in respect to other properties such as pH-dependence. The activity of the *L.casei* enzyme is also affected by Mn^{++} ions. A comparison of the *L.casei* and streptococcal lactate dehydrogenases is of interest in relation to the reported close similarity between both the malic enzyme and the fructose diphosphate aldolase of *L.casei* and the corresponding enzymes in certain streptococci.

Evidence for an Anaerobic Electron Transfer Chain in the Rumen Bacterium *BACTEROIDES RUMINICOLA*

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Bacteroides ruminicola has been shown to have an unusual energy metabolism, as evidenced by high growth yields (ratio of dry weight production to carbohydrate fermented). This can be due either to unknown ATP-generating reactions, or to a high Y_{ATP} (g dry weight per mol ATP), or to a low maintenance energy.

If the first explanation is correct, the unknown site of ATP formation would be most likely to occur during fumarate reduction to succinate. De Vries has postulated this step to be coupled to the formation of 2 ATP molecules in certain other bacteria. We are examining this reaction in some detail. The fumarate reductase activity was assayed anaerobically in a membrane fraction. Inhibitors of electron transport in mammalian mitochondria were tested, and whilst antimycin A and rotenone did not inhibit, HOQNO fully inhibits the reaction, 50% inhibition occurring at $6.5 \times 10^{-6}\text{M}$.

When a difference spectrum of the membrane fraction with and without HOQNO was examined in the presence of NADH and fumarate, absorbance peaks of 427 nm and 563 nm appeared. This suggests that the b-type cytochrome known to be present may be involved in the reduction of fumarate by NADH on the fumarate side of the HOQNO block, though it could be on a side path.

HOQNO is a naphthoquinone analogue and extraction of cells with non-polar solvents revealed that vitamin K (menaquinone) is present. Examination of a possible role of flavoprotein in the fumarate reductase reaction is under current investigation. The above results suggest that an anaerobic electron transport chain bound to the bacterial membrane exists, though any relationship to possible ATP production by anaerobic oxidative phosphorylation remains to be demonstrated.

Growth Yield Measurements in *BACTEROIDES RUMINICOLA*

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Bacteroides ruminicola, strain B 4, produces much greater yields than might be expected from its fermentation pathways. Experiments have been carried out using D-glucose, D-xylose and L-arabinose as substrates in an attempt to differentiate between two possible reasons for this. These are:

- (i) Anaerobic electron transport occurs coupled to oxidative phosphorylation;
or
(ii) Maintenance energy may be less than in most other bacteria, thus making ATP utilisation more efficient.
If calculations of Y_{ATP} (g dry weight per mol ATP) are made assuming that (i) occurs, and that 2 ATP are made per mol of fumarate reduced to succinate, then Y_{ATP} during glucose and xylose fermentation becomes 10.5, the normal value.

The fermentations of xylose and arabinose are thought to occur by the same pathway, as judged by fermentation products (though growth on arabinose is faster). However, $Y_{arabinose}$ is higher than Y_{xylose} ; and thus Y_{ATP} during arabinose fermentation may be estimated to be greater than 10.5 even when 2 ATP (per succinate) are assumed to be formed by oxidative phosphorylation! Corrections for storage polysaccharide have been made in all the above experiments.

No definitive interpretation of these results can be made, but it does seem likely that explanation (ii) is valid and that (i) cannot be ruled out as a possible additional factor.

Growth Characteristics of *C. ALBICANS* When Grown in Continuous Culture

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The growth characteristics of *Candida albicans* CMI 45,348 has been examined under aerobic conditions in a chemostat. At different steady states the environment was controlled with respect to the dissolved oxygen, the concentration of the carbon and nitrogen source, the pH and the temperature. At each steady state a series of parameters such as RQ, dry weight of cells, glucose and nitrogen utilised, extra-cellular polysaccharide and acid produced, were determined. With maltose as the carbon source the morphology was mycelial whereas with lactate as a carbon source a yeast culture was obtained. Fructose or glucose as a carbon source produced a mixed morphology of yeast, pseudo-mycelial and mycelial cells.

Purification of Thymine Oxidase from *NOCARDIA CORALLINA*

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Thymine oxidase (1), an inducible enzyme in several bacterial species (2, 3, 4) which catalyses the initial oxidation of the pyrimidines, uracil and thymine, has not previously been purified from any source.

Purification of the enzyme from *Nocardia corallina* involved disruption of the organisms using a French press followed by fractionation of the extract using calcium phosphate gel, ammonium sulfate, Sepharose 4B, DEAE cellulose, calcium phosphate gel deposited on cellulose, DEAE Sephadex A50 and finally Sephadex G200.

The enzyme from Sephadex G200 was 55 fold purified and represented 25% of the original activity in the crude extract. Studies using acrylamide gel electrophoresis showed the enzyme to be approximately 95% pure. The molecular weight of thymine oxidase from *N. corallina* was $297,000 \pm 15,000$ as determined by sedimentation equilibrium analysis (6) and the K_m values for thymine and uracil at pH8.85 were 8.4×10^{-5} and 4.0×10^{-4} mole per litre respectively. The absorption spectrum of the enzyme was strongly suggestive of a flavoprotein.

Assay of thymine oxidase involves the coupling of the oxidation of substrates to reduction of methylene blue. Preliminary studies have suggested that oxygen is directly involved in the oxidation of thymine as well as in the reduction of methylene blue.

References:

1. Hayaishi, O., & Kornberg, A., *J. Am. Chem. Soc.* (1951), 73, 2975.
2. Hayaishi, O., & Kornberg, A., *J. Biol. Chem.*, (1952), 197, 717.
3. Lara, F. J. S., *J. Bact.*, (1952), 64, 271.
4. Batt, R. D. & Woods, D. D., *Biochem. J.*, (1951), 49, ix.
5. Batt, R. D., *J. Bact.*, (1961), 81, 59.
6. Yphantis, D. A., *Biochem.* (1964), 3, 297.

Physical Studies of Biological Polymers

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Biological polymers are often separated into size ranges by rate zonal centrifugation in a sucrose density gradient. The sedimentation of such molecules has been computer-simulated, and thus the mean sedimentation coefficient S for each of twenty well-defined glycogen fractions calculated. The calculation involves computing the viscosity and density of the sucrose as a function of distance down the centrifuge cell and methods of approximating these functions have been critically examined.

Each fraction has also been studied using dynamic light-scattering. According to this method, the rate of Brownian motion of solute molecules is measured by analysing the Doppler shifts in the frequency of light scattered by the solution. A laser light source must be used, and the analysis of signal from the scattered light is performed by an auto-correlator commanded by an on-line computer. The parameter thus obtained is the mean diffusion coefficient \bar{D} of the polymer fraction.

Provided the partial specific volume, \bar{v}_0 , of the polymer material is known, the mean molecular weight \bar{M} for each fraction can be obtained from the Svedberg equation

$$M = \frac{S}{D} \frac{RT}{(1-\bar{v}_0)}$$

The molecular weight distribution of glycogen has thus been obtained. The vast majority of this material, as extracted, lies in the molecular weight range:

$$10^7 < M < 2 \times 10^8$$

Electron microscopy shows that glycogen molecules consist of spheres and conglomerates of these spheres. A series of models has been built from small silica spheres to represent glycogen molecules from various fractions. The frictional ratio f_r , found by sedimenting the models through glycerine under gravity, correlates well with the f_r value obtained from S and M for the corresponding glycogen fraction.

Drug Binding and Displacement to Serum Albumin

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It has been known for some years that blood contains substances which compete with drugs for binding sites and thereby alter the apparent affinity constants of the protein-drug complexes, e.g. salicylates will displace bilirubin from plasma proteins. Since these displacement interactions may occur with pharmacologically inactive compounds, then a situation where two or more drugs are administered will likely produce even further complicating factors. If the drug must be administered close to its toxic level, then any increase in concentration as by displacement by another species will cause a significant problem.

This project has attempted to obtain detailed binding isotherms for the interactions of salicylic acid and indomethacin in physiological serum albumin concentrations.

It is remarkable that only a handful of investigators appear to have made a detailed study of albumin binding capacity in the physiological ranges.

Initial studies using classical equilibrium dialysis indicated very significant decreases (possibly up to 40%) in the binding of salicylate on addition of physiological levels of indomethacin, but factors including time and accuracy have led to the use of the relatively new continuous dialfiltration technique. Up to 60% salicylate displacement has been demonstrated up to date, but it must be noted that these large displacements involve the use of indomethacin at greater than physiological levels.

These studies so far have encompassed the comparison of binding to pure BSA, pure HSA, and both normal and dialysed HSA, as provided by the Commonwealth Serum Laboratories. Significant differences have been noted.

Dynamic Light-Scattering from Biological Macromolecules

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The method of dynamic light-scattering, or photon correlation spectroscopy, enables the diffusion coefficients (D) of macromolecules to be determined rapidly and precisely. The diffusion coefficient may be related to the effective hydrodynamic radius (a) by means of the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\eta a}$$

Evaluation of a or D allows conformation changes to be described in terms of environmental parameters e.g. temperature, pH, ionic strength etc. Analysis of the scattered light may be made either by analogue autocorrelation or by photon correlation and comparisons of the two methods have been made utilising protein solutions as the scattering source. The sensitivity of the method depends both on the size and shape of the scattering particle and upon the intensity of the laser light source. The present apparatus allows measurements to be made down to the $\mu\text{g./ml.}$ range (depending on particle size). This enables the extrapolation of D to zero concentration to be made with high confidence.

Dynamic light-scattering has also been performed on electrophoresing macromolecules. It has proved possible to identify various species by spectral analysis.

The Concept of Semi-Synthetic Proteins, with Particular Reference to the Chemical Synthesis of an Immunoglobulin

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The chemical synthesis of proteins can only be achieved with a tremendous expenditure of time, as the work load involved increases exponentially with the size of the protein. Although the Merrifield Solid Phase Method allows automation of the synthetic procedure the large size of proteins does not allow isolation of pure products due to the accumulation of impurities formed from incomplete coupling reactions.

The preparation of semi-synthetic proteins, however, can allow the study of structure-function relationships by chemical synthesis of even large proteins such as immunoglobulins. A semi-synthetic protein is prepared by combination of a synthetic peptide with the fragment corresponding to the rest of the native protein.

This paper will describe initial work directed towards the partial synthesis of thyroglobulin auto-antibodies. This goal has been approached from two different directions, namely the purification of thyroglobulin antibodies by affinity chromatography and isolation of light chain fragments, and the development of methods for the synthesis of peptides which are suitably protected for combination with native fragments.

Synthetic and Structural Studies on Peptides : Somatostatin

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Somatostatin (growth hormone-release inhibiting factor) continues to produce increasing interest in the literature as a possible method for controlling growth hormone levels. Synthesis of the active pure hormone, therefore, would be highly desirable to many research groups. The chemical synthesis of somatostatin should produce relatively large amounts of biologically active material as well as offering the added advantage of being able to introduce radioactive amino acids into the peptide chain.

Automated solid phase synthesis of somatostatin has been achieved by conventional Merrifield techniques. Of particular interest in this synthesis is the use of protected sulphhydryl groups (with the *p*-methoxybenzyl moiety) such that this tetradecapeptide can be cyclised to the desired intramolecular disulphide form.

Recently it has been shown that *o*-nitrophenyl esters of amino acids may prove superior to the conventional dicyclohexylcarbodiimide method of peptide bond formation. The fact that the *o*-nitrophenyl ester method leads to fewer by-products and the recovery of unused amino acid derivatives should result in an overall reduction in the cost of synthesizing biologically active hormones. The synthesis of the appropriate amino acid derivatives and somatostatin itself will be discussed in this paper.

Intracellular Localization and Properties of Aldehyde Dehydrogenase from Sheep Liver

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The distribution of aldehyde dehydrogenase in sheep liver was studied. Activity was found in the cytoplasm, mitochondria and microsomes. Cross-contamination of activities from different sub-cellular fractions during the isolation procedures used was shown to be insignificant. Accordingly, the level of aldehyde dehydrogenase activity found in each fraction should reflect the distribution pattern *in vivo*.

Aldehyde dehydrogenases from cytoplasm and mitochondria were isolated, and some of their catalytic properties examined. The results show that the enzymes from the two fractions are not identical.

Biochemical Effects involved in the Development of Aspirin-induced Gastric Damage

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Aspirin (acetyl salicylic acid) produces gastric damage which can result in the loss of considerable quantities of blood (Smith, 1966a; Salter, 1968). The work reported here is part of a long term project to study the biochemical factors involved in the development of damage by this drug. The relationship of these effects to structural damage observed under the light and electron microscopes is also being studied.

Previous studies (Roth & Valdes-Dapena, 1963; Rainsford, Watkins and Sith, 1968; Hingson & Ito, 1971) indicate that the early effects of aspirin are of a physical nature involving sloughing of the protective mucus layer and direct physical damage by particles of the drug. The physical effects have, in part, been shown to be due to an effect of aspirin and salicylate on the interactions between some components of the soluble fraction of mucus, (Rainsford, Watkins &

Smith, 1968). This effect only occurs under the acidic conditions (pH 3.5) present in the stomach and not at pH 7.0. Further studies involving the sedimentation analyses of the gel-like fraction of mucus (as developed by Johnson & Rainsford, 1972) will be reported. The results show that 50mM salicylates cause an increase in the interactions between the gel-like components of mucus.

The biochemical effects which follow the initial physical effects seem to involve inhibition of a wide variety of biosynthetic and other biochemical processes (Smith, 1966b; Rainsford & Smith, 1969). Most important of these is the possibility of inhibiting the biosynthesis of protective mucus, a suggestion made from *in vitro* studies (Kent & Allen, 1968; Rainsford & Smith, 1969). In the work a single oral dose of 50 or 200mg/kg aspirin to rats was found to inhibit the incorporation of radioactively labelled precursors (e.g. $^{35}\text{SO}_4$) into the mucus glycoproteins isolated (and characterised) from the gastric mucosa.

The relationship of these studies to the development of cellular damage by aspirin in the stomach will be discussed.

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REFERENCES:

- Hingson, D. J. & Ito, S. (1971) *Gastroenterology*, 61, 156-177.
Johnson, P. & Rainsford, K. D. (1972) *Biochim. Biophys. Acta*, 286, 72-78.
Kent, P. W. & Allen, A. (1968) *Biochem. J.* 106, 645-658.
Rainsford, K. D., Watkins, J. & Smith, M. J. H. (1968) *J. Pharm. Pharmacol.* 20, 941-943.
Rainsford, K. D. & Smith, M. J. H. (1969) *Biochem. J.* 111, 37P.
Roth, J. L. A. & Valdes-Dapena, A. (1963) in "*Salicylates — an International Symposium*". Editors: Dixon, A. St. J., Martin, B. K., Smith, M. J. H. & Wood, P. H. N. pp. 224-225. London: J. & A. Churchill.
Smith, M. J. H. (1966a) in "*The Salicylates. A Critical Bibliographic Review*", pp. 223-306, New York: Interscience.
Smith, M. J. H. (1966b) *ibid* pp.49-105.

The Contribution of General Base Catalysis by Imidazole to Catalysis by Chymotrypsin

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An attempt to estimate the importance of general acid-base catalysis in enzymic catalysis has been made, using the hydrolysis of the ester group of *N,O*-diacetylserinamide as a model for the deacylation of acylchymotrypsins. General base catalysis of this reaction by imidazole is estimated to reduce the activation energy by at least 31 kJ mol⁻¹. The rate of reaction, however, is not greatly enhanced because of an unfavourable change in the entropy of activation from -132 to -197 J K⁻¹ mol⁻¹. At about 300 K, a typical temperature for enzyme catalysed reactions, the reduction in activation energy would cause a rate enhancement of about 3 × 10⁵ fold if the unfavourable entropy change did not occur. For specific acyl-chymotrypsins the entropy of activation for deacylation is about -89 J K⁻¹ mol⁻¹, allowing the full effect of general base catalysis by imidazole to be realised. It is therefore postulated that in the active site of an enzyme a properly oriented imidazole side chain may catalyse the rate of a reaction 10⁵ fold by general base catalysis.

Methylation of Tryptamines by Human Enzymes

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Evidence exists that the psychotomimetic methylated indoleamines, dimethyltryptamine, bufotenin and 5-methoxydimethyltryptamine may play a role in the schizophrenias.

We have found enzymatic N-methylation of tryptamine and of N-methyltryptamine by ^{14}C S-adenosylmethionine in extracts of "normal" human liver and other organs. A sensitive two-dimensional thin layer chromatography assay system was created to give better separations and lower blank activities for simultaneous assay of a number of indoleamine derivatives than other reported radiochemical assays.

A potent dialysable inhibitor of the indoleamine N-methyltransferase was found in human liver tissue.

The widespread distribution of the indoleamine N-methyltransferase and its potent dialysable inhibitor in liver is of interest in relation to the biochemical model being examined.

Studies on the Effects of Anti-Tumour Drugs and other Compounds on ATPases of Cellular Membranes

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An investigation of the adenosine triphosphatase (ATPase) activity of smooth and rough endoplasmic reticulum, and of lysosomes in mouse liver is described. Methods of isolating mouse liver smooth and rough endoplasmic reticulum and mouse liver lysosomes have been developed, and assays for ATPase activity using each of these materials have also been developed.

The ATPase activity of each membrane fraction has been characterised. Smooth and rough reticular membranes have both Mg²⁺-stimulated, and Na⁺/K⁺-stimulated, Mg²⁺-dependent ATPase activities. A powerful Mg²⁺-stimulated ATPase is associated with mouse liver lysosomal membranes.

The *in vitro* effect of various antitumour drugs, of the carcinogen carbon tetrachloride, and of chemicals such as adenosine-3', 5'-cyclic phosphate (cAMP), mepacrine and Triton X-100 on the ATPase activities of these membranes has been investigated. Results obtained are consistent with dependence of ATPase activity on membrane conformation, and agents perturbing the membrane state result in altered ATPase activities.

Novel Transaminations and their relation to Phenylketonuria

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Brain and/or plasma serotonin (5-HT) is reduced in clinical and experimental phenylketonuria. The associated rise in the urinary excretion of non-hydroxylated indolic acids suggests an increased transamination of tryptophan. This transamination may lower brain tryptophan, the availability of which is rate-limiting for 5-HT synthesis. The increased transamination may be due to transamination between tryptophan and phenylpyruvate (present in high levels in phenylketonuria). Phenylpyruvate and other aromatic keto acids are transaminated by tryptophan more readily than is α -ketoglutarate (α -KG). For both rat and human aminotransferases,

this is due to an apparent change in affinity for tryptophan in the presence of aromatic keto acids. The apparent K_m for tryptophan is 2 mM in the presence of phenylpyruvate and 55 mM in the presence of α -KG. The affinity of the enzymes for keto acids and the relative reaction velocities would also favour transamination of aromatic keto acids rather than α -KG by tryptophan at physiological concentrations of substrates. Kinetic analysis of the transaminations occurring with phenylalanine, tyrosine and DOPA suggest that aromatic keto acids are the preferred substrates for brain aromatic amino acid aminotransferases.

Myocardial Adenyl Cyclase

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A crude membrane preparation has been prepared from guinea pig myocardium, and the activity of adenyl cyclase in the presence and absence of various physiologically active agents has been studied. Conditions for the incubation of the membrane preparation and assay of cAMP will be presented.

An Hydroxyproline-Rich Arabinogalactan-Peptide from Wheat Endosperm

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The water-soluble polysaccharides from wheat endosperm can be separated by ammonium sulphate fractionation or by gel filtration chromatography into an arabinoxylan and an arabinogalactan-peptide. The arabinogalactan-peptide has been shown to be a non-associating, polydisperse macromolecule ($\bar{M}_w = 22,000$). The molecule consists of 8% peptide material associated with polysaccharide composed of galactose and arabinose in the ratio 1.5:1 (w/w).

Chemical and enzymic degradation studies show that the polysaccharide is a β -galactan substituted with arabinofuranosyl residues. The peptide is rich in hydroxyproline (16-20% on a molar basis). The linkage between carbohydrate and peptide is stable to hot alkaline treatment and the present evidence suggests that it involves galactose and hydroxyproline in glycosidic linkage.

Metabolism of Mucopolysaccharide and Collagen During Remodelling of the Healing Tendon

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The left hindlimbs of adult, male New Zealand white rabbits were completely relaxed by proximal neurectomy and distal tenotomy. Extensive tissue remodelling accompanied the healing of the divided tendo achilles. Histology showed a gross appearance of mucopolysaccharide (MPS) in the relaxed tendon zones distant from the site of divisions, and distinct from the healing response. Only a $28.2 \pm 19.6\%$ ($p < 0.05$) increase in MPS was found by analysis, on comparing relaxed tendon with corresponding areas from the unoperated, control legs. Radiochemical studies showed little change between test and control tendons in the metabolism of MPS formed before operation. A massive turnover of newly-synthesised MPS was observed post-operatively, throughout the healing tendon.

The release of tension resulted in a change in collagen organisation from large, straight, ordered bundles to smaller,

randomly orientated bundles. A parallel change in staining by the Masson trichrome method occurred, from red to green. However, there was no significant difference between the total collagen contents of the normal and relaxed organs. Of more importance, soluble collagen levels were also similar and low (about 1% of the total collagen).

A hypothesis will be presented linking these diverse findings, based on the extensive interaction of changed residues on the relaxed, disaggregated collagen, which had previously been maintained apart under normal tension.

Gallstone Metabolism in Rabbits

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Rabbits fed a diet composed of 15% oleic acid, 45% standard laboratory pellets, and 40% casein have been variously reported to form gallstones composed principally of cholesterol or calcium glycoallodeoxycholate.

In this laboratory, three rabbits given the gallstone-inducing diet formed stones of calcium glycoallodeoxycholate and some glycodeoxycholate. Control biles contain ratios of allodeoxycholic acid to deoxycholic acid of 1:5 - 1:10 and in gallstone forming biles this ratio is increased to 1:3 - 1:5. Five rabbits which were fed the gallstone-inducing diet plus kanamycin, a non-absorbable antibiotic, produced biles containing little or no allodeoxycholic acid. Thus bacteria acting on the bile acid pool during intestinal transit are responsible for increased concentrations of the less soluble bile acid in rabbits eating the gallstone diet.

It was proposed that cholesterol gallstones might be formed by animals fed gallstone diet plus kanamycin to prevent formation of glycoallodeoxycholate stones, since hepatic cholesterol concentrations increase several fold in animals fed the gallstone diet, and the excess cholesterol could be excreted into the bile. However, there was no significant difference in biliary cholesterol concentrations in each of twelve animals on either diet (0.009 ± 0.0008 micromols/ml (control), 0.019 ± 0.018 micromols/ml (GS); 80 samples).

Total bile salt pools had expanded two to three times in animals fed the gallstone diet (174.3 ± 58.8 mg (control); 299.3 ± 103.3 mg (GS); 6 animals). Therefore these animals seem to be protected against cholesterol gallstone formation by conversion of excess hepatic cholesterol to bile acids prior to secretion into bile. Gallstone formation is controlled by an interplay of effects of intestinal bacterial flora and hepatic regulatory mechanisms.

Mitochondrial DNA of Ram Spermatozoa

T. A. Stewart* and I. T. Forrester

Department of Biochemistry, University of Otago

A possible role for mitochondria in spermatozoon motility and the isolation of a distinct mitochondrial DNA from diploid cells of a variety of organisms has prompted our search for extra-nuclear DNA in ram spermatozoa.

The normal cell fractionation procedures coupling mechanical disruption of the cell membrane followed by isolation of mitochondria by differential and isopycnic centrifugation proved difficult with spermatozoa. This may be due to the resistant outer membrane of the spermatozoa. To overcome this a selective chemical procedure was developed in which the membrane surrounding the head was degraded and the released nuclear DNA digested.

The remaining cell fraction, consisting principally of intact spermatozoon tails, contained DNA that could be isolated and resolved by equilibrium CsCl centrifugation into two species; one with the same buoyant density as nuclear DNA and one at a higher buoyant density.

The heavier of these two species was consistent with a mitochondrial DNA due to its increased concentration in a tail enriched fraction, together with similar banding characteristics in CsCl to DNA isolated from purified lamb heart mitochondria and ram testes mitochondria.

The molecular weight of the heavier DNA species from ram spermatozoa has been determined by band sedimentation and reassociation kinetics.

Work is at present concerned with the isolation of intact mitochondria from mature ram spermatozoa to demonstrate that the heavier DNA species is mitochondrial in origin.

Preparative Gel Electrophoresis as a Tool for the Study of Bacteriophage Messenger RNA Species

M. P. Bodger and M. G. Smith*

Department of Biochemistry, University of Otago

Preparative gel electrophoresis has been used for isolation in high yield of T5 messenger RNA species and also for analytical purpose by comparison of the mobility of the various species with reference RNAs. These methods combined with hybridisation procedures have shown that *E. coli* ribosomal RNA synthesis ceases on infection and that the T5 messenger RNAs are possibly derived from large precursor molecules.

Nucleic Acid Synthesis Induced by a Small RNA Virus

J. R. Bedbrook*, and R. E. F. Matthews

Department of Cell Biology, University of Auckland

Turnip yellow mosaic virus (TYMV) is a small icosahedral virus containing single-stranded RNA of 6.5 kb. In its experimental host Chinese cabbage, the major cytological and biochemical changes, induced by virus replication, appear in the chloroplasts.

The replicative form (double-stranded) RNA of the virus has been found to be associated with the outer chloroplast membrane. In the experiments reported here double-stranded RNA has also been found associated with the nucleus of infected cells.

Nuclear DNA synthesis is affected by TYMV replication. In particular two physically distinct species of DNA are induced by virus replication. Both species appear to contain some RNA. The physical nature and the possible biological significance of these DNA species will be discussed.

The Biosynthesis of Plant Proteins

A. R. Cashmore

Applied Biochemistry Division, DSIR, Palmerston North

Protein synthesis in pea seedlings has been examined from three viewpoints.

1. The majority of proteins in green plants are synthesised either within the chloroplast or the cell cytoplasm. A primary requirement in the study of plant protein biosynthesis is to distinguish between these two sites of synthesis. ³⁵S-methionine labelled proteins from green pea seedlings have been fractionated by acrylamide gel electrophoresis in sodium dodecyl sulphate. By the use of selective inhibitors the sites of synthesis of the major proteins have been determined. Of particular interest are the results concerning the two subunits of Fraction I protein and the major proteins of the chloroplast lamellae.

2. One of the more obvious regulatory phenomena exhibited by plants is the greening response to light. This light stimulated development of chloroplasts involves considerable synthesis of proteins. A study has been made of the nature and time course of protein synthesis resulting from exposure of etiolated pea seedlings to light.

3. *In vitro* systems provide a powerful means of looking at the mechanism of protein biosynthesis. An *in vitro* protein synthesising system prepared from wheat embryos has been primed for protein synthesis with cytoplasmic polyosomes from green pea seedlings. The products of this highly active protein synthesising system have been compared with the *in vivo* synthesised proteins.

The Effect of Oxygen on Carbon Dioxide Fixation by Isolated Chloroplasts

J. W. Lyttleton

Applied Biochemistry Division, DSIR, Palmerston North

It has for some time been known that oxygen reduces the rate of photosynthetic carbon dioxide incorporation by plants, and that this effect is also shown by intact chloroplasts *in vitro*. Until recently a satisfactory explanation of the effect was lacking, but this was provided when it was shown that ribulose diphosphate (RuDP) carboxylase, the enzyme responsible for carbon dioxide fixation, can also catalyse a reaction between RuDP and oxygen, producing phosphoglycerate and phosphoglycolate. Oxygen acts as a competitive inhibitor of the carboxylase reaction, and it also represses fixation by removing material from the Calvin cycle in the form of phosphoglycolate, thus reducing the amount of RuDP available.

Experiments will be described to investigate whether the action on RuDP carboxylase can be considered a sufficient explanation for the effect of oxygen on carbon dioxide incorporation by isolated chloroplasts.

Glycerolipid Involvement in the Biosynthesis of Polyunsaturated Fatty Acids in Plants

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Linoleic and α -linolenic acids are quantitatively by far the most important fatty acids of plant glycerolipids, but the mechanism of their biosynthesis is only now being elucidated.

Early studies with intact leaves showed that 1-¹⁴C-acetate was incorporated quite rapidly into oleic acid and more slowly into linoleic and α -linolenic acids. The time course of labelling suggested the biosynthetic sequence oleic \rightarrow linoleic \rightarrow linolenic.

Later studies, again using intact leaves, indicated that this desaturation took place with phosphatidyl choline-bound fatty acids and not, as had been assumed, with coenzyme A or acyl-carrier protein derivatives of the fatty acids.

Until recently it had not been possible to demonstrate oleate desaturation in cell-free extracts of plant material, but it has now been shown that microsomal preparations from various sources are capable of converting oleic to linoleic and linolenic acids. Very convincing evidence has been obtained for a direct desaturation of oleyl phosphatidyl choline to linoleyl phosphatidyl choline on microsomes isolated from a yeast.

Cyclic AMP Phosphodiesterase in Plant Tissues

D. I. Ozich* and E. Moustafa

Department of Biochemistry, University of Auckland

Cyclic AMP phosphodiesterase was partially purified from seedlings of several plant species. The properties of the enzyme isolated from lupin seedlings were studied. The rate of reaction catalysed by this enzyme was determined in seedlings at various stages of germination.

Some Aspects of Phytol Metabolism

R. P. Hansen

Applied Biochemistry Division, DSIR, Palmerston North

Phytol (3,7,11,15-tetramethylhexadec-*trans*-2-en-1-ol) constitutes about 30% of the chlorophyll molecule. Although small quantities of this isoprenoid alcohol are found in the free state, more frequently its fatty acid derivative phytanic acid (3,7,11,15-tetramethylhexadecanoic acid) is detected, together with its oxidative degradation homologues pristanic acid (2,6,10,14-tetramethylpentadecanoic) and 4,8,12-trimethyltridecanoic acid. These multibranched fatty acids have been identified in small amounts in the lipids from many sources, including those of ruminants, terrestrial and marine mammals, fish, zooplankton, some crude petroleum oils and certain geological deposits. Phytanic acid alone has been isolated from rumen bacteria. High levels of this C₂₀ acid have been identified in the lipids of people afflicted with Refsum's syndrome. Recent investigations have shown that phytanic, pristanic and 4,8,12-trimethyltridecanoic acids are present in appreciable proportions in the fatty acids from earthworms. It is postulated that the isoprenoid acids in earthworms originated in plant phytol and were assimilated in the gut from ingested soil containing living and dead microorganisms and other fauna.

Casein Conformation and the Fluorescence of Bound Anilino-naphthalene-Sulphonate (ANS)

L. K. Creamer

N.Z. Dairy Research Institute, Palmerston North

Anilino-naphthalenesulphonate (ANS), which changes its fluorescent properties in differing solvents and on being bound to many proteins, has frequently been used as a probe of protein structure. An analysis of the fluorescent changes of ANS in solutions containing α_{s1} - and β -casein under a variety of conditions has been undertaken. It was found that conditions that favoured the formation of large stable protein aggregates also favoured an increase in ANS fluorescence from the protein solution. The effect of Ca²⁺ on the aggregation of α_{s1} -, β - and a mixture of α_{s1} - and β -casein was examined. At 38°C, 0.08 M NaCl, pH 6.7, increases in Ca²⁺ caused steady increases in the ANS fluorescence from β -casein solutions, although the solution became steadily more cloudy. In contrast, the fluorescence from α_{s1} -casein solutions increased markedly when a critical level of added Ca²⁺ (0.005M) was reached. This was accompanied by protein aggregation and precipitation. When the proteins were mixed, and the Ca²⁺ level increased, the marked increase of ANS fluorescence at 0.005M Ca²⁺ was even greater but it was not accompanied by protein precipitation. These and other results show that α_{s1} - and β -casein interact in a specific manner and that many properties of the natural casein micelle system can be explained in terms of the interactions and behaviour of α_{s1} - and β -casein alone.

Modifications of Triglyceride Structure in Bovine Milk Fat

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Lactating monozygous twin cows were used to study modifications in the triglyceride structure of milk fat arising from the feeding of a diet high in linoleate, in which the linoleate was protected against the normal process of biohydrogenation in the rumen. The linoleate content of the experimental milk was 19.8% compared with 1.5% for the control milk. When the proportions of linoleate increased the proportions of myristate and palmitate decreased. A

small decrease in the proportions of butyrate was also evident.

G.L.C. analysis of the total milk fat triglycerides showed that the increase in linoleate content gave rise to increases in the relative proportions of triglyceride species with carbon numbers of 40 and 54, and decreases in those with carbon numbers of 32, 34, 36, 38 and 50.

Fractionation of the samples were carried out by silicic acid chromatography to give fractions of low, medium, and high molecular weight. Relative proportions by weight of these fractions were 35%, 20% and 45% respectively in the milk high in linoleate, compared with 40%, 20% and 40% for the control milk. G.L.C. analysis of the triglycerides and fatty acids of the three fractions showed the same trends as for the total milk fat.

The fractions were further fractionated by degree of unsaturation using silver nitrate T.L.C. Analysis showed an increase in diene, triene, and tetraene triglyceride species with proportionate decreases in the relative proportions of saturated and monoene triglyceride species, when compared with the control milk.

The Involvement of the Lysosome in Glycogen Metabolism

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Glycogen, isolated rapidly from the livers of rabbits or rats, can be effectively and consistently fractionated on sucrose density gradients. The fractions so obtained have been examined by electron-microscopy and dynamic laser light-scattering. The former method shows that the fractions are of good purity with symmetrical size distributions within fractions and confirm previous descriptions of glycogen structure by electron micrographs. Utilising diffusion coefficients for each fraction obtained by dynamic light-scattering, molecular weight distributions are obtained and the incorporation of isotopically-labelled precursors into glycogen may be described as plots of c.p.m./mg glycogen versus molecular weight. This allows speculation concerning

- the course of incorporation of the isotope and
- the metabolic inhomogeneity of "low" and "high" molecular weight glycogen. ("Low" molecular weight glycogen is arbitrarily defined as of less than 10⁶ daltons, "high" molecular weight is of the order of 10⁹ daltons).

Separation of glycogen which is located within a cytoplasmic organelle has led to the conclusions that:

- a significant proportion of cellular glycogen in the liver is localised within an organelle—probably the lysosome
- the glycogen thus separated from the cytosol glycogen is predominately of "high molecular weight", predominately of "high" molecular weight.

The presence of two separate pools of glycogen of different size ranges is of obviously great significance in energy metabolism.

Aspects of Mannosidosis, an Inherited Lysosomal Storage Disease

B. G. Winchester* and R. D. Jolly

Queen Elizabeth College, University of London, and Veterinary, Pathology, and Public Health Department, Massey University, Palmerston North

Enzymes of Carbohydrate Metabolism, and the Classification of RHIZOBIUM

L. D. Kennedy* and A. S. Craig

Applied Biochemistry Division, DSIR, Palmerston North

The genus *Rhizobium* is usually subdivided into fast growing acid producing strains, and slow growing non-acid producing strains. Other workers have found that NADP-linked

6-phosphogluconate dehydrogenase is present in fast growing *Rhizobium* strains, but not in slow growing strains. Previous work in this Division has shown that the occurrence of nuclear inclusion bodies in the bacteroids, cytochemically identified as polyphosphate, correlates well with slow growth rate and the lack of acid production in culture. We have examined several strains that have anomalous characteristics, and find complete agreement between the presence of polyphosphate bodies, the absence of NADP-linked 6-phosphogluconate dehydrogenase and slow growth rate.

Rhizobium strains NZP2227 and NZP2237 (CC 1005) produce no acid in culture but have fast growth rates, and otherwise behave more as acid producers. We find that both strains contain NADP-linked 6-phosphogluconate dehydrogenase and do not produce polyphosphate bodies in the bacteroids. These strains also have greater glucose 6-phosphate dehydrogenase activities than polyphosphate body producing strains.

Effect of Nucleotides on Isocitrate Dehydrogenases of Rhizobia and Bacteroids of Legume Root Nodules

E. Moustafa* and C. K. Leong
Department of Biochemistry, University of Auckland

NAD⁺-specific isocitrate dehydrogenase was purified from cell-free extracts of rhizobia. The properties of this enzyme were compared to the properties of the enzyme obtained from the corresponding bacteroids. Rhizobial NAD⁺-specific isocitrate dehydrogenase is inhibited by AMP, ADP, ATP and cyclic AMP whereas the enzyme from the corresponding bacteroids is not affected by these nucleotides. This is due to competition with NAD⁺ for the site of interaction with the enzyme.

Symbiotic Nitrogen Fixation—Ammonia Assimilation

K. J. F. Farnden*, D. B. Scott, J. M. Banks, and L. C. Stevenson
Department of Biochemistry, University of Otago

Although the detailed biochemistry of the conversion of nitrogen to ammonia by leguminous root nodules is rapidly unfolding, the role of the bacteroid or host in the assimilation of this ammonia is less clear. Evidence has recently been presented (Kennedy, I. R., *Proc. Aust. Biochem. Soc.* (1973), 6, 33) which supports a pathway of ammonia assimilation involving glutamate synthase and glutamine synthetase but not glutamate dehydrogenase. The glutamate synthase is located within the bacteroid, but the relative significance of a plant or bacteroid glutamine synthetase in ammonia assimilation is not known. Likewise, the role of asparagine biosynthesis in ammonia assimilation has not been examined in the nodule system.

We are currently investigating the biosynthesis of asparagine and glutamine by *Rhizobia*, bacteroids and legume host tissue with a view to determining the significance, if any, of these compounds in ammonia assimilation.

Effect of Dibutyryl Cyclic Amp and other Nucleotides on Symbiotic Legume Nitrogen Fixation

T. Wilson* and E. Moustafa
Department of Biochemistry, University of Auckland

The rate of nitrogen fixation by legume root nodules is increased by low concentrations (below about 10 n moles/ml) and decreased by higher concentrations (above about 100 n moles/ml) of dibutyryl cyclic AMP. The effect of the nucleotide on symbiotic nitrogen fixation is not due to

butyrate which could result from the breakdown of dibutyryl cyclic AMP.

Results of investigations carried out in an attempt to understand the mode of action of dibutyryl cyclic AMP on symbiotic nitrogen fixation will be presented.

Chemical Education

The Third Man

L. H. Boulton
Auckland Technical Institute

Chemical and related industries have been developing in New Zealand at a quickening pace over the past decade. Along with this changing emphasis in our economy, the past few years have seen the emergence and growth of the technical institutes as tertiary education centres for industrial personnel. Traditionally the Universities have provided industry with graduates whilst the technical institutes have trained the technicians. The present graduate to technician output is about two to one, which appears to be too high for New Zealand.

A better balance could be achieved if we gave serious consideration to the training of a third man—the technologist. He is not necessarily a graduate, but is a professional in an area of applied chemistry. Overseas countries have long recognised the educational needs of the professional, non-graduate chemist and it is time that New Zealand followed suit.

The teaching of post-NZCS courses at diploma or professional level would be a natural extension of the technical institute function. Professional engineers, accountants, pharmacists and others already receive their tertiary training at technical institutes. It is time for the Institute of Chemistry to use its influence. The third man should be allowed in from the cold.

New Syllabuses for New Zealand Certificates in Science (Chemistry)

A. L. Odell
Department of Chemistry, University of Auckland

New syllabuses have been drafted for Chemistry III and IV and preliminary drafts for Chemistry V.

A survey by N.Z.I.C. of opinions of employers on existing syllabuses show a wide variety of opinions. Many thought the syllabuses too "academic" and others hoped that revised syllabuses would make the candidates more useful to their employers earlier in the course.

A committee having four employers' representatives and four tutors from technical institutes and chaired by the author has been meeting for over twelve months. Draft syllabuses will be handed out at the Conference.

Experimental Chemistry in Schools

A. H. Wooff
Christchurch Boys' High School

While it is generally agreed that school chemistry should have an experimental basis, it appears that little attention has been given to either the defining of its purpose or to the design of experiments that might achieve them. In this context the various types of experimental work will be surveyed and particular attention will be paid to the role of the quantitative experiment and to the largely unsolved problems of introductory organic chemistry.

Some future developments and the role of the practising teacher in shaping them will be discussed. The assumed level is that of the 6th and 7th form.

Recent Trends in Chemical Education

G. R. White

Department of Chemistry, University of Auckland

One consequence of the decreasing popularity of chemistry as a school or university subject (particularly in the U.K.) has been a fundamental rethinking of the aims and objectives of the teaching of chemistry by those interested in chemical education. The last few years have seen the development of numerous new courses aimed at making chemistry more interesting for the student and of greater relevance to everyday life (e.g. Nuffield and Chem. Study courses for schools and courses such as "Chemistry and Society", "Chemistry and Industry" etc. at the tertiary level.) The effectiveness of traditional teaching methods has also been questioned and many innovations in teaching strategy have been attempted by some teachers of chemistry (e.g. use of self-instructional systems, emphasis on small group learning situations, development of open-ended laboratory projects, etc.) Assessment procedures have been re-examined and objective test items are now widely used. One advantage of these is that student responses can be readily analysed to improve feedback on chemistry courses. However, the sophisticated analyses now routinely carried out by many educators do little to make bad questions good or bad chemistry better.

The effectiveness (or otherwise) of these and other recent trends in chemical education will be discussed.

A Survey of the Perceived Aims of Chemistry Teaching in Form 7

D. M. McGrath

Secondary Teachers College, Auckland

Chemistry has long been taught as a major subject in the secondary school curriculum. This paper follows the approach of a Council of Europe study (1972) which surveyed the aims of 7th form chemistry teaching in European countries.

New Zealand 7th form chemistry teachers and students will be surveyed to find their perceptions of the aims of chemistry teaching.

Expected outcomes are:

- a comparison between aims of New Zealand 7th form chemistry teachers and their European counterparts
- the extent to which perceived aims of teachers and students agree
- possible suggestions for the University Bursary Chemistry revision committee.

Can Chemistry Appropriate to Modern Society be Taught?

J. G. Gregory

Information Service, DSIR, Wellington

If education can be blamed for some evils of present society, it is a past education system in which school chemistry was taught largely as history, of great men and great ideas. In present educational experimentation it still seems impossible to lose history—ideas are comparatively easy to select with hindsight, and chemical innovations so quickly date. The only noticeable change is to logic, emphasising the techniques of reasoning. However, these conceptual skills are taught at a micro-level and in a vocational manner, with the few potentially great chemists among the pupils in mind rather than the many ordinary chemists and the potential teachers, businessmen, clerks, etc. Is this what is needed for future society?

A complete change to a macroconceptual, or systems approach, at the sociological rather than the technical level is needed. This can encompass change and facilitate curriculum selection. Examples of case studies show changing inputs to and outputs from industrial chemical systems in response to changing demands of industries, workers, consumers and environmental groups. The approach has problems — considerable teacher retraining would be required; and is it chemistry, if it ever was.

Chromatography

A Review of Methods Suggested for the Prediction of Retention Indices and Their Application to Qualitative Analysis by Gas Chromatography

P. G. Robinson

School of Medicine, University of Auckland

Retention indices [methylene units (MU), equivalent chain lengths (ECL)] were first suggested by Kovats in 1958. Since then their use, and that of the similar MU and ECL values, has become widely accepted. To date these are the only reproducible way of reporting data for qualitative analysis.

Because of this, many attempts have been made to predict retention indices from other data, e.g. boiling points, structural features, etc. Some of these methods will be reviewed and examples of their application in qualitative analysis will be given.

Picogram Analysis with Specific Detection Using a Combined G.C./M.S.

P. T. Holland* and R. F. Henzell

Ruakura Agricultural Research Centre, Hamilton

The limit of sensitivity obtainable in a g.c./m.s. system is found to be determined by the amount of column "bleed". A lower limit of 10-100 ng is generally possible using stable stationary phases such as SE-30 and OV-17 up to a temperature of 250°. At higher temperatures or with crude samples of biological origin this limit may increase to 1 µg.

Thus the mass-spectrometer provides comparable sensitivity to a FID, and in addition gives complete spectra of the separated components. To extend the sensitivity into the electron capture region, specific ions can be monitored instead of scanning the whole spectrum. This enables the background signal to be bucked out and the amplification greatly increased. The mass-chromatogram now produced represents a sensitivity increase of 10-1000 fold depending on the relative abundance of the particular ion in the spectrum. As well as increased sensitivity, response of other components is reduced or eliminated. Further increases in specificity can be obtained by monitoring two or more significant ions in the spectrum.

We have employed this technique in a variety of non-routine analyses covering various aspects of agricultural chemistry. For example, long chain fatty acetates have been detected in crude extracts of female pest moths and correlated with the bioassay for sex attractiveness to male moths. Other analyses include pesticide and herbicide residues and plant and animal hormone assays. In a high accuracy study of animal respiration, monitoring of blood O₂ and CO₂ levels was carried out using a modification of the above technique.

Limitations of the technique generally depend on the gas-chromatographic properties of the substance being analysed. For routine analyses further development of inexpensive reliable mass analysers is required.

Computer Acquisition of Chromatographic Data

P. P. Williams

Chemistry Division, DSIR, Gracefield

Chemistry Division is currently analysing annually about 10,000 samples of blood taken from drivers of motor vehicles for ethanol content. This number is expected to increase possibly to as much as 20,000 over the next three years. To cope with this work, the Division is installing an automatic gas chromatographic analysis system incorporating a mini-

computer. It is intended that the equipment shall present the results of analyses typed on a certificate acceptable in the courts, and maintain a complete record of all samples analysed. Although a number of manufacturers now offer packages designed for computer processing of chromatographic data, none of the available packages is suitable for this task. Accordingly, a system has been designed which uses a general purpose real-time software operating system. The total system will be described, and problems of sample identification, peak detection and integration, peak area calibration and recovery from mishaps and breakdowns will be discussed.

The Gas-Liquid Chromatography of Carbohydrates — A Review

I. K. Gray

N.Z. Dairy Research Institute, Palmerston North

The methods of converting sugars into volatile derivatives, with particular emphasis on trimethylsilyl ethers, followed by their gas-liquid chromatography (GLC) will be reviewed. The application of GLC of sugars as a research tool and possible use for routine quality control in the food industry will be discussed.

Review of Amino Acid Analysis By G.L.C.

M. J. Reeves and G. M. Wallace*

Food Technology Department, Massey University, Palmerston North

By the use of volatile N-trifluoroacetyl n-butyl ester derivatives of amino acids it has been possible overseas to effectively separate the 20 natural protein amino acids, and the procedure has been developed for detection at nanogram level. This review will include the results of investigations into the use of the procedure in New Zealand laboratories as well as reporting on the overseas work. The usefulness of the technique will also be considered.

A Review of the Analysis of Pesticides by Gas Chromatography

J. O'Kane

Tasman Vaccine Laboratories, Upper Hutt

The analysis of pesticides will be reviewed from three points:

1. The types of pesticides which must be analysed.
2. Methods of extraction and clean-up.
3. Column packings and detectors.

A Review of Affinity Chromatography

B. Norman

Pharmacia (South Seas) Pty. Ltd., Australia

During the last 3-4 years the field of affinity chromatography has been subjected to an enormous expansion that probably would not have taken place had it not been for the recent development of suitable matrixes and mild, efficient and uncomplicated coupling methods.

Since the choice of the right type of matrix and coupling method is so essential for maximum efficiency in affinity chromatography, this review will mainly deal with the aspects of these two important choices.

A special part of the review will be devoted to the right use of spacer gels in affinity chromatography. The principle and applications of hydrophobic chromatography as an extension of the use of spacer gels will also be mentioned.

The Use of Silver Oxide in Reaction Gas Chromatography

C. B. Johnson* and E. Wong

Applied Biochemistry Division, DSIR, Palmerston North

As part of a programme concerned with the study of the volatile constituents of mutton, a method was developed for the collection and esterification of micro-gram quantities of fatty acids for structural elucidation by combined gas chromatography-mass spectrometry. Available methods of esterification, with emphasis on those that are suitable for the aforesaid application, will be briefly reviewed. Methylation with $\text{Ag}_2\text{O}/\text{CH}_3\text{I}$ was found to be suitable for the analysis of acids containing five or more carbon atoms.

The possibility of abstracting fatty acids from a complex mixture of organic compounds followed by esterification of the abstracted acids, was investigated. Limitations of this method and a comparison with zinc oxide abstraction of acids will be discussed.

Acetylated Methyl Xylosides in Structural Studies of Hardwood Methylated Xylans

V. D. Harwood

Forest Research Institute, Rotorua

In structural investigations of polysaccharides it is customary to hydrolyse the methylated product and quantitatively estimate the methylated aldoses as their acetylated methyl alditols. A recent publication on the partial methylation of methyl beta-D-xyloside has suggested that these glycosides could be used in identification of the methanolytate of a hard beech xylan. Separations of the acetylated mono- and di-methyl xylosides by gas-liquid chromatography helps to resolve mixtures of the corresponding alditol acetates. Quantitative data comparing the two methods are appended and some observations on demethylation prior to analysis are noted.

The Nature of the Wax Esters from the Rumen Liquor of Cows Fed White Clover

D. R. Body

Applied Biochemistry Division, DSIR, Palmerston North

The wax esters were isolated from bovine rumen liquor and white clover leaves by means of silicic acid column and preparative thin-layer chromatography. Gas-liquid chromatography (GLC) was utilised to analyse the individual fatty acid and fatty alcohol compositions.

The main rumen liquor wax esters' fatty acids were stearic, palmitic and phytanic acids correlated to a range of fatty alcohols comprised mainly of dihydrophytol and triacontanol (n-30). From this information the occurrence of novel dihydrophytyl wax esters (including dihydrophytyl phytanate) was established, and this was confirmed by comparing their intact wax ester GLC data with those of synthesised authentic components. Although palmitic, linolenic, linoleic and stearic acids, together with triacontanol are principal contributors to the white clover wax ester compositions, the most striking difference was the absence of isoprenoid derivatives of the plant wax ester structure.

Details of the composition and chromatographic properties of the wax esters from both rumen liquor and white clover tissues, together with any relationship will be discussed. Reference to the formation of the isoprenoids and their association with the rumen liquor neutral lipids under investigation will be included.

Evaluation of Flavour by Sensory Methods and by Gas Chromatography

N. Lodge

Dairy Division, Ministry of Agriculture and Fisheries, Auckland

Flavour is defined as the mingled sensation of taste, olfaction and texture. In most cases the aroma properties of a substance exert the greatest influence on flavour. This paper deals with the assessment of carrot flavour by subjective testing and an attempt to measure this factor by gas chromatography and mass spectrometry. The approach may be applied to flavour evaluation of a variety of foodstuffs where odour is considered the most important aspect of flavour.

Since aroma is caused by compounds volatile enough to reach our odour receptors it was decided to try to remove volatiles from the non-volatile food constituents. The volatiles were extracted by a Likens extraction apparatus and added to a carrot-base liquid for sensory evaluation by flavour panel. Differences in quality between different varieties of carrots were noted. The characteristic volatile fraction was chromatographed on a 30 metre S.C.O.T. column coated with Carbowax 20M. The individual components were identified after GLC separation by leading part of the eluate to a mass spectrometer and scanning at the start of a peak, apex, downward slope and tail. Synergism was found to play a large part in the odour of carrot root as in the flavour of many foodstuffs.

Glass Scot Capillary GC Analysis of Plant Constituents

J. A. Zabkiewicz

Forest Research Institute, Rotorua

A previous lecture outlined the uses and disadvantages of metal capillary column gc analysis. Most, if not all, of these disadvantages can be overcome by the use of glass capillary columns.

Recent technological developments have made such columns available and easier to use. A comparison will be made of the effectiveness of such commercially available and of "home-made" SCOT columns. Examples of various analyses of labile substances, such as are found in plants, will be given and compared with the results from packed columns.

Electrochemistry

Quantitative I.R. Spectra of Water in Aqueous Solutions. The Librational Band

R. F. Armishaw

Department of Medicine, University of Auckland

Quantitative IR Spectra of numerous aqueous electrolyte solutions have been obtained with a $7\ \mu$ film cell fitted with KRS-5 windows. Corrections for reflection losses were made.

The main features of the broad librational bands ($\sim 700\text{cm}^{-1}$) were:

1. Low concentrations of electrolyte have little effect on the water librational bands. Above 2M however, significant effects were observed.
2. The sets of librational bands for solutions of an electrolyte of increasing concentrations possessed a common frequency, termed the isosbestic frequency, for which all bands have equal intensity. This indicated that the band comprised components from at least two distinct water species in equilibrium, and analysis into 2 components was possible.

(i) Contributors to the low frequency component were thought to be water molecules involved in primary hydration of ion pairs (4-6 H_2O s/ion pair).

(ii) Contributors to the high frequency component were all the remaining water molecules not involved in primary hydration, which had librational properties identical with bulk water.

3. All electrolytes, except NH_4F , shifted the band to lower frequencies and increased the integrated intensity. Large weakly polarising cations and large weakly H-bonding anions produced the largest shift to lower frequencies.

Frequency; Cation Trend $\text{H}_2\text{O} > \text{Li}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+$
Anion Trend $\text{F}^- > \text{H}_2\text{O} > \text{NO}_3^- > \text{Cl}^- > \text{Br}^- > \text{Cl}_4^- > \text{I}^-$

The band intensity was increased most by small strongly polarising cations and large anions.

Intensity; Cation Trend $\text{Li}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+$
Anion Trend $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^- > \text{F}^-$

All observed frequency and intensity data can be explained in terms of direct ion-water interactions.

The Electrochemical Thermodynamics of the Silver-Water System at Elevated Temperatures

B. Pound* and D. D. Macdonald

Chemistry Department, Victoria University of Wellington

Potential/pH diagrams have been constructed for the silver/water system at 25, 60, 100, 150, 200, 250 and 300° by integrating free energy functions for various species over the above temperature range using heat capacity (non-dissolved components) and absolute ionic entropy (dissolved species) data. The diagrams are used to predict the electrochemical behaviour of silver as a function of temperature, and are tested by comparing calculated parameters (e.g. solubility, electrode potential) with data from the literature.

The Anodic Dissolution of Bismuth in Halide Solutions

D. E. Williams and P. T. Wilson*

Department of Chemistry, University of Auckland, and Chemistry Division, DSIR, Gracefield

A potentiostatic sweep technique was used to study the kinetics of the anodic dissolution of bismuth from a rotating disc electrode into acidic halide solutions. The current was measured as a function of electrode potential and halide ion concentration in solutions maintained at a constant ionic strength with perchloric acid. The Tafel slopes and halide reaction orders were calculated from the experimental results after making corrections for the ohmic potential drop in solution, and after deriving the surface halide concentration using equations which describe mass transfer at a rotating disc electrode.

The results were analysed in terms of the pseudo-equilibrium hypothesis, in which it is supposed that all steps prior to the rate determining one in the reaction sequence are in equilibrium. In all three solutions, the results are in accord with a mechanism in which the rate determining step is the desorption from the electrode surface of a Bi(II) halide intermediate, accompanied by a single electron transfer, to form a free Bi(III) halide complex in solution. The fractional surface coverage of the Bi(II) halide intermediate is described by a Temkin isotherm which allows for the intrinsic heterogeneity of the metal surface.

Sodium Hydroxymethane Sulphinate — A Polarographic Investigation

J. S. Edgar

Wool Research Organisation, Christchurch

Polarographic studies on sodium hydroxymethane sulphinate ($\text{HOCH}_2\text{SO}_2\text{Na}$) in acid solution using a rotating platinum microelectrode show an irreversible wave at approximately $E_{\frac{1}{2}} = +0.7\text{V}$ (vs.S.C.E.). Evidence that this wave arises

from the oxidation of the sulphoxylate anion HSO_2^- is given. Kinetic studies on the rate of formation of the species show a strong pH and temperature dependence.

The results correlate well with the chemistry of other S (IV) reactions, and explain the powerful bleaching properties of $\text{HOCH}_2\text{SO}_2\text{Na}$ in textile applications.

Kinetics of Electrochemical Dissolution of Thallium in Aqueous Solution

R. B. Williamson

Chemistry Division, DSIR, Gracefield

Over a wide pH range thallium metal dissolves anodically to form Tl^+ , with no surface films of oxide or hydroxide. Steady state current-potential curves were measured at a rotating disc electrode using a potentiostatic sweep technique. By extrapolation to high rotation rates, it was possible to eliminate the effect of mass transport and the reverse reaction, and the kinetics of the pure anodic process could be determined. It was found that the anodic Tafel slope, $b = dE/d\log i = 59 \pm 8$ mV. This result does not support a rate determining charge transfer step, but is consistent with the rate determining desorption of adsorbed Tl^+ on the electrode surface. The electron transfer takes place in a relatively fast pre-equilibrium step to form Tl^+ (adsorbed).

Cyclic Voltammetry of Monel 400 in High Temperature Lithium Hydroxide Solution

D. D. Macdonald

Chemistry Department, Victoria University of Wellington

The electrochemical behaviour of Monel 400 (~70% Ni, 30% Cu) in 1 mol kg^{-1} lithium hydroxide solution at temperatures to 250°C has been investigated using the technique of cyclic voltammetry in which the potential is cyclically swept between hydrogen and oxygen evolution. The cyclic voltammograms exhibit peaks which are correlated with the formation of both dissolved species and oxide films at the metal/solution interface.

Electrochemical Problems Associated with Corrosion of Tins Used for Canned Foods

G. G. Page*, J. T. Hughes and P. T. Wilson

Chemistry Division, DSIR, Gracefield

Economics, hygiene and modern high speed tin-plate and canning techniques are altering the significance of the corrosion problems that may occur within sealed food cans. One trend is to use lighter weights of tin coatings, and to protect them by application of lacquers either to the sheets or after the cans are formed. The lacquer will not give adequate corrosion protection if it is applied over crevices, therefore the side seam must now be filled with solder, so as to form a sound substrate for the lacquer. The cut edges of the lap seams at either end of the can must also be protected from corrosion, as the sharp cut edges tend to form weak points in the lacquer. If local failure in the lacquer coating occurs at the sharp edges, the exposed steel will not be protected by the sacrificial wastage of the tin coating, and rapid corrosion may occur.

All these features have a significant bearing on the electrochemical reactions which occur in the can as the residual oxygen is depleted. Some of the practical problems that have arisen will be outlined and future approaches discussed.

Kinetics of the Electrochemical Nucleation and Growth of Anodic Sulphide Films

M. L. Daroux* and G. A. Wright

Department of Chemistry, University of Auckland

The formation of sulphide films on Ti, Pb, Co and Bi anodes in alkaline solutions of hydrogen sulphide ions has been demonstrated, using the technique of cyclic voltammetry. A detailed kinetic study has been carried out in the case of the thallium anode. The experimental variables were the pH, concentration of HS^- , electrode rotation rate, potential sweep rate, and the range of potential covered by the cyclic voltammetry programme.

Below 1 mmol/l of HS^- a dissolution-precipitation mechanism prevails and a loosely attached, porous layer of thallic sulphide appears on the metal surface. At higher concentrations of HS^- a monolayer of thallic sulphide forms directly on the metal surface and grows thicker by the solid-state electromigration of thallic ions. This coherent film breaks down at high electrode potentials and the anodic reaction reverts to the dissolution-precipitation mechanism.

Spontaneous oscillations of current at a frequency of 2 to 4 Hz were discovered in the anodic region, and these could be ascribed to a coupling of film growth and film dissolution reactions.

Industrial

Anti-Oxidants in Plastics Packaging

A. C. Kennett

Chemistry Division, DSIR, Auckland

The anti-oxidants used in plastics packaging formulations are additives which may migrate and break down to form other products. As a result the identification and determination of the compounds present in films and varying in amounts from 0.02 to 0.05 percent is made complex.

Analytical methods for the extraction and determination of anti-oxidants are reviewed. The main analytical methods which are being employed at present are colorimetry, spectrophotometry, thin-layer and gas chromatography.

Internal Polymer Formation in Wool

A. J. McKinnon

Wool Research Organisation of N.Z. (Inc.), Christchurch

Some techniques for the *in-situ* formation of addition polymers within the wool fibre will be discussed. Such internal polymers are largely chemically grafted to the wool substrate through the large numbers of disulphide and thio groups within the fibre, and in many cases may be regarded as graft copolymers.

Details of the reaction mechanisms and the role of diffusion will be described where it has been possible to infer these from experimental data.

The distribution of polymer deposits within the fibre will be discussed in particular cases at both the supra molecular and macroscopic level.

Some data on the effects on the mechanical properties of the fibres will be presented.

An Experiment in Industrial Chemistry with a Methanol-Dehydrogenation Plant

R. B. Keey

Department of Chemical Engineering, University of Canterbury

One of the concerns of industrial chemistry is the management of materials and energy on a large scale. Stoichiometry provides essential inventories for this management. As both an example of technique and a learning experience, Chemical Process Technology students at the University

The Perkin Elmer model F33

A new compact gas chromatograph

Injectors and detectors mounted on temperature controlled block

Hinged lid for simple column changing

Linear temperature programmer

Low thermal mass oven

Wide-range ionization amplifier

Temperature readout meter

Digital temperature settings

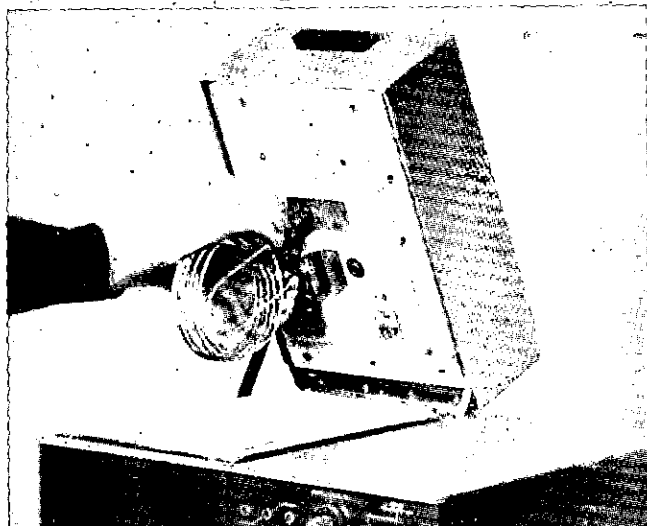


Model F33 Gas Chromatograph

The Model F33 is the successor to the well known Model F11 and contains all those features which made its predecessor so successful, together with a number of technological improvements which add to the performance of the instrument.

Compact

The compact modular design has been retained even though the internal volume of the oven has been increased. The low thermal mass oven has excellent temperature stability and the introduction of digital temperature setting ensures long term reproducibility. An integral full cycle proportional control circuit eliminates any possibility of electrical interaction with other equipment. Readout of oven temperature is onto a built-in front panel meter which can be switched to read other zone temperatures. The hinged lid of the oven is used to mount the chromatographic system, injectors, columns and detectors and, when fully opened, provides easy access for column changing.

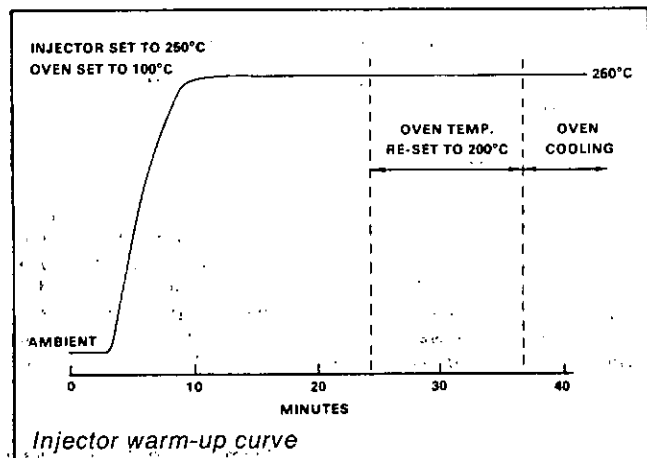


Column changing

Versatile

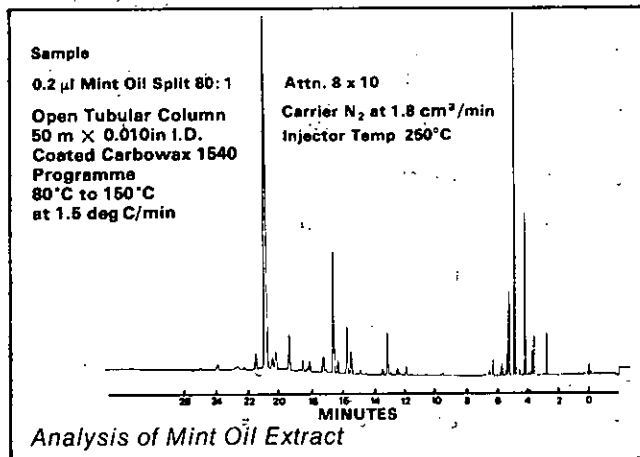
The lid of the oven contains a temperature controlled block on which are mounted the injectors and detectors. Injectors for different diameter columns are interchangeable making it possible to achieve optimum performance for any column size, either metal or glass, with a minimum of expense. Temperature control of the injector/detector zone is by means of an integral half cycle proportional control system and settings are made on a digital switch to ensure reproducibility.

The ionization detectors are also easily interchanged thus allowing single or dual FID, single ECD or FID/ECD operation.



High Performance

The detectors have the same advanced design as those used on the Perkin Elmer Models F17 and F30 and provide the highest possible levels of performance incorporating as they do the results of many years of research and development. Signals from the detectors are fed to a wide range Ionization Amplifier which combines high sensitivity, low drift and long term stability with exceptional reliability. The linear range is better than 10^9 so that major and part per million components can be analysed in the same mixture.



Modular

The gas controls are completely modular. Provision is made on the rear of the oven unit for mounting a carrier gas flow controller in either channel. In addition, single pressure control modules are available for carrier gas or for air and hydrogen for the FID. These units can be combined in whatever configuration is determined by the particular instrumental combination.

A Linear Temperature Programmer is available as an optional accessory which provides a wide range of reproducible programme rates starting at 0.5 deg C/min and going up to 30 deg C/min. An electronic timer allows a period of automatic isothermal operation at the start of a run up to a maximum of twenty minutes. Adjustable stops are provided for setting the initial and final temperatures and they can be locked in position to ensure reproducibility; an appropriate panel light indicates the state of the programme.

For the end user, probably the most important feature is the exceptional reliability which is the result of ten years experience with the Model F11 in large numbers throughout the world.

Further Information

For further information on the new Perkin-Elmer model F33 gas chromatograph contact Fletcher Health and Science, Private Bag, Auckland, Telephone 592-869.

Fletcher

HEALTH+SCIENCE

A division of the Fletcher Industries Ltd.
Private Bag, Auckland. Telephone 592-869.

of Canterbury tried to strike mass and heat-energy balances around a local methanol-dehydrogenation plant from data they themselves had obtained from the plant. This exercise is described, and some of the conclusions that can be drawn from it discussed. In particular, the exercise illustrates the manipulation of uncertain data under imperfectly controlled conditions.

Radiochemical Studies of Milk Protein Interactions at Stainless Steel Surfaces

T. J. Nisbet

Department of Chemistry, University of Waikato

The adsorption of protein at hard surfaces is of importance in food technology and medical science. In the dairy industry when the milk protein is in combination with a number of minerals, the formation of troublesome deposits of varying composition known collectively as "milkstone" results. The bacteria often associated with these deposits are a major cause of low quality milk products. The maintenance of milk quality is dependent upon the limitation of "milkstone" formation to the minimum level, consistent with the realities of farm and factory procedures.

Fundamental studies of protein adsorption and deposition at a stainless steel surface have been initiated using ^{131}I iodinated casein to obtain a better understanding of the factors which led to the formation of these deposits.

The desorption of milk protein has also been investigated using different detergents, allowing the efficiency of a detergent to be monitored.

A number of results from these radiochemical studies will be discussed.

Thermodynamic Description of the Stability of Minerals in Aqueous Solutions

G. J. Churchman* and M. L. Jackson

Soil Bureau, DSIR, and University of Wisconsin, U.S.A.

Minerals are often formed in an aqueous environment in nature. Thermodynamic properties, e.g. free energies of formation of minerals, are used to predict the composition of the solid phase which will be in equilibrium with a particular aqueous solution environment. Such properties have often been determined from the compositions of solutions resulting from the long term contact of each particular mineral with an aqueous phase of known initial composition. The principal assumptions underlying the application of this method are:

1. the reaction taking place is a congruent dissociation of the mineral into its constituents and
2. the reaction is reversible.

The results of treatments of the clay mineral, montmorillonite, with solutions encompassing a wide range of pH values did not conform to the conditions defined in these assumptions. The compositions of solutions resulting from these treatments can be described by a reversible equilibrium reaction between the solution phase and another solid phase besides montmorillonite. This particular solid phase is derived from montmorillonite at an early stage of the dissolution process. It is considered that the interactions of aqueous solutions with montmorillonite and also with many other minerals are more accurately described as multi-step irreversible processes than as a single-step reversible reaction.

Isolation of the Steroidal Alkaloid Solasodine from Native New Zealand Solanum Plants and its Use for the Production of Steroid Drugs

R. J. Weston

Chemistry Division, DSIR, Petone

Solasodine is the nitrogen isomer of diosgenin which is almost the sole source of starting material for the manufacture of steroid drugs throughout the world; thus solasodine could share this role equally with diosgenin.

Solasodine occurs in two native plants. The bench-scale isolation of this product will be described. Basically a simple process, the isolation and purification of solasodine involves a large number of variables, and successful production on a large scale involves careful selection of the appropriate variables. The combination of a number of these variables which has led to the pilot-scale isolation and purification of solasodine will be discussed.

Extractives of the New Zealand Beeches

J. A. Lloyd

Forest Research Institute, Rotorua

The New Zealand beeches are a rich source of polyphenolic extractives which may be extracted from the wood with methanol. The amount varies with species and heartwood and sapwood tissue, though is usually 4-14% of the wood. In addition to these phenolic compounds, smaller amounts of non-polar, petroleum-soluble compounds are also present.

Tannins which form ellagic acid and cyanidin on acid hydrolysis comprise most of the methanol-soluble material though considerable monomeric material is also present. Catechin, dihydroquercetin, quercetin and gallic acid were the major compounds isolated from red and mountain beeches while hard beech also contained abundant resveratrol. Silver beech extractives included ellagic acid, 3,3'-dimethyl ellagic acid, gallic acid and phloroglucinol. Sapwood contained more glycosides than heartwood.

The principal resin components were palmitic acid, oleic acid, C14-35 alkanes, behenyl and linoceryl alcohols and β -sitosterol.

The effects these extractives will have on the pulping and subsequent bleaching of beech wood is discussed.

Inorganic

Thiocarbonyl Complexes

K. R. Grundy, R. O. Harris, and W. R. Roper*

Departments of Chemistry, Universities of Auckland and Toronto

The various methods which lead to thiocarbonyl complexes will be reviewed. A new approach involves methylation of π -bound carbon disulphide to give a dithioester group which chelates through carbon and sulphur. Further reaction of this group with acid results in elimination of methylthiol and production of a thiocarbonyl ligand. The situations in which this approach has been successful will be described, together with some reactions of the thiocarbonyl ligand which lead to carbene complexes.

An Interesting Mercurial Reaction

K. M. Mackay*, N. Hosmane, and E. A. V. Ebsworth

Departments of Chemistry, Universities of Waikato and Edinburgh

Following the observation by Hosmane that the reaction of SiH_3Br on $(\text{Me}_3\text{Si})_2\text{Hg}$ yields the unsymmetric disilane $\text{Me}_3\text{SiSiH}_3$, it has been shown that silylgermanes may be produced by the similar reaction of GeH_3Br or $\text{CH}_3\text{GeH}_2\text{Br}$. Use of excess germyl bromide yields digermanes. The reactions were followed by nmr, and the mercury intermediate was characterised by the INDOR method on the ^{199}Hg satellites.

Stereochemistry and Structure of Some Rhenium-Silicon Derivatives

M. Claire Couldwell*, W. T. Robinson, and T. J. Simpson

Departments of Chemistry, Universities of Otago and Canterbury

The crystal and molecular structures of $\text{Me}_3\text{SiRe}(\text{CO})_5$ and $(\text{Me}_3\text{Si})_3\text{SiRe}(\text{CO})_5$ will be presented. These represent the first examples of structure determinations on compounds containing non-bridging rhenium-silicon bonds. The structures will be compared with those of the corresponding manganese compounds, particular attention being paid to the significance of metal-metal bond lengths and the stereochemistry around the transition metal atom.

"Routine" X-Ray Crystal Structure Analysis of Organic Compounds

T. J. McLennan

Department of Chemistry, University of Canterbury

Computer development has been accompanied by a remarkable increase in the rate at which new crystal structures appear in the literature. One might be tempted to conclude that automatic diffractometers, and program packages for automatically processing the data they produce, provide all the essentials for accurate and reliably rapid elucidation of crystal structures. Such is not necessarily the case. Present day control programs for X-ray data collection experiments are, unfortunately, of greatly differing efficiency as are the various "structure solving" programs.

The "all light atom" nature of organic compounds no longer presents formidable computational barriers, except for one class of compounds which unfortunately includes all optically active substances. Organic substances that include several "heavy" atoms, especially when the molecules are optically active, are often quite difficult analyses.

In this paper the nature of some of these problems will be explained and discussed with reference to a recent crystallographic look at Canterbury on structures of long-standing difficulty.

The Synthesis, Characterisation and Some Chemical Properties of Bis(Methylgermyl) Tetracarbonyl Iron and Hydrido-(Methylgermyl) Tetracarbonyl Iron

A. Bonny

Department of Chemistry, University of Waikato

$(\text{CH}_3\text{GeH}_2)_2\text{Fe}(\text{CO})_4$ (I) and $\text{H}(\text{CH}_3\text{GeH}_2)\text{Fe}(\text{CO})_4$ (II) have been synthesised and characterised. Their vibrational, proton nmr, and mass spectra will be reported and indicate a *cis* structure.

Reactions with Group IV tetrahalides lead to stepwise substitution of Ge-H bonds in (I), while mercuric halides present a balance between Ge-H and Ge-Fe cleavage.

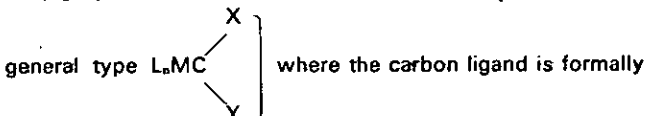
Metal cluster formation may occur (a) in thermal decomposition of (I) and (b) in the reaction of (I) with $\text{CO}_2(\text{CO})_8$. Preliminary evidence for these reactions will be presented.

Cyclic Carbene Complexes

T. J. Collins*, K. R. Grundy, and W. R. Roper

Department of Chemistry, University of Auckland

This lecture is concerned with metal complexes of the



a cyclic carbene $:\text{CXCR}_2\text{CR}_2\text{Y}$ or $:\text{CXCR}=\text{CRY}$ (X = N, O

or S). The various synthetic routes to this type of complex will be reviewed, and some new approaches which have been developed will be discussed in detail. These include: (a) ring-closing reactions involving metal co-ordinated tosylmethylisocyanide with aldehydes or ketones, (b) reaction of π -bound carbon disulphide with difunctional alkyl halides.

Some Chemistry of the Pyridine Adduct of C-Bromo-ortho-Carborane

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Department of Chemistry, Worcester Polytechnic Institut, Massachusetts, U.S.A.

1Visiting Lecturer, Department of Chemistry, University of Canterbury

Previous workers² have shown that halogenated derivatives of the icosahedral carboranes will form stable adducts with amines and, in particular, have isolated a compound (I) which is the *bis* pyridine adduct of C-bromo-*ortho*-carborane (1-bromo-1,2-dicarba-*closo*-dodecaborane [12]). An X-ray study in our laboratory of recrystallised (I) however, did not give results compatible with what was expected for (I), but indicated that we had studied a new compound (II) in which an OH group was bonded to boron atom 9 of the carborane cage with both pyridine molecules hydrogen-bonded to the hydrogen atom of this OH group. Infrared and nuclear magnetic resonance spectroscopy was performed to substantiate the proposed structure of (II), and further reactions were run to show that the OH group present in (II) is formed by hydrolysis of (I) during intended recrystallisation. It was also found that one of the two pyridine molecules of (II) can be removed by heating to form (III), the mono pyridine adduct of 9-hydroxy-1-bromo-*ortho*-carborane. The reactions and structures involved will be discussed in terms of known chemistry and calculated electronic charge distributions of the icosahedral carboranes and other boron compounds.

(2) J. Plešek, T. Hanslík, F. Hanousek and S. Hermanek, *Coll. Czech. Chem. Comm.*, (1972), 37, 3403.

Small Metalloboron Cage and Cluster Compounds of Iron, Cobalt, and Nickel. Synthesis, Structure, and Electronic Considerations

R. N. Grimes

Department of Chemistry, University of Virginia, U.S.A.

The metallocarboranes are electron-deficient polyhedral or polyhedral-fragment clusters containing boron, carbon, and one or more transition or main-group metal atoms in the cage framework. A wide variety of such species is known, consisting for the most part of air-stable crystalline solids, and an extremely rich and diverse chemistry has developed in this area within a short time. Although metallocarborane polyhedra having up to 14 vertices have been characterised, the present paper is concerned with smaller systems with as few as five framework atoms, which have a close structural and electronic relationship to the metal clusters, the metallocenes and other organometallic cage molecules. The preparation, structural characterisation and reactions of the small metallocarboranes are reviewed with emphasis on recent developments. Thus, reactions of metal salts or organometallic reagents with the polyhedral carboranes $\text{C}_2\text{B}_3\text{H}_5$, $\text{C}_2\text{B}_4\text{H}_6$, and $\text{C}_2\text{B}_5\text{H}_7$, or with the open-cage species of $\text{C}_2\text{B}_4\text{H}_8$, generate numerous open- and closed-cage mono-, di-, and trimetallocarboranes. For example, treatment of trigonal bipyramidal $\text{C}_2\text{B}_3\text{H}_5$ with $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ in the gas phase results in insertion of cobalt into the cage, giving octahedral $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_3\text{H}_5$; this species is an isoelectronic and isostructural analog of metal clusters such as $(\text{C}_2\text{H}_5)_2\text{C}_2\text{Co}_4(\text{CO})_{10}$, as well as the carborane $\text{C}_2\text{B}_4\text{H}_8$ and the borane

dianion $B_6H_6^{2-}$. Further, reaction of $(\eta-C_5H_5)_2CoC_2B_3H_5$ with $(\eta-C_5H_5)Co(CO)_2$ produces the dicobalt isomers 1,2,3,5- and 1,7,2,4- $(\eta-C_5H_5)_2Co_2C_2B_3H_5$, in both of which the cage system has the gross geometry of a pentagonal bipyramid. At least two additional isomers have also been prepared. Metal insertions into the pentagonal pyramidal $C_2B_3H_7^-$ ion generate a variety of metallocarboranes; similar treatment of $B_5H_9^-$ ion produces metalloboranes, which contain metal and boron atoms, but no carbon, in the cage framework.

Novel structural features and spectroscopic properties of several compounds are discussed, and the reactions, inter-conversions and thermal rearrangements of the small metallo-boron cages are described and correlated.

Recent References:

- V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Amer. Chem. Soc.*, (1974), 96, 3090.
 R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, (1974), 13, 1138.
 L. G. Sneddon, D. C. Beer and R. N. Grimes, *J. Amer. Chem. Soc.*, (1973), 95, 6623.
 V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, (1973), 95, 2830, and 95, 5078.
 D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Amer. Chem. Soc.*, (1973), 95, 3046.

Optically Active cis-Dianionobis (Ethyl-enediamine) Chromium (III) Complexes

I. J. Kindred, and D. A. House*

Department of Chemistry, University of Canterbury

The relatively inert Cr(III) cations, *cis*-Cr(NCS)₂(en)₂⁺ and *cis*-Cr(N₃)₂(en)₂⁺ have been resolved by conventional means using the antimonyl tartrate anion, and ion exchange techniques have been used to separate the active cations from the diastereoisomerides. Using these as starting materials the following chemical transformations have been carried out while preserving at least some of the optical activity:

- (1) A-(or D)-(-)₄₃₆-Cr(NCS)₂(en)₂⁺ $\xrightarrow{H_3O^+}$ (-)₄₃₆-Cr(NCS)(en)₂(OH₂)²⁺ + NCS⁻
- (2) (+)-Cr(N₃)₂(en)₂⁺ $\xrightarrow{H_3O^+}$ (+)-Cr(N₃)(en)₂(OH₂)²⁺ + N₃⁻
- (3) (+)-Cr(N₃)₂(en)₂⁺ $\xrightarrow{H^+/NO_2^-}$ (+)₅₀₀-Cr(en)₂(OH₂)³⁺
- (4) (+)-Cr(N₃)₂(en)₂⁺ \xrightarrow{HCl} (+)-CrCl₂(en)₂⁺
- (5) (+)-CrCl₂(en)₂⁺ $\xrightarrow{H_3O^+}$ (+)-CrCl(en)₂(OH₂)²⁺

A comparison of the ORD and CD spectrum of these Cr(III) complexes with those of the analogous Co(III) complexes whose absolute configuration has been determined, suggests that the absolute configuration of the Cr(III) complexes is retained in these transformations. The rate of the mutarotation reaction (2) depends on the acidity and in 0.118 M HClO₄, $10^3k_{obs} = 4.61 \text{ sec}^{-1}$ ($t_{1/2} = 4.17 \text{ hr}$) at 25.0°C, $E_a = 82.8 \text{ kJ mol}^{-1}$, $\log PZ = 10.173 \text{ sec}^{-1}$ and $\Delta S_{298} = -58 \text{ J K}^{-1} \text{ mol}^{-1}$.

Catalysis of Some Inorganic Reactions by Surfactant Solubilised Water

Charmian J. O'Connor

Department of Chemistry, University of Auckland

Rate constants for a variety of inorganic reactions have been investigated in water solubilised by alkylammonium carboxylate surfactants. These surfactants form reversed micelles in non-polar solvents and possess an interior cavity surrounded by the polar headgroups in which both water and the inorganic complex may be solubilised. Rates of reactions depend upon the structure of the surfactant, the

amount of water solubilised and the nature of the inorganic substrate.

The rate constant for the aquation of $Cr(C_2O_4)_3^{3-}$ in the presence of micellar octylammonium tetradecanoate in benzene is at least a factor of 10^6 greater than that in aqueous solution at the same temperature. This remarkable rate acceleration is discussed in terms of pre-equilibrium proton transfer from the ammonium ion of the surfactant and enhanced activity of water in the micelle cavity.

The results for both of these reactions are interpreted. $Cr(C_2O_4)_2(H_2O)_2^-$ are also markedly enhanced when both the reactant and water are brought into close proximity in the interior of reversed micelles.

The rate constants for *trans-cis* isomerisation of in terms of aquation of the "one-ended dissociated" intermediates followed by rate determining attack of water. Catalysis of other reactions is discussed.

Ultra-High Resolution Gas Chromatography and Applications in Tritium Labelling of Hydrocarbons

K. A. Hunter* and A. L. Odell

Urey Radiochemical Laboratory, University of Auckland

Isotopic isomers of tritium labelled methane, viz. CH₃T, CH₂T₂, CHT₃, CT₄, have been separated by gas adsorption chromatography on active charcoal. The separating ability of the columns has been extended virtually indefinitely by a method of recycling the mixture of isomers through two columns in series.

The apparatus was used to study the products of exchange between tritium gas (T₂) and methane on a silica gel catalyst. It was found that the products vary in their isotopic composition according to both the order in which the reactants are admitted and whether or not the catalyst has been irradiated with Co-60 γ radiation. When tritium is admitted first to the catalyst, irradiation is observed to not only increase the yield of exchanged methane, but also to change the mechanism of exchange from multiple exchange of tritium to a single exchange producing only CH₃T. In contrast, when CH₄ is admitted first to the catalyst the yield of labelled methane is not significantly changed by irradiation. The irradiated catalyst, however, produces an additional exchange product CT₄.

Intramolecular Hydrolysis of Nitriles Co-ordinated to Cobalt (III)

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The complex *cis*-[Co(en)₂(NH₂CH₂CN)(OH)]²⁺ undergoes rapid reaction at pH 7 to form the N,O bound amide, [Co(en)₂(NH₂CH₂CONH₂)]³⁺ as sole product. The reaction involves intramolecular attack by the co-ordinated OH on the nitrile carbon atom. Compared to typical intermolecular nitrile base hydrolysis ($k_{obs} \sim 10^{-12} \text{ sec}^{-1}$ at pH 7, $\Delta H \neq \sim 15 \text{ kcal mole}^{-1}$, $\Delta S \neq \sim -15$ to $-20 \text{ cal deg}^{-1} \text{ mole}^{-1}$), reaction of the cobalt (III) complex occurs $\sim 10^{12}$ times faster with about half this acceleration coming from a decrease in the $\Delta H \neq$ term (to 6.41) and half from an increase in $\Delta S \neq$ (to +8.1).

The presence of metal ions such as Hg²⁺, Ag⁺, Zn²⁺ and Cd²⁺ further accelerates conversion of *cis*-[Co(en)₂(NH₂CH₂CN)(OH)]²⁺ to the amide complex. These reactions are all first order in the metal ion except for Ag⁺ where there appears to be an additional path, second order in Ag⁺.

Hydrolysis of the analogous bromo complex *cis*-[Co(en)₂(NH₂CH₂CN)-Br]²⁺ in the presence of Hg²⁺ leads to both N,O (95%) and N,N' (5%) bound amide products.

The Oxidation of SO₂ By Oxygen in Aqueous Solution

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The rate of oxidation of SO₂ by oxygen in "pure" water was found to vary with pH, having a maximum rate at pH 6 where the half life for the reaction was 300 ± 50 min. It is believed that the variable results for the oxidation in "pure" water were due to contamination by trace amounts of Fe(III) (about 5 × 10⁻⁸ M). It was shown that Fe(III) at 10⁻⁶ M concentration is a true catalyst for SO₂ solution oxidation and that its catalytic role can be explained by a free radical chain reaction. Such a chain reaction can be used to explain much of the data obtained for SO₂ solution oxidation in the presence of metal ions.

Organic

Arylation Involving Polyfluoroaromatic Systems

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The thermal decomposition of aroyl peroxides in polyfluoroaromatic solvents gives good yields of the appropriate polyfluorobiaryl through homolytic displacement of fluorine by the aryl radical. Mechanisms proposed by analogy with the reaction with benzene are unable to explain (i) the catalytic effect of added aroic acids and (ii) the vanishingly small yields of 2,3,4,5,6-pentafluorobiphenyl formed when phenylazotriphenylmethane (PAT) is used as the source of phenyl radical in the attack of hexafluorobenzene.

Partial rate factors for the phenylation of hexafluorobenzene, pentafluorobenzene, bromopentafluorobenzene, and octafluorotoluene by the thermal decomposition of benzoyl peroxide are inconsistent, and suggest that the concept of a free phenyl radical, able to differentiate between potential substrates and sites of attack easily, is incorrect. A similar lack of consistency is found in the pentafluorophenylation of some mono- and di-substituted benzenes by radicals generated from the interaction of pentafluoroaniline and pentyl nitrite.

The assumptions inherent in determining the relative rates of arylation of aromatic substrates by measurement of the relative yields of the corresponding biaryls are reviewed.

Reactions of Allylic Systems in Carbohydrates

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Cyclic monosaccharides with double bonds in the 1,2-position (glyc-1-enoses) undergo reaction with a variety of compounds to give rise to products having the double bond at the 2,3-position. This reaction has been used in the synthesis of several compounds of biological importance.

The reverse type of allylic rearrangement (glyc-2-enose → glyc-1-enose), has now been observed under various conditions, and the continued rearrangement (glyc-2-enose → glyc-3-enose) can also be achieved to yield further compounds of significance in natural product chemistry. Allylic reactions of unsaturated sugar derivatives which proceed by the S_N2' route appear to be uncommon.

Bromine Addition to Mesityl Oxide

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The addition of bromine to mesityl oxide (4-methyl-3-penten-2-one) was investigated in acetic acid under a variety of conditions.

A clear distinction between an acid and a non-acid catalysed mechanism is found. It is proposed that where acid catalysis is absent the mechanism is electrophilic, and in the presence of acid the addition is probably electrophilic to an activated alkene formed by 1,2 addition across the C=O bond. Nucleophilic addition to the protonated substrate is considered an unlikely mode of reaction.

Biochemistry of Lower Terpenoids in Plants

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The biosynthesis of lower terpenoids (C₅, C₁₀, C₁₅) in plants is generally characterised by a high degree of metabolic compartmentalisation. In most cases, carbon from sugars or from photosynthetically fixed CO₂ is incorporated more readily than is exogenous mevalonate (MVA). The hemiterpene isoprene has recently been recognised as a common natural compound, produced by many plant species. It is emitted by leaves in the light and formed preferentially from CO₂.

Most plants incorporate MVA label poorly into mono- and sesquiterpenes, and at biosynthetic sites which appear to be energy-deficient (lacking carbohydrates) and appear to contain endogenous pools of dimethylallyl pyrophosphate (DMAPP). Incorporation of labelled MVA into mono- and sesquiterpenes of peppermint is stimulated several-fold by sucrose, or by 5% CO₂ in the light. Labelled precursors are incorporated preferentially into the isopentenyl pyrophosphate (IPP) derived portions of monoterpenes in several species, and of caryophyllene (C₁₅) in peppermint.

In contrast, the glandular epidermis of rose petals incorporates MVA readily into monoterpenes with no apparent DMAPP pools, and appears to be energy-rich.

Several enzymes of monoterpene metabolism have been demonstrated in cell-free plant extracts. These include: a geraniol-nerol isomerase; a neryl pyrophosphate cyclase, producing α-terpineol; two α-terpineol dehydratases, producing limonene and terpinolene; and several dehydrogenases.

The Decompositions of GEM-Dichloro- arocyclopropenes

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The ready availability of gem-dichloroarocyclopropenes has recently resulted in their use as precursors to members of the series unavailable by other routes.^{1,2} However, these halogen-containing compounds exhibit only limited stability under a variety of conditions and the results of a study on their various modes of decomposition will be presented.

1. B. Halton, *Chem.Rev.*, (1973), 73, 113.
2. P. Muller, *Chem.Comm.*, (1973), 895.

The Synthesis of Sporidesmin Analogues for Immunological Work Against Facial Eczema

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Facial eczema is a disease in cattle and sheep caused by a poisonous fungus that grows in North Island pastures. An immunological approach to the prevention of this disease has been proposed — to produce antibodies specific to the toxin called Sporidesmin.

An outline of the causes of facial eczema will be given, along with a basic outline of immunology, as it applies in this study. The production of a vaccine has required the synthesis of compounds related to sporidesmin. A recent synthesis at Harvard will be given, and compared with the approach proposed for this study. There will be a discussion of the synthesis of compounds at present being used, which will be compared with the toxin. The use of these compounds to produce antibodies against sporidesmin will then be discussed, and the testing methods used to characterise the antibodies will be shown. Finally a brief outline of the steps to a useful vaccine will be given.

Some Aspects of the Conjugate Addition Reaction of Organocuprates to α, β -Unsaturated Ketones

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A study of the conjugate addition reaction of lithium dialkyl cuprates with α, β -unsaturated ketones will be presented. The effect of nitro aromatic compounds and substituted nitrosobenzenes on the conjugate addition reaction will be discussed. A mechanism will be proposed in which a one-electron transfer process from the cuprate to the α, β -unsaturated ketone occurs with subsequent alkylation of the β carbon to give the 1,4 addition products.

Hyperconjugation in Co-ordinated Ligands — When is a Single Bond a Double Bond ?

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Hyperconjugation has been a contentious area of organic chemistry for some time, and arguments based on the dimensions of small molecules have been questioned on various grounds. New evidence from the structure of N,N'-alkyl-salicylaldimine complexes of copper (II) which strongly supports the theory of hyperconjugation is presented, and the role of first and second order hyperconjugation in stabilising chelates involving N-alkyl substituted salicylaldimine ligands is discussed.

Intramolecular Vinylic Substitution by Palladium II

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Organometallic complexes containing metal σ -carbon bonds formed from arenes are well documented in the literature but few are found for alkenes.

Intramolecular electrophilic attack by palladium occurs when α, β -unsaturated oximes, such as 1-acetylcyclohexene oxime are co-ordinated with lithium tetrachloropalladate in methanol solution, giving dimeric complexes containing a stable σ -palladium-vinyl carbon bond.

PFT ^{13}C -NMR Probes to Electronic and Field Effects in Conjugated Systems

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The value of ^{13}C data in assessing structural and electronic features of π -systems has become evident during recent years. Three studies, which demonstrate the strength of this spectroscopic technique, will be reported.

(i) The natural abundance of ^{13}C magnetic resonance spectra of sydnone and related meso-ionic compounds have been measured. The data indicate considerable shielding of the carbon-4 in sydnones (observed *ca* δCTms 95) as predicted by *ab initio* SCF-M.O. and semiempirical M.O. calculations. The influence of substituents and heteroatom contributions have been determined and generally follow that observed in other heterocyclic systems. This new data provide support for the most recent structural refinements based on core electron binding energy studies.

(ii) Diphenylcyclopropenone is known from dipole moment studies to be a highly polarised molecule (5.14D) a factor reflected also in its high basicity ($H_o = 2.5$). Proposals have been advanced, based on chemical reactivity as well as Huckel M.O. charge density and D.E. calculations, which suggest that the zwitterion resonance form contributes substantially to the ground state. The ^{13}C spectra of a range of cyclopropenone derivatives support this conclusion, the carbonyl carbon being observed near δCTms 155.0 (30 - 70 ppm to higher field compared to cyclic ketones). This indicative shift due to the delocalised carbenium character was reflected also in the other ring and substituents resonances.

(iii) The ^{13}C -spectra of a range of *cis*- and *trans*-alk-3-en-1-yne and their 1-trimethylsilyl derivatives have been determined. Analysis of the spectra permits an evaluation of the diamagnetic effect of the acetylenic bond and the localised contribution of the C-Si $d\pi p\pi$ bonding.

The Natural Products Chemistry of Liverworts: Its Taxonomic Implications

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Liverworts are one of the most morphologically primitive groups in the plant kingdom. As a result their classification has presented great difficulties to plant taxonomists. In some cases, for example, species differences are based on criteria that would be considered inconsequential in higher plants.

Chemical differences based on the structures of secondary plant metabolites present a stable taxonomic character traditionally not utilised in plant classification. We have studied the flavonoid chemistry of liverworts with special emphasis on those species belonging to the order Marchantiales. The results obtained are sufficiently encouraging for us to suggest that chemotaxonomy could have a revolutionary role to play in liverwort classification. For example, the species so far studied have yielded a number of novel flavone glycosides unknown in the plant kingdom outside the liverworts.

Studies by other workers have revealed that some genera of leafy liverworts (order Jungermanniales) have a rich sesquiterpene chemistry. As is the case with the flavone glycosides a number of structures unique to the liverworts have been discovered. More interesting aspects of these results will be discussed and their implications as to the phylogenetic status of liverworts will be discussed.

PSEUDOMONAD Phytotoxins Associated with Leaf Chlorosis

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Phytopathogenic *Pseudomonad* bacteria are responsible for a wide range of diseases of plants in New Zealand. Of the numerous species, five can cause a chlorosis in infected leaves as part of the overall disease symptom. The chlorosis appears as a "halo" beyond the infection-site, and is generally accepted as being caused by an extracellular toxin produced by the bacteria within the plant tissue. To date only one such toxin has been isolated and its structure elucidated, that being tabtoxin, the chlorosis-inducing toxin of the "wildfire" disease of tobacco.

After summarising the current status of this group of phytotoxins, I will discuss the purification of the toxin involved in the "halo-blight" of beans, and present some information on its nature. The techniques used, although certainly not new in theory, have been developed for this class of natural product and may be generally applicable to the isolation of peptides and/or water soluble substances.

Applications of Lanthanide Shift Reagents in Structural Elucidation

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Department of Chemistry, University of Auckland

Two applications of the use of the lanthanide shift reagent $\text{Eu}(\text{fod})_3$ in n.m.r. spectroscopy will be discussed. The first concerns the structural and stereochemical assignment of a product isolated from reaction of 2 α -bromo-5 α -cholestan-3-one with allyl bormide, and the second concerns the characterisation of a non-racemic enantiomeric mixture formed during demethylation of a podocarpic acid derivative.

Regiospecificity and Regioselectivity in Di- π -Methane Photoisomerisations

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The acetone sensitised di-methane rearrangement of 11,12-dicarbomethoxy-9,10-dihydro-9,10-ethenoanthracenes is affected by substituents at C-9. There are two possible pathways whereby these unsymmetrical ethenoanthracenes can rearrange. Where the substituent is acetoxy or bromo the rearrangement occurs exclusively via pathway 'A' to give 5-substituted dibenzotricyclo[3,3,0,0] octadienes. If the substituent is methyl the rearrangement takes place via both pathways to give the 5-substituted (major product) and 8-substituted octadienes. For the hydroxy or amino substituents the rearrangement occurs via pathway 'B' to give finally the same indeno [1,2a] indene. The rearrangement occurs mainly via pathway 'A' for acetamido, methoxy and ethoxy substituents.

The formation of these various products is discussed in terms of the effects of the different substituents on the stability of the intermediate diradical species and hence on the course of the rearrangements. The factors involved include hydrogen bonding, and through space interaction of lone pairs of electrons with neighbouring radical sites.

Reactions of Quinone Methides in Water

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Quinone methides occur as intermediates in several biological processes. They are reactive molecules and only highly hindered, stabilised types have been isolated for study. However, an unhindered quinone methide is produced as a transient by flash photolysis of the lignin precursor, coniferyl alcohol.

The rates of reaction of this quinone methide have been measured in aqueous solution over the pH range 2-13. The pH dependence of the rate fits a rate equation of the form

$$\mu = (k_0 + k_{1130} [\text{H}_3\text{O}^+] + k_{011} [\text{OH}^-]) [\text{QM}]$$

and the individual rate constants have been determined. In acetate buffer's terms in the buffer components are also observed. The chemical reactions of quinone methides implied by these rates are discussed.

Steroids as Probes of the Relative Reactivities of Enophiles and Dienophiles Reactions of Dicyanoacetylene with Ergosterol Derivatives

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Ergosteryl acetate with dicyanoacetylene gives the two 7 α -ene adducts resulting from abstraction of the 9 α - and 14 α -hydrogens of the diene; 9(11)-dehydroergosteryl acetate gives both possible ring-B Diels-Alder adducts and also the 7 α -ene adduct having an 8(14),9(11)-diene system.

This ene-adduct undergoes allylic rearrangement of the maleonitrile substituent on alumina or silica gel plates. Ergosteryl-B₃ benzoate with dicyanoacetylene gives the Diels-Alder adduct only. These three steroids are suggested as convenient substrates for comparative assessment of the reactivities and steric requirements of enophiles and dienophiles.

A Commercial Synthesis of Guaioxide

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An industrial investigation of some reactions of the essential oil of guaiwood, obtained from a South American tree, will be described. The aim of the work was to synthesise the sesquiterpene ether guaioxide on a commercial scale for the perfumery industry. The two main constituents of guaiwood oil are the isomeric alcohols guaiol and bulnesol. The research consisted of their dehydration and isomerisation reactions using acid catalysts, and in particular their treatment with performic and peracetic acids. The manufacture of guaioxide was finally carried out by the treatment of guaiwood oil with formic acid.

New Synthetic Reactions : Allylic Alkylation

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This paper describes a new synthetic reaction utilising a carbon-carbon double bond to activate the alpha position for alkylation. The method involves treatment of the olefin with palladium chloride in the presence of a weak base followed by condensation of the thus formed π -allylpalladium chloride dimers with polarisable anions. Thus, alkylation of 2-methyl-1-octene, 4-methyl-3-heptene, and 2-*n*-propyl-1-pentene with the anions of dimethyl malonate, methyl methylsulfanylacetate, and methyl methylsulfonylacetate is described. With the unsymmetrical allyl system high to exclusive preference for the less substituted end occurs. In the case of methyl methylsulfonyl acetate, only one geometric isomer is obtained. Further transformations of the alkylation products derived from the sulfur stabilised anions allowed wide modification of the structural unit introduced. For example, hydrolysis, decarboxylation, and desulfonation converted methyl 2-methylsulfonyl-4-*n*-propyl-*cis*-4-heptenoate into 4-ethyl-*trans*-3-heptene representing a net homologation of a methyl olefin into an ethyl olefin.

The Autoxidation and Isomerisation of Cholest-5-en-3-one in Acetic Acid

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Treatment of cholest-5-en-3-one with air in acetic acid yields: cholest-4-en-3-one (ca. 30%), 6 α -hydroperoxycholest-4-en-3-one (ca. 6%), 6 β -hydroperoxycholest-4-en-3-one (ca. 20%), 6 α -hydroxycholest-4-en-3-one (ca. 4%), 6 β -hydroxycholest-4-en-3-one (ca. 10%), and cholest-4-en-3, 6-dione (ca. 30%). The mechanisms involved in the formation of the first five of these products have been investigated and their main details have been elucidated.

It is proposed that cholest-4-en-3-one arises by the isomerisation of cholest-5-en-3-one catalysed by HOAc, and, to a very small extent by OAc⁻. The hydroperoxides are formed by the autoxidation of cholesta-3, 5-dien-3-ol (produced by the tautomeric rearrangement of cholest-5-en-3-one cata-

lysed by HOAc and H₂OAc⁺) via a free-radical chain mechanism. The hydroperoxides then expoxidise, the dienol and the epoxide ring is opened by the interaction of HOAc or H₂OAc⁺ yielding a molecule of 6-hydroxycholest-4-en-3-one; in the process the hydroperoxide is reduced to the corresponding alcohol. Cholest-4-en-3,6-dione apparently arises by some free-radical process involving the hydroperoxides and possibly the alcohols.

Aldehyde-Catalysed Hydrolysis of Phenyl Esters of Amino Acids

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The catalytic effect of aromatic aldehydes on the hydrolyses of phenyl esters of amino acids has been interpreted as involving intramolecular catalysis in carbinolamine intermediates.

Studies of these reactions have been extended to find (a) comparative catalytic rates for esters of glycine and proline, and (b) the effect of ionisation of salicylaldehyde (2-hydroxybenzaldehyde) on its catalytic properties.

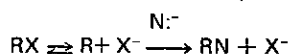
Attempts are also under way to find an analogous catalysis by imines (Schiff bases) derived from aromatic aldehydes.

The Question of Ion-Pair Intermediates in Nucleophilic Substitution Reactions at Secondary Carbon

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The traditional dichotomy of mechanisms S_N1 and S_N2 for

nucleophilic attack at saturated carbon have recently been challenged by Snee. His suggestion is that all such reactions proceed via nucleophilic attack on a pre-formed ion-pair, and that the kinetic order is dependent on which of the steps is



rate-determining. He has claimed that the 2-octyl mesylate NaN₃/H₂O-dioxan system displays borderline behaviour symptomatic only of an ion-pair mechanism.

The kinetics and products of the reaction of 2-octyl mesylate with azide ion and water in 25% dioxan-water have been re-investigated, using 2M NaClO₄ as an ionic strength "buffer" to swamp out salt effects. The results are in accordance with the occurrence of simultaneous first-order and second order processes, and the rate-determining and product-determining steps are identical. The mechanistic consequences of the rejection of the borderline suggestion are examined.

Conformational Studies of 2,2-Dibenzyl-5,5-Dimethylcyclohexane-1,3-Dione, 3,3-Dimethyl-7,111-Diphenylspiro [5,5] Undecane-1,5,9-Trione and Derivatives

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Earlier studies of the pmr spectra of the title compounds led to proposed structures which showed severe steric crowding within the molecules. X-ray crystallographic studies, performed by M. D. Brice and J. Browning at the University of Canterbury have confirmed the structure for the trione, but shown an alternative, less sterically crowded structure for the dione. Further studies on the conformational dynamics and chemistry of the title compounds will be presented. Included in the discussion will be information obtained from the cmr spectra of the compounds.

Demethylation of Aryl Methyl Ethers

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The demethylation of aryl methyl ethers in high yield using powerful nucleophiles in dipolar aprotic solvents has recently been added to the synthetic armoury. The first such reagent, sodium thioethoxide in dimethyl formamide, has been shown to exhibit some selectivity in its action. This paper will summarise the general procedure and show some applications of the synthetic utility of the reaction.

Physical

The Computation of NMR Lineshapes by the Density Matrix Method

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Experimentally observed temperature dependent changes in NMR spectra may be interpreted in terms of some rate process involving interchange of spins between different magnetic environments. Depending upon the complexity of the spin system involved in the exchange process, estimates of the rate of exchange can be made by the use of approximations based on the Bloch equations. It has long been known however that these approximation treatments are quantitatively unreliable, and that the most satisfactory method of determining rate constants and activation parameters is by a full steady state lineshape fitting over the temperature range where exchange effects can be observed.

For weakly coupled spin systems undergoing exchange it is possible to compute theoretical lineshapes using modified Bloch equations but strongly coupled systems require a full density matrix treatment.

The density matrix method will be reviewed and the results of the investigation into the internal rotation of the nitroso group of N,N-dimethyl, and N,N-diethyl-*p*-nitrosoaniline in various solvents will be presented.

Quenching and Trapping of Cd 228.8 nm Resonance Radiation Studied by a Phase-Shift Method

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Cadmium vapour at temperatures around 560 K has been irradiated with 228.8 nm resonance radiation from a modulated microwave discharge lamp. The phase angle of the 228.8 nm fluorescence relative to a fixed reference signal has been measured as a function of the partial pressure of added quenching gas. Under the above conditions, which are those of large optical depth, the radiation trapping time T obeys a Stern-Volmer relationship of the form

$$T_0/T = 1 + k_0 N_0 T_0$$

where T_0 is the trapping time in absence of quencher Q ; N_0 is the concentration of Q ; and k_0 is the rate constant for quenching of Cd(¹P₁) by Q . Values of k_0 and quenching rates will be presented for $Q = \text{He, Ar, H}_2, \text{N}_2, \text{NH}_3, \text{N}_2\text{O, CO}_2, \text{CO, propene, and n-butane}$. The values of k_0 range from 5.2×10^{-12} to $1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and T_0 is typically 1.3 μs .

Some Applications of ESR Spectroscopy to the Study of Transition Metals

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An introduction and review of the analytical applications of ESR to the study of transition metal ions in solution will be given. Results of the application of this method to Cu^{2+} and Mn^{2+} will be discussed.

A Computer Simulation of Cheesemaking

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Cheesemaking is started by the addition of rennet and bacteria to milk which results in the formation of a coagulum. This is cut into curd particles which synerese or shrink with the expulsion of whey. The lactose concentration and acidity in the curd are affected by the growth of trapped bacteria. These changes result in diffusion between the curd and whey.

The object of simulating this system was to demonstrate the relationship between the whey acidity and the conditions within the curd.

The digital computer programme consisted of three functional sub-programmes which simulated bacterial growth, syneresis and diffusion. These three problems were considered one at a time so that independent models could be developed and tested. These models were then coupled together to simulate the whole system.

The curd particles were represented in the models as spheres divided into 10 spherical shell elements or sections between which solutions could pass by diffusion and syneresis. The method of simulation was to calculate the change in each variable in the system during a short time interval. This resulted in a new set of conditions so that the changes in the next short time interval would be modified accordingly.

ESR Studies of Some Organic Radical Anions in Solution

A. S. Huffadine and B. M. Peake*
Department of Chemistry, University of Otago

Results of the analysis of the ESR spectra of the radical anions of some derivatives of spirobifluorene in different ether solvents will be discussed in terms of spin localisation.

Nuclear Quadrupole Resonance Studies of Copper (I) Complexes

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The nuclear quadrupole resonance (n.q.r.) frequencies of ^{63}Cu and ^{65}Cu have been measured in several Copper (I) complexes with phosphine and arsine sulphide ligands. The resonance frequencies lie in the range 25-30 MHz for ^{63}Cu . These results will be compared with the n.q.r. frequencies of ^{63}Cu and ^{65}Cu measured in other copper (I) compounds, and will be discussed in terms of molecular structure and various bonding schemes for copper (I).

ESR Studies of Copper Complexes Extracted into Organic Solvents by Carboxylic Acids

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Past studies of the distribution of Cu^{11} , between an aqueous phase and an organic phase containing a carboxylic acid have indicated the presence of dimeric Cu^{11} species in the organic phase. We report here the results of e.s.r. studies on such systems. These reveal the presence in the organic phase of monomeric and dimeric Cu^{11} species, which show $S = \frac{1}{2}$ and $S = 1$ spectra respectively. Physical and chemical evidence concerning the nature of the extracted species will be discussed.

Internal Pressure of Methanol-DMSO Mixtures

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Internal pressures $(\delta U/\delta V)_T$, have been derived from experimentally measured thermal pressure coefficients, $(\delta P/\delta T)_V$, for methanol-DMSO mixtures. These data, together with the temperature dependence of the thermal pressure coefficient, are used to interpret structural changes in the solvent system as a function of composition. Thermodynamic parameters of mixing at constant volume for this system are also discussed.

Kinetics of the Glass Transition

A. J. Easteal
Department of Chemistry, University of Auckland

The kinetics of the glass transition of super-cooled liquids were investigated with a differential scanning calorimeter. Measurements of the heat capacity as a function of heating or cooling rates yielded data on the kinetics of conversion of the crystalline phase to the glassy state.

The Design of High Conductivity Ionic Solids and Liquids

J. W. Tomlinson
Department of Chemistry, Victoria University of Wellington

The effective functioning of electrochemical energy conversion devices — batteries with high energy and power density, fuel cells etc. — and of all kinds of electrochemical ionic medium with a sufficiently high electrolytic conductivity. Material problems make it desirable that temperature should be as low as possible, and there is therefore great interest in the design of low temperature high conductivity media. The theoretical background to ionic migration tends to be somewhat obscure, and it is useful to take a broad and simple view of the problem in the solid, glassy and fluid states. In this review the relation between ionic migration and structure, temperature and pressure will be examined, and the factors which may be especially important to consider in developing high conductivity electrolytes will be discussed in the light of recent developments in solid and fluid state chemistry.

Transport in Very Concentrated Calcium Nitrate Solutions as a Function of Temperature and Volume

S. I. Smedley
Department of Chemistry, Victoria University of Wellington

We have measured the electrical conductivity and compressibility of concentrated calcium nitrate solutions from 25°C to 150°C and up to 5 kbar. The results are interpreted in terms of modern theories of transport in liquids.

Mass Spectrometry

MASS SPECTROMETRIC DATA TRANSFER TO REMOTE COMPUTER

L. N. Nixon* and P. D. Mintoft, A.B.D., D.S.I.R.
Palmerston North

The presence of a well established automatic data handling unit associated with the mass spectrometer at Massey University suggested the possibility that use could be made of this system for processing data from the mass spectrometer at Applied Biochemistry Division, D.S.I.R.

Both "on-line" and "off-line" techniques for transferring m.s. data to the computer (distant about 1300 metres) were investigated with particular reference to cost. For "off-line" transfer trials were made using a video recorder. An inexpensive "on-line" link-up has been developed employing transmission of the analogue mass spectrometer output signal.

DATA REDUCTION FROM PHOTOGRAPHIC PLATES IN SPARK SOURCE MASS SPECTROMETRY

P. C. Rankin*
Soil Bureau, D.S.I.R., Taita

Ion sensitive photographic emulsion have been extensively used for quantitative analysis in spark source mass spectrometry. Such ion detectors effectively integrate the fluctuating ion currents produced by a spark discharge. They can permanently record a large mass range (viz. 7-240) and permit rapid visual qualitative assessment of element concentration in a sample. On the other hand emulsion detectors are time consuming, have a limited linear range and have plate to plate variation in emulsion response to ion impact. This paper will discuss the experience gained at Soil Bureau in the use of emulsion detectors and outline some of the procedures used to compensate for emulsion variation.

CARBON ISOTOPES AS A TOOL IN THE STUDY OF WATER POLLUTION

C. H. Hendy
Department of Chemistry, University of Waikato, Hamilton

The results of as yet unpublished research, conducted by the speaker while at Lamont-Doherty Geological Observatory, will be discussed.

EXPERIENCES WITH THE MICROMASS 602C ISOTOPE MASS SPECTROMETER

J. R. Hulston
Institute of Nuclear Sciences, D.S.I.R., Lower Hutt

The Micromass 602C isotope mass spectrometer has recently been installed for natural deuterium measurements at I.N.S. The all-metal vacuum system, without refrigerant, and the electronics units which use an integrated circuit amplifier for almost every adjustment represent a radical change from traditional isotope mass spectrometers. The consequences of these changes will be discussed together with the reliability record since installation.

MASS SPECTROMETERS USED AS TOOLS IN STUDYING FAST GAS REACTIONS OF ATOMS, RADICALS AND IONS

C. G. Freeman*
Chemistry Department, University of Canterbury

Some aspects of the work of this group will be reviewed.



EXECUTIVE SECRETARY APPOINTED

Council recently appointed Mrs N. E. Wignall, to this position. She was born in Christchurch, graduated B.H.Sc. 1949. She spent three years as the only science teacher at Waikato Diocesan School for Girls. During an overseas trip she worked for a year at the Post-Graduate Medical School in London. Her first year back in New Zealand was a frustrating one, trying to find another niche in a laboratory. Finally she joined D.S.I.R. in Wellington, where for four years she worked in the Food & Drugs Section. She resigned on marriage and returned to Christchurch. Three teenage children keep her busy, but she still has time for Duplicate Bridge, Scottish Country Dancing, and catching tiddlers with hook and line (cod don't come to the upper reaches of Queen Charlotte Sound as they did before the increase in ferry traffic).

OBITUARY—

R. M. ALLISON, M.Sc., Ph.D. (Wis.) F.N.Z.I.C.

Russell Allison, for many years Officer in Charge of the Lincoln Substation of Applied Biochemistry Division, DSIR, died on 13th June.

Russell graduated M.Sc. in Chemistry from Canterbury in 1940, and joined the staff of Wheat Research Institute. After the war he worked in Auckland at Plant Disease Division on timber preservation, and later at the then Plant Chemistry Laboratory, Palmerston North, before coming to D.S.I.R. Lincoln in 1949 to establish a biochemical laboratory. Here he interested himself in a wide range of problems provided by the locale.

His major interest was in nutrition in the broadest sense and this combined with his strong humanitarian views fitted him well for the leaf protein project that was his principal task in latter years, and he brought to this both enthusiasm and skill.

He took an active part in the affairs of the Institute, serving as Branch Chairman in 1957. He also made a large contribution to the scientific life of the community, for instance as a leading member of the Royal Society and as one of the founders of both the Nutrition Society and the Christchurch Biochemistry Group. On a more personal basis his time and experience was always available to his fellows.

A man of wide interests in education, music and the outdoors he leaves many friends. He is survived by his wife and three daughters. RWC

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30th APRIL, 1974

1973		1973	
EXPENDITURE:		INCOME:	
\$		\$	
2472	Administration Expenses:	7505	Subscriptions — Annual
	Printing, Stationery,		Interest Received:
	Postages, Tolls, etc.	265	Bank of New Zealand
1200	Salary, Registrar	192	Local Body Stock
929	Travelling Expenses		
535	Honoraria (Less Proportion Charged to Journal)	(457)	
		401	Net Proceeds — Sundry Publications
700	Branch Expenses Allowances		—Environment in Industry Stock
165	Audit Fees		Less Net Cost
—	Conference Costs paid by Institute		
70	Donation—S.A.N.Z.		
20	Royal Socy. of N.Z. Membership Fee		
—	Publicity		
13	Depreciation		
50	Donation—N.Z. Institute of Engineers		
—	Prizes	34	Excess of Expenditure over Income for Year
(6154)			
5079	PUBLICATIONS:		
—	Cost of Journal		
—	“List of Members”		
—	“Rules” — Covers only		
—2836	Less Revenue from Advertising		
(2243)			
\$8397		\$8397	

We have audited the books of The New Zealand Institute of Chemistry (Inc.) for the year ended 30th April 1974, and have received all the information and explanations we have required. In our opinion, according to the best of our information and the explanations given to us as shown by the books of account, the Balance Sheet, Income and Expenditure Account, and Trust Fund Account are properly drawn up so as to give a true and fair view of the state of the Institute's affairs as at 30th April, 1974.

SHANANAN AND WINDER,
Chartered Accountants.
M. P. Winder.

OVERSEAS VISITORS TRAVELLING FUND

181	Balance 30.4.73	—	625	Balance 30.4.73	373.70
70	Travelling Expenses Paid During Year	339.80		Conference Profits	766.15
374	Balance, 30.4.74	688.05		Less Audit Fee	112.00
					654.15
				Balance 30.4.74	
\$625		\$1,027.85	\$625		\$1,027.85

Members are reminded that exemption from payment of the annual subscription is available on application to Council to all

members over 65 years and to those over 60 years who have retired and have paid at least 10 years subscription.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

BALANCE SHEET AS AT 30th APRIL, 1974

1973			1973		
\$			\$		
	CURRENT LIABILITIES			CURRENT ASSETS:	
—	Bank of New Zealand	2,248.59	33	Petty Cash Funds	9.98
185	Sundry Creditors	541.19	1912	Bank of New Zealand	—
334	Subscriptions Received in Advance	213.25	1146	Subscriptions in Arrears	862.00
400	Royal Institute of Chem- istry Funds Held in Advance	—	377	Sundry Debtors	1,194.14
			671	Publications on Hand	1,810.34
			(4139)	TOTAL CURRENT ASSETS	3,876.46
(919)	TOTAL CURRENT LIABILITIES	3,003.03		TRUST FUND INVEST- MENTS (AT COST):	
	SPECIAL FUNDS:		96	Post Office Savings Bank	98.50
140	Education Fund (School Bulletin)	140.00	1000	Hutt County Council, Redemption Loan	1,000.00
374	Overseas Visitors Trav- elling Fund	688.05	1500	Lyttelton Harbour Board Loan	1,500.00
—	Easterfield Fund	400.00			
(514)	TOTAL SPECIAL FUNDS	1,228.05	(2596)	GENERAL FUND INVEST- MENT:	2,598.50
	TRUST FUND:		1000	North Canterbury Hos- pital Board Stock	1,000.00
2593	Balance 30.4.73	2,595.65	5000	Bank of New Zealand Ltd.—Term Deposit	5,000.00
3	Plus interest credited	2.85			
(2596)		2,598.50	(6000)	FIXED ASSETS (AT COST):	6,000.00
	ACCUMULATED FUNDS:			Office Equipment	317.80
8795	Balance 30.4.73	8,761.44		Less Depreciation	274.80
34	Excess of Expenditure over Income for Year	3,071.06	53	Addressograph Plates	62.35
(8761)	Balance 30.4.74	5,690.38		Less Depreciation	60.35
			2		2.00
			(55)	TOTAL FIXED ASSETS	45.00
\$12790		\$12,519.96	\$12790		\$12,519.96

**THE NEW ZEALAND INSTITUTE OF CHEMISTRY
(INCORPORATED)**

Notice of Meeting

ANNUAL GENERAL MEETING

**to be held at the University of Auckland
Wednesday, August 28, 1974, at 5.00 p.m.
Canterbury**

Acting General Secretary.

D. J. Hogan,

Sir Thomas Easterfield in his time

An essay towards a Biography

by E. Christie and T. A. Turney

Introduction

This is an account of the life and work of Sir Thomas Easterfield. There would appear to be sufficient material to write a full biography but both authors being engaged in other major tasks do not possess the time at present to embark on this project. They have accordingly written the material available from primary sources as an essay towards a biography. They hope this will be of interest to the readers of this journal and will enable a future historian to embark on a full scale biography. The authors are grateful to Dr C. R. Barnicoat and to the Librarian of the Cawthron Institute for providing help and assistance. They note with regret that two individuals, E. Marsden and E. Beaglehole, who might have provided helpful information have passed away since this project was commenced.

THE FORMATIVE YEARS 1866—1900

Victorian England

At the time of Easterfield's birth in 1866 England had reached a peaceful era.

Samuel Smiles had published his *Self Help* in 1859 in which was extolled the Victorian Virtues of Thrift, Character and Duty; in the same year there had appeared Darwin's *Origin of Species* which was to influence the scientific environment of the era described in the next section. A good description of a typical Victorian is given by Bowra in his book, *Memories*: "My father in his youth had been deeply influenced by Huxley's assaults on established religion and never reverted to the Christianity in which he had been brought up. He liked to expose its absurdities and to confirm my own doubts. But he kept to the highest degree the full code of Victorian morality. I never knew him to do a mean or dishonest thing and he was deeply shocked when others did." It was the age of the established church; how seriously this influenced events is shown in the case of Henry Sidgwick as described by Broad in *British Philosophy in Mid Century*.

"Sidgwick became a Fellow of Trinity College, Cambridge, in 1859 and a lecturer in moral science in 1867. At that time a holder of a college fellowship had to express formally his assent to the doctrines of the Church of England. This obligation was not usually taken very seriously; but Sidgwick was an exceptionally conscientious man and by 1869 had reached a theological position which he felt obliged him to resign office held under these conditions." Such was the influence of the established church. Easterfield himself records that he was brought up to conduct his life's work "to the glory of God and his fellow men." It was an era that created the Salvation Army (1878).

It was the era of free trade. The farmer suffered while the textile manufacturers profited, and Leeds, the centre of Easterfield's early life, was a centre of textile production. The overseas investments in the Empire balanced an unfavourable export-import balance. In the words of the *Cambridge Modern History*, "Mid Victorian England had developed India as an economic colony, Latin America as a sphere of private trade and investment. There was no sharp change in the late Victorian period. Investment continued to flow to non Empire as well as Empire countries" and the climate of opinion summed up by the *Times* 30/12/1899, was, 'Trade was never better, wages were never so good, nor were there ever fewer workmen unemployed'.

Politically, Britain, in the middle of the Victorian era, was the greatest power in the world. Her navy dominated the world and she held large territorial possessions on four continents. It was a period of empire expansion (the British

Empire reached its maximum by 1900). It was an age of missionary zeal, the gospel message being spread throughout Africa. The monarchy of Victoria was supreme, with her relatives married into all the Royal Houses of Europe. Disraeli and Gladstone competed for political supremacy; Irish Home Rule was the most damaging political cause. It was an era of electoral reform as the franchise was gradually extended. The colonies were populated with British emigrants of whom Easterfield was to be one.

In the same period there were changes in the educational pattern. Most of the universities in Britain date their foundation to the period after 1870. The ancient foundations of Scotland provided a different pattern and Easterfield was to find echoes of this on his appointment to Wellington. The class stratification of England was reflected in its public schools. The Elementary Education Act of 1870 was, however, instrumental in broadening the opportunities open to the masses. This was assisted by the development in 1873 at Cambridge of the University Extension movement, an activity in which Easterfield was subsequently to take part. Cambridge was the home of personalities such as Oscar Browning, who was to influence the young Curzon, later Viceroy of India, while at Oxford, Jowett the trainer of Empire rulers, held sway. T. H. Huxley had a large influence on education with his belief in the value of science in a liberal education—beliefs to be echoed later by Easterfield. Women fought for and gained acceptance in the universities.

Adding colour to this formal background was the cultural environment that was being created by the writers and artists of this period. The period was mirrored by novelists, most of whom are now regarded as minor, such as Hardy, Butler and Stevenson. Walter Pater at Oxford wrote his unique prose. Wilde the playwright was overshadowed by Shaw, but perhaps Lewis Carroll captured the period for the longest time with his 'Alice in Wonderland.' Reflecting the scientific spirit of the era is H. G. Wells whose life spans almost the same period as Easterfield. Among the poets were Hopkins and Yeats, while in art the era was dominated by the impressionist painters.

It was in this period and environment in which Easterfield grew. He was to receive his formal university education at Leeds which lies on the river Aire, and which was to be the subject of a paper by him on pollution. The town Leeds in the county of Yorkshire became a city in 1893. Beaglehole in his *History of Victoria University College* notes that Easterfield had the characteristics of a Yorkshireman. The major industry in 1855 was the wholesale clothing industry; in 1874 the Yorkshire College of Science was established.

CHEMISTRY AND SCIENCE 1866-1900

Science and technology became closely related in this period. Mendeleeff formulated his periodic table in 1869, but the importance of this was not perceived until later. A clarification of the theories of thermodynamics enabled the development of the steam engine. Electricity developed from the scientific work of Maxwell (1873). Studies of light were concerned with speculation on the nature of light and with developments in spectroscopy that led to the spectacular discovery of helium. In physics it was an age of climax and it was thought that all discoverable physical phenomena had been found. (A significant change was to take place with the discovery of nuclear physics.) This peak of physics was exemplified in the work of Kelvin at Glasgow where a vast range of practical and theoretical physical problems were studied. In biology Darwin's *Origin of Species* set the stage for controversial thinking and his ideas were vigorously promulgated in the face of religious opposition by

T. H. Huxley. Pasteur discovered optical activity, opening new vistas in chemistry and the subject for one of Easterfield's early papers. Lister by his discovery of antiseptics revolutionized medicine to increase the length of human life. But the most important area of scientific development, and the one in which Easterfield was professionally concerned, was that of organic chemistry.

Organic chemistry had been concerned with the range of substances that could be obtained from plants and animals, but Wohler's discovery in 1829 that these could be synthesized artificially caused a considerable change in emphasis. In 1856 W. H. Perkin broke through into an important new area with his discovery of synthetic dyes and the subsequent establishment of the British dye industry. Important theoretical progress was made at the same time by Kekulé's discovery of the structure of benzene.

Pasteur's discovery of optical activity was followed through vigorously by the chemists Le Bel and Van't Hoff. At the same time as these developments were taking place there was a vigorous rise in the new science of physical chemistry. Van't Hoff himself had studied the problems of solutions; Arrhenius discovered the electrical properties of solutions containing common salt. These views were then further extended by Ostwald. It is noteworthy that Arrhenius, Ostwald and Van't Hoff were invited to expound their theories at a meeting of the British Association in Leeds in 1890, a meeting which the young Easterfield attended.

Concurrent with these developments in science were developments in technologies. The most striking of these was the development of electricity, the large scale generation of electricity being established in the 1880's. This was followed by the development of electric light through the efforts of Edison and Swan. The development of the telegraph speeded up communication leading to the invention of the radio and telephone. The development of electricity power led to electrochemical industries. Thus in the 1880's the production of aluminium became feasible, and new methods of producing the commercially important chemicals caustic soda and sulphuric acid were developed. An important development mentioned by Easterfield many times in subsequent addresses was the establishment by Lawes in 1843 of the first superphosphate factory.

Concurrently with developments in chemical industry were changes in metallurgical processes which were to contribute to changes in technology in the period. The production of steel was revolutionised. Sail gave way to steam and the widespread discovery of oil in America was to revolutionize the development of transport in the twentieth century. It is in this background of rapid scientific and technological progress that Easterfield was educated, and as the ascendancy established by Perkin in the British dyestuff industry had been rapidly lost to the Germans, it was natural that after his initial training in British universities Easterfield should go to Germany for doctoral training.

THE YOUNG EASTERFIELD

Thomas Hill Easterfield was born at Doncaster on the 1st March, 1866. No information is available on his life prior to 1878, except that his father was the local manager of the Yorkshire Savings Bank.

In 1878 he entered Doncaster Grammar School. In 1879 he won two prizes in modern languages and in 1881 a science prize. His earliest recorded paper was published in 1883 in the Leeds Photographic Society journal when he was seventeen. This was followed by an account of a glacial deposit near Doncaster in the same year. His entrance to Cambridge is marked by a paper in 1887 in the *Cambridge Philosophical Society Journal* on permanganic acid, work to which Easterfield was to return on his retirement from the Cawthron Institute. His interest in the development of apparatus and equipment is shown in papers on a simple water bath regulator and a trough for Hofmann vapour density published in 1889.

Easterfield entered the Yorkshire College (now the University of Leeds), a somewhat primitive environment. Later he became a Senior Foundation Scholar of Clare College, Cambridge, and in 1886 was awarded a First Class in the Natural Science Tripos, Chemistry, Physics, Geology and Zoology.

During his undergraduate period Easterfield was a prominent miler and three miler, gaining his athletic blue. After graduation he worked first in the Federal Polytechnic, Zurich, working under renowned chemist Emil Fischer, in the University of Wurzburg obtained a Ph.D. in 1894 for a dissertation on citrazinic acid. In 1888 Easterfield returned to Cambridge to become a lecturer in the University Extension Movement, and to work in the Organic Laboratory of the University. Easterfield had been trained as an organic chemist, but his training in Germany had brought him into contact with the newer developing area of physical chemistry.

That he may have had an association with the most eminent physical chemists of his time is indicated by the fact that in 1890 he read a paper on the pollution of the River Aire with J. M. Wilson, a meeting we have already noted as being attended by Ostwald, Arrhenius and Van't Hoff.

Since Leeds was an industrial town and since pollution has become a live problem in the present the conclusions of this paper may be quoted with interest.

- (1) The river, originally a limpid stream, receives pollution from all the townships on its banks until it passes Leeds where the pollution becomes so great that the effect of the smaller towns below it becomes inappreciable.
- (2) That between each centre of population the river appears to clean itself to a small extent by natural causes.
- (3) That nearly all impurities rise and fall simultaneously but not in the same proportion.

Easterfield's association with ideas developed by Pasteur, Le Bel and van't Hoff are shown in his next paper in which he cites phenylbromacetic acid as an apparent exception to the principle of optical activity. It would, however, appear from knowledge now available that the compound as prepared had been racemized rather than being truly inactive. A further paper on the oxidation of mannitol is recorded in this same period.

The fruit of Easterfield's labours in the Extension Movement can be seen in the publication of the *Chemistry of Common Life* by the Cambridge University Press in 1892. Further papers on the anhydro derivatives of citric and aconitic acids (1892), the oxidation of charcoal by nitric acid (1893) and on salts of a new platinum base (1893) follow in this period, culminated by the publication of the work on citrazinic acid, the results of the Ph.D. thesis at Wurzburg, published as a dissertation in 1894.

A beginning of the work on natural products to be followed through later at Victoria is seen in a study of the constituents of Indian hemp resin. This is followed by a paper on cannabinol, of interest in relation to the current use of marijuana, and one on derivatives of dibenzylmesitylene. In 1899 Easterfield received a letter announcing his appointment as Professor of Chemistry and Physics at the newly established Victoria University of Wellington.

THE PIONEER 1900-1920

New Zealand in the Early 20th Century

The general election of 1899 was the most languid held in fifteen years, the main item of interest being the New Zealand troops sent to South Africa for the Boer War. The Liberal party had held office for the twenty-one years from 1891 to 1912, and this period was marked by the passage of important industrial and social legislation. In 1892 the lease in perpetuity system of land tenure was introduced as a not wholly successful attempt to prevent land from coming into the possession of large land owners. In 1893 the franchise was extended to women. In 1894 the Industrial Conciliation Act set up the Arbitration Court. In 1898 the Old Age Pensions Act was passed and in 1899 Labour Day initiated. In 1901 the Duke and Duchess of York visited New Zealand; the Cook and other Pacific Islands were annexed. The death of the Rt. Hon. R. J. Seddon, premier since 1893, was the end of a colourful era.

In 1907 New Zealand was constituted as a Dominion, the first of many events in weakening political ties with Great Britain. Other important events were the establishment of through railway communication between Wellington and Auckland and the introduction of C.M.T. in 1909, the first poll on national prohibition in 1911 and the laying of the foundation stone of Parliament Buildings in 1912. The Lib-

eral party in 1912 had held office for twenty-one years, relying on the support given by the smaller farmers and by the working class. It was replaced in 1912 by a more conservative Reform party. Labour began to break away from the Liberals and after 1910 New Zealand labour followed the example of Australia and formed its own party. Large scale strikes occurred in 1913, 1916 and 1921-22. During World War I a coalition ministry was formed with Massey as Prime Minister and Ward as Finance Minister. The war placed a very heavy drain on New Zealand resources at this time. Social legislation was, however, more or less at a standstill during the war. It is hard to assess this period of New Zealand history which in retrospect seems a period of tranquil progress. Population increased from 800,000 at the turn of the century to about 1½ million in 1920. There were steady increases in education but it is important to remember this was a period when most children left school in standard six and only a fortunate minority went to secondary school and an even smaller minority to university. It was a period of relatively favourable economic climate which ended with the depression of the twenties and from which the country was not to fully recover until the return of the first Labour Government in 1935.

It was to this social environment that Easterfield arrived in 1900. Victoria University College, a college of the University of New Zealand, had been established out of controversy. Easterfield came as one of the four foundation professors and was to be one of its leaders for the next twenty years.

Chemistry and Science in the Early 20th Century

The first part of the twentieth century was a less optimistic period in scientific development. The optimism of the late Victorian era was diminished by the first World War and it was only after this conflict that science gained new momentum. It is partly this change of climate which may have concerned Easterfield to look for new fields in the early twenties when he transferred his allegiance from Victoria University College to the newly founded Cawthron Institute. His address in 1917 on the aims of the Institute and a later address to A.N.Z.A.A.S. however still contain the spirit of Victorian scientific optimism. Within New Zealand science was a comparatively neglected area of activity and it was not until the establishment of the D.S.I.R. under Marsden in 1926 that science in New Zealand could be said to have gained momentum. Chemistry was to be changed by the experiments and theories of physics; thus in 1908 Rutherford and Geiger gave experimental proof of the identity of the α particle which paved the way for future important discoveries in radioactivity and in nuclear physics. At the same time Aston showed the existence of isotopic forms of the same atom such as Cl^{35} and Cl^{37} . Simultaneously Moseley from the study of X-ray spectra discovered the importance of atomic number as a property of atoms. All these experiments led to tentative ideas on the nature of the atom. In 1904 Thomson regarded atoms as consisting of electrons embedded in a sphere of positive electricity; this idea was elaborated by G. N. Lewis to stable octets of electrons, then exploited to a fuller extent by N. V. Sidgwick, a relative of the earlier Sidgwick we have mentioned. The Thomson atom gave way to the Rutherford atom in which the mass of the atom was concentrated in a small central nucleus, the electrons being disposed in orbits around it. This was extended in a rigorous mathematical form by Bohr, and the Bohr-Rutherford atom became the new basis of physical thinking.

In physics other important developments were taking place. In 1900 from a study of black body radiation by Planck came the first ideas of the quantum theory, applied by Einstein in 1905 to a study of the photoelectric effect. These developments did not greatly affect the ideas of Easterfield, inbred with a spirit of Victorian optimism tempered by a German-trained skill in organic chemistry.

Easterfield the Pioneer

Most of the background of this period can be obtained from a reading of Beaglehole's *History of Victoria University College*. The environment in which he found himself on

arrival has been described in the Jubilee number of *Spike*, when Easterfield was the only surviving member of the four professors who had founded the university. Easterfield was surprised to find that his contract of appointment also required him to teach physics, which he did until 1909. Easterfield had liberal interests and considered that culture could be derived from almost any subject if it were sufficiently well taught. He was also the advocate of the development at Victoria of an independent spirit despite the conflicting claims of university models based on the English, Scottish and Continental systems. Arriving at Wellington, Easterfield was told that if the professors came out for the Seddon Government they could obtain all they wanted for the College, otherwise they would get very little.

The College was inaugurated with great enthusiasm and Easterfield expressed thanks on behalf of his colleagues for the warm welcome they had been given on their arrival in Wellington. The Inaugural Lectures followed. Easterfield's "Research as a prime factor in scientific education" was delivered without notes, and in his own opinion contained several howlers. The main points stated were that it is equally the duty of a scientific teacher to make new knowledge as to teach what is already known; that every science student could be regarded as potentially a research student if given opportunity and encouragement; that research is a great educator in itself, and that research habits carried into practice are of fundamental value to the human race. The lecture was well received. Some days later Easterfield was visited by a man who asked him to assist in research on making gold from sawdust in which he claimed to have been already successful.

There was controversy over the site of the university, and until this was established makeshift accommodation was found in the Girls' College. Easterfield furnished competing architects with his ideas for the building which was opened in 1906. Writing to leading citizens was not very rewarding in producing funds for the new institution. There was also an unfortunate start with regard to the quality and quantity of apparatus and equipment that had been ordered for the new institution.

Like many who change institutions Easterfield continued to collaborate with former colleagues. Starting from his inaugural address with its strongly Huxlian flavour Easterfield with characteristic energy proceeded to look at the challenges of the new environment.

Losses of animal stock were being caused by the consumption of the poisonous tutu plant, so Easterfield with the vigorous Aston, chemist to the Department of Agriculture, commenced studies of the N.Z. flora. The first isolation of tutin was reported in 1900, but the structural problem, a difficult one chemically, was not finally solved until the work of Johns in the fifties. Concurrently with this work was a series of physico-chemical experiments conducted with Easterfield's own research students; with Bee (1901) an account of the Raoult method for molecular weight determination; with Robertson (1901) (Easterfield's most brilliant student and his successor at Victoria) a study of the vapour densities of fatty acids; studies on the N.Z. flora were continued with a paper on the karaka berry (1901); Cambridge work with Mills on derivatives of dibenzoyl mesitylene and a study of colophony, the residue remaining in the stil when crude turpentine is worked with oil or spirit (1902); work on rimu resin appeared in 1903 as Part 3 of the studies on N.Z. flora; with Silberrad papers on the synthesis of α - α glutaric acid (1903) and studies on ethyl carboxylglutarate (1904). The work book for 1903 still extant in the Cawthron Institute Library contains observations on podocarpic acid in Easterfield's own handwriting. A paper on the resin acids of the coniferae appeared in 1904. In 1909 Easterfield and his students presented a series of papers at the Australasian Association for the Advancement of Science. Work on the N.Z. flora was summarized in 1910, followed by a series of fatty acid chemistry in 1911. Part V of the chemistry of the N.Z. flora appeared in 1916.

This flow of papers was to change in 1917 when Easterfield was asked to act as Secretary to a Committee set up to consider the best means of dealing with a bequest made by Thomas Cawthron to found a scientific institution. As the result of his work as Secretary to this Committee, Easterfield was nominated as the first Director.

Nelson in the Twenties

Nelson was one of the earliest founded parts of New Zealand and the victories of Nelson at Trafalgar are celebrated in the names of its streets. The area has always been isolated by land and sea from other parts of the country. It is celebrated for its high quota of sunshine and is noted for its specialized agricultural industries such as hops, tobacco and fruit. Its character in the twenties was not greatly different from today, except for the primitive nature of the roading and in the lack of electricity. It was to this area that Easterfield came in the early twenties.

Miller, in his book *Thomas Cawthron and the Cawthron Institute* has given us a good account of the man who was so important in effecting the shift in Easterfield's interests. Cawthron came to New Zealand as a weakly boy but eventually became a strong man and developed a strong character. Frugal in his habits and shrewd in business, he was liberal in matters of public welfare. Thus at the time of his death he had endowed the Cawthron Park with seven thousand acres of mountain and forest, the Nelson Institute and Library Building, the School of Music and the Cathedral steps. In his will he left the sum of £240,000 for the founding of a scientific institute.

Easterfield gave the first Cawthron Lecture on the aims and ideals of the Institute in 1917, in which his Victorian ideals can be seen. "In this time of stress our natural desire is to honour those who are risking their all in fighting on behalf of the ideals for which the British Empire stands." Easterfield's definition of utility is interesting. "By utility I understand anything which makes for good—which makes life sweeter—which develops an appreciation of art, music or literature or which tends to the raising of public ideals." He began with an account of the scientific development of agriculture, the work of Liebig, Gilbert and Lawes. He then turned his attention to the romance of coal tar for industry discussed the foundations of the electrochemical industry made by Davy and Faraday, and considered the development of electromagnetic radiation.

He then considered the agricultural problems that were facing the country. These were bush sickness causing ill thrift in animals, and problems of the fruit industry. "At the present day we hear constant complaint of blights and insect pests, of bitter pit, black spots, aphids and codlin moth." He also noted that the flax and forestry industries provided problems of scientific worth. He did not think the Institute should carry out researches of obvious economic importance only, and considered practical schemes for the implementation of the proposed Institute.

The address must have impressed the Trustees, for in 1919 Easterfield was asked to and accepted an offer to become the first Director of the Institute with opportunity to select staff for the new Institute.

Chemistry and Science in the 1920's

In biology the trend was to a quantitative type of measurement using the techniques of chemistry and physics. Physics was dominated by the work of Rutherford, though progress was made in other directions. Thus in 1922 experiments on the ejection of electrons from atoms by X-rays lead to a discovery of the Compton effect. In 1924 de Broglie discovered the duality of particles and waves. In 1932 Anderson in America discovered the positron and in the same period Chadwick discovered the neutron. A further discovery was that of artificial radioactivity by the Joliot Curies in 1934. In 1925 wave mechanics was developed through the thinking of Schrodinger and of Heisenberg.

The era however belonged to Rutherford and from his Cavendish laboratory came a continuous stream of discoveries in the field of radioactivity. In 1921 the artificial disintegration of light elements. In 1925 the disintegration of atomic nuclei. In 1931 an analysis of α particles and in 1935 a most significant paper on the accurate determination of the energy released in nuclear transformation. In chemistry there were changes. Sidgwick's *Electronic Theory of Valency* (1926) revolutionized the thinking on the nature of chemical elements and compounds, and in 1922 Mellor's monumental work on inorganic chemistry appeared. Organic

chemistry advanced in a systematic way and was strongly influenced in 1923 by Ingold whose theories of organic structure were to prove as fruitful and as revolutionary as those of Sidgwick in the inorganic area. Perhaps the greatest area of advance was that of physical chemistry. The development of the quantum theory gave great impetus to the study of spectroscopy and after 1930 there were great advances in this and in X-ray crystallography. The Raman effect discovered by C. V. Raman in 1928 gave added impetus to these investigations. Advances in the kinetic theory of gases led to fresh thinking by Hinshelwood on the rates of chemical reactions. There were concurrent developments on the theory of chemical bonds associated with the work of Heitler and London (1927). It was against this background of rapid scientific change that Easterfield came to the Cawthron Institute in 1919, but here again as at Victoria University, Easterfield's thinking was to be brought to local rather than to international scientific problems.

Easterfield the Leader

The shift to the Cawthron Institute resulted in a considerable change in Easterfield's interests and demanded greater administrative activity on his part. Detailed information on this has not been obtained but it is clear that he would have been concerned with the problems of setting up laboratories and acquiring equipment, of the recruitment of suitable staff, with the provision of adequate finance and with important decisions concerning the research policy of the Institute, some part of which had already been considered in the Cawthron Lecture of 1917.

Easterfield got away to a rapid start in the new institution. One paper from the Cawthron Institute records notes on naphthalene trouble at the gas works (1921). The practical ramifications of the Institute's work were exemplified in an early pamphlet written with Rigg on lucerne growing (1921). The evangelical Huxlean Easterfield was still to be found; his presidential address to the N.Z. Institute Science Congress in 1921 still had the scientific evangelical tone of earlier lectures. An interest in national problems was revealed in a discussion of the Taranaki petroleum supplies, delivered at the Pan-Pacific Science Congress in 1923. Nostalgia had its place in an account of the development of science at Victoria University College in the *Spike* for Easter 1924. The New Zealand mineral oils received more formal treatment in articles in the *New Zealand Journal of Science and Technology* (1924). The relation of chemistry to pharmacy was the subject of a Cawthron Bulletin in 1928. Nostalgia played a hand again with reminiscences in the *Leeds University Magazine* for 1928. The soil surveys initiated by the Institute in the Nelson area began in a paper on pakihi lands. Large areas of marshy lands on the West Coast of the South Island are known as pakihi land, and this term is now applied to all areas of a similar nature in the Nelson Province. Interest in agricultural problems was extended in a paper on the occurrence of xanthin calculi in sheep (1929). The scientific achievements of the Institute in this era have been well summarized by David Miller in his book. Finally, in the later years before retirement there are a number of more general addresses and papers—the achievements of the Cawthron Institute, Cawthron Lecture 1933, *Chemistry in New Zealand 1940, 'A Foundation Professor Looks at the Early Years,' 1949.*

The Retirement Years

In 1933 Easterfield retired from the Cawthron Institute and was succeeded by one of his able students, Rigg, who had trained at Cambridge. In retirement he was knighted, but retained a position with the Institute as an honorary research chemist.

H. O. Askew in his obituary of Easterfield writes. "Besides being an enthusiastic chemist, Easterfield took a leading part in the organization and administration of scientific affairs in general. He was a foundation member of the New Zealand Institute which later became the Royal Society of New Zealand. He was President of the Society in 1921-22 and was awarded the Hector Medal of that Society for his researches in chemistry. Throughout his twenty-nine years of residence in Nelson he was a member, being President on several

occasions, of the Nelson Philosophical Society. An active member of the Australasian Association for the Advancement of Science he was President of the Chemistry Section in 1909. The New Zealand Institute of Chemistry, of which he was a foundation member and its second President, owed a great deal to him in its formative years."

Later he became an Honorary Fellow of this Institute. He was also a Life Fellow of the Royal Institute of Chemistry of Great Britain and Ireland.

Easterfield himself records the names of students who published as a result of their student work. "Of these Robertson was the outstanding investigator, publishing no less than ten papers during his student days, this is probably a record among New Zealand chemists." He also records, "The first session had scarcely commenced when a request was received from a number of legal practitioners that a course of lectures on chemistry 'suitable for lawyers'" be given and he records the subsequently distinguished lawyers who attended.

In Nelson Sir Thomas was an enthusiastic supporter of the Philosophical Society, Suter Art Society and the Nelson Rotary Club. He was President of the Nelson Harmonic Society for several years. He was a member of the Nelson Diocesan Synod for a number of years and on three occasions was one of the representatives of the diocese on the General Synod of the Anglican Church.

At the time of his death (1949) he was survived by one son, Dr T. E. Easterfield, and four daughters, Dr Helen Deem, Dr Theo Hall, Miss Daisy Easterfield and Miss Beatrice Easterfield. The authors have not had the opportunity of making contact with surviving relatives.

Publications

1. The interaction of solutions of alum and sodium thio-sulphate. T. H. Easterfield, *Leeds Photographic Society* (1883).
2. A glacial deposit near Doncaster. T. H. Easterfield, *Yorkshire Geological Society*, (1883), 8.
3. Some remarks on permanganic acid. T. H. Easterfield, *Cambridge Philosophical Society*, (1887), 106.
4. A simple water bath regulator. T. H. Easterfield, *Chemical News*, (1889).
5. A trough for Hofman vapour density determination. T. H. Easterfield, *Chemical News*, (1889), 60, 250.
6. The River Aire, A study in river pollution. T. H. Easterfield and J. M. Wilson, Read before the British Association, 8/9/1890.
7. Phenylbromacetic acid, an apparent exception to the Le Bel-Vant Hoff hypothesis. T. H. Easterfield, (1891), 59, 71.
8. The oxidation of mannitol by nitric acid. α -mannosaccharic acid. T. H. Easterfield, *Transactions of the Chemical Society*, (1891), 59, 306.
9. The chemistry of common life. T. H. Easterfield, *Cambridge University Press*, 1892.
10. Anhydro derivatives of citric and aconitic acids. T. H. Easterfield and W. J. Sell, *Transactions of the Chemical Society*, (1892), 61, 1003.
11. The oxidation of charcoal by nitric acid. T. H. Easterfield, *Transactions of the Chemical Society*, (1893), p. 163.
12. Salts of a new platinum sulphuric base. T. H. Easterfield and W. J. Sell, *Chemical News*, (1893) 223.
13. Studies on citrazinic acid. T. H. Easterfield and W. J. Sell, *Transactions of the Chemical Society, Part I*, (1893), 63, 1035.
14. Studies on citrazinic acid. T. H. Easterfield and W. J. Sell, *Transactions of the Chemical Society, Part II*, (1894), 65, 28.
15. Studies on citrazinic acid. T. H. Easterfield and W. J. Sell, *Transactions of the Chemical Society, Part III*, (1894), 65, 828.
16. "Citrazinic acid", T. H. Easterfield, Inaugural Dissertation, Ph.D., University of Wurzburg, 1894.
17. The constituents of Indian Hemp Resin. T. H. Easterfield and T. B. Wood, *Proceedings of the Cambridge Philosophical Society*, (1896), 9, 144.
18. Charas. The resin of Indian Hemp. T. H. Easterfield, T. B. Wood and W. T. N. Spivey, *Transactions of the Chemical Society*, (1896), 69, 539.

19. Cannabinol Part I. T. H. Easterfield, W. T. N. Spivey and T. B. Wood, *Transactions of the Chemical Society*, (1899), 75, 20.
20. Derivatives of dibenzylmesitylene. T. H. Easterfield and W. H. Mills, *Proceedings of the Chemical Society*, (1899), 22.
21. Research as the prime factor in scientific education. T. H. Easterfield, Inaugural Address, Victoria University College, Wellington, 1899.
22. Studies on the chemistry of the N.Z. flora. Part I. The tutu plant. T. H. Easterfield and B. C. Aston, *Transactions of the New Zealand Institute*, (1900), 33, 345.
23. Tutu, Part I. Tutin and coriamyrtin. T. H. Easterfield and B. C. Aston, *Transactions of the Chemical Society*, (1901), 79, 120.
24. Racults law for molecular weight determination. T. H. Easterfield and J. Bee, *Transactions of the New Zealand Institute*, (1901), 34, 497.
25. The vapour densities of fatty acids. T. H. Easterfield and P. W. Robertson, *Transactions of the New Zealand Institute*, (1901), 34, 499.
26. Studies on the chemistry of the N.Z. flora. Part II. The karaka nut, T. H. Easterfield and B. C. Aston, *Transactions of the New Zealand Institute*, (1901), 34, 495.
27. Derivatives of dibenzylmesitylene. T. H. Easterfield and W. H. Mills, *Transactions of the Chemical Society* (1902), 81, 1311.
28. A contribution to the chemistry of colophony. T. H. Easterfield and G. Bagley, *Transactions of the New Zealand Institute*, (1902), 35, 476.
29. Studies on the chemistry of the N.Z. flora. Part III. Rimu resin. T. H. Easterfield and B. C. Aston, *Transactions of the New Zealand Institute*, (1903), 36, 483.
30. The synthesis of α - α diglutamic acid. Easterfield, T. H. and Silberrard, O., *Journal of the Chemical Society*, (1903), 38.
31. The karaka fruit. T. H. Easterfield and B. C. Aston, *Journal of the Chemical Society*, (1903), 191.
32. Studies on ethylcarboxyglutarate. T. H. Easterfield and O. Silberrard, *Transactions of the Chemical Society*, (1904), 862.
33. The resin acids of the coniferae. Part I. The constitution of abietic acid. T. H. Easterfield and G. Bagley, *Transactions of the Chemical Society*, (1904), 1238.
34. The resin acids of the coniferae. Part II. The chemistry of colophony. T. H. Easterfield and G. Bagley, *Report of the Australian Association for the Advancement of Science*, (1904), 10, 155.
35. The acids of some New Zealand timber trees. T. H. Easterfield, *Transactions of the Australian Association for the Advancement of Science*, (1904), 10, 157.
36. The position of chemical research in Australia. T. H. Easterfield, Sec. B, *Report of the Australian Association for the Advancement of Science*, (1909), 12, 115.
37. New types of ebullioscopes. T. H. Easterfield, *Report of the Australian Association for the Advancement of Science*, (1909), 12, 155.
38. Oleone the ketone from oleic acid. T. H. Easterfield and C. N. Taylor, *Report of the Australian Association for the Advancement of Science*, (1909), 12, 156.
39. Isoretene. T. H. Easterfield and R. E. Rudman, *Report of the Australian Association for the Advancement of Science*, (1909), 12, 158.
40. Note on the physical chemistry of phosphorous acid. T. H. Easterfield and H. T. Revell, *Report of the Australian Association for the Advancement of Science*, (1909), 12, 153.
41. Matai-resinol. T. H. Easterfield and J. Bee, *Report of the Australian Association for the Advancement of Science*, (1909), 12, 154.
42. Studies on the chemistry of the New Zealand flora. Part IV. The chemistry of the podocarpi. *Transactions of the New Zealand Institute*, (1910), 43, 53.
43. The resin acids of the coniferae. Part III. Matai-resinol. T. H. Easterfield and J. Bee, *Transactions of the Chemical Society*, (1910), 1028.

44. The interaction of iron with higher fatty acids. T. H. Easterfield and Miss C. M. Taylor, *Transactions of the New Zealand Institute*, (1911), 44, 301.
45. The preparation of the ketones of the higher fatty acids. T. H. Easterfield and C. N. Taylor, *Transactions of the Chemical Society*, (1911), 99, 2298.
46. Studies in the chemistry of the New Zealand flora. Part V. The chemistry of podocarpus totara and podocarpus spicatus. T. H. Easterfield and J. C. McDowall, *Transactions of the New Zealand Institute*, (1916), 48, 518.
47. The aims and ideals of the Cawthron Institute. Cawthron Lecture 1917, T. H. Easterfield, Nelson 1921.
48. Lucerne growing in the Nelson district. T. H. Easterfield and T. Rigg, *Cawthron Institute Bulletin*, 1921.
49. Some aspects of scientific research. T. H. Easterfield, Presidential Address, New Zealand Institute Science Congress, *Proceedings of the New Zealand Institute*, (1921), 53, 26.
50. Discussion on petroleum supplies of the Pacific. T. H. Easterfield, Pan Pacific Congress, 1923.
51. Development of science at Victoria University. T. H. Easterfield, *Spike*, Easter, 1924.
52. New Zealand mineral oils. T. H. Easterfield and N. McClelland, *New Zealand Journal of Science and Technology*, (1924), 6, 274.
53. The relation of chemistry to pharmacy. T. H. Easterfield, *Cawthron Institute Bulletin*, 1928.
54. Reminiscences, T. H. Easterfield, *Leeds University Magazine*, 1928.
55. Pakihi lands of the Nelson Province. T. H. Easterfield, T. Rigg and J. A. Bruce, *New Zealand Journal of Science and Technology*, (1929), 11, 231.
56. A widespread occurrence of xanthin calculi in sheep. T. H. Easterfield, T. Rigg, H. O. Askew and J. A. Bruce, *The Journal of Agricultural Science*, (1929), 19, 573.
57. The occurrence of xanthin calculi in New Zealand sheep, T. H. Easterfield and J. A. Bruce, *New Zealand Journal of Science and Technology*, (1930), 11, 357.
58. The conversion of pakihi into dairy pasture. T. H. Easterfield, T. Rigg, H. O. Askew and J. A. Bruce, *Cawthron Institute Bulletin*, 1931.
59. The achievements of the Cawthron Institute. T. H. Easterfield, Cawthron Lecture, 1933.
60. "Chemistry in New Zealand" in "Chemistry in the development of New Zealand industry". T. H. Easterfield, New Zealand Section Institute of Chemistry of Great Britain and Ireland and New Zealand Institute of Chemistry 1940.
61. A foundation professor writes of the early years. T. H. Easterfield, Jubilee Number of *Spike*, Victoria University College Students Association, 1949.
62. Some abnormal concretions of the animal body. T. H. Easterfield, Undated lecture.
63. Cements: their solved and unsolved problems. T. H. Easterfield, Undated lecture.

Background Material

1. Easterfield, T. H., Laboratory notebook c. 1908, Cawthron Institute Library.
2. Findlay, A., *A hundred years of chemistry*, Gerald Duckworth, 1947.
3. Easterfield, T. H., Obituary, H. O. Askew, *Nelson Evening Mail*, 1949.
4. Easterfield, T. H., Obituary, T. H. Rigg, *Journal of the New Zealand Institute of Chemistry*, 63, 1949.
5. Easterfield, T. H., Obituary, E. Marsden, *Journal of the Chemical Society*, 1557, 1952.
6. Beaglehole, J. C., *History of Victoria University College*, Victoria University College, 1956.
7. Miller, D., Thomas Cawthron and the Cawthron Institute The Cawthron Institute, 1963. Appendix on personalia contains notes on T. H. Easterfield.
8. *Encyclopaedia of New Zealand*, Government Printer, 1966. Contains articles on the Cawthron Institute and on T. H. Easterfield.

9. *Encyclopaedia Britannica* was consulted for general scientific background.

10. *New Zealand Year Book* was consulted for historical details.

All other sources of material have been noted internally.

ONE MAN'S MEAT IS ANOTHER MAN'S POISON

The Auckland Industrial Develoapment Division of DSIR is exploring the feasibility of an advisory service on the re-use of industrial waste materials. Virtually every industrial process carries with it the production of waste materials, and disposal of these waste products can be difficult and expensive. Dangers of environmental pollution and the growing awareness of the possible exhaustion of some important raw-material sources emphasise the need to recycle waste products from industry whenever possible.

With this in mind AIDD is proposing a scheme whereby all industrial and commercial undertakings are invited to supply information on their waste products: quantity, quality, and present method of disposal etc. The information will then be correlated and published at regular intervals in industrial publications such as "Environment & Pollution Control Equipment News", "Chemistry & Industry", and "Science in Industry News". Information will be disseminated to as wide a readership as possible; names of firms supplying the information will not appear. Any company can refer to the list of materials available. If a company can employ one, or more, of them in its own processes further details can be obtained from AIDD.

The role of AIDD will be to collect and publish information about waste material, to answer inquiries on individual items and, if required, to check the material to establish that it is suitable for the purpose intended. Finally both firms will be put in contact with each other to come to a mutually advantageous arrangement. If a particular material is available in sufficient quantity it may well be in a form unsuitable for re-cycling. In this case AIDD will endeavour to assist directly or by reference to another source of aid.

The success of the proposed service depends upon the whole-hearted co-operation of industry, not only in Auckland but throughout New Zealand. Because the problem is national, naturally the offer of assistance will cover the whole country; a waste material in Christchurch could be a raw material in Auckland or vice-versa. For all information on waste products, inquiries about these products, requests for further details of the scheme, and other information about how you and AIDD can help New Zealand; while you are helping yourself, please phone or write:

H. Green at
Auckland Industrial Development Division, DSIR,
P.O. Box 2225, Auckland. (Tel.: 34-116)

APPOINTMENT

Dr H. J. Percival has recently taken up his appointment as Director of the New Zealand Pottery and Ceramics Research Association, Gracefield.

Dr Percival returns to P.A.C.R.A. after a period of several years including two years in the Department of Industrial Chemistry, Universite Libre de Bruxelles, Brussels, Belgium, and eight months on the staff of the New Zealand Fertiliser Manufacturers' Research Association, Otago. In Belgium Dr Percival carried out post-doctoral studies under Professor W. L. De Kayser on the hydrothermal synthesis of dolomite and the sintering properties of dolomite at high temperature.

Dr Percival gained his M.Sc (Hons) and Ph.D (1970) degrees in Chemistry from Victoria University of Wellington. He was a Victoria University Fellow in the P.A.C.R.A. Fellowship scheme for Ph.D. students.

BRANCH NEWS

Auckland

The activities of the Auckland Branch recently can only be described as "hectic" with the following overseas visitors attending various meetings.

Mr J. D. Pankhurst and Mr R. A. Canham, president and executive secretary respectively of the International Water Pollution Control Federation, and both from the United States visited New Zealand from 28th to 30th April. The New Zealand Water Supply and Disposal Association which is affiliated to the N.Z.I.C. among other groups, organised a meeting addressed by these visitors.

Dr B. S. Friedman, President of the American Chemical Society, was on holiday in New Zealand, and met Auckland members of the N.Z.I.C. for a brief address and cocktails on the 10th of May.

Professor W. W. Eckenfelder, a chemical engineering authority, of Vanderbilt University, Nashville Tennessee, held a seminar on "Modern Methods of Waste Water Treatment" on May 11.

Dr Egan, Government Chemist, London United Kingdom and Mr L. G. Clark, New South Wales Government Analyst, Sydney, Australia both presented papers at a one day symposium on "Toxicology", organised by the Auckland branch, on May 13.

Dr J. A. Turner, Radiochemical Centre, Amersham, England spoke on "Preparation and use of Labelled Compounds" on May 15.

Apart from these overseas visitors, a New Zealander well known for his travels, the Hon. Mr J. A. Walding, addressed the branch on "The Role of the Chemist in the Environment" at the branch's graduate luncheon meeting on May 9.

On the local front, congratulations are forwarded to Associate Professor C. J. O'Connor of the Auckland University on her award of a D.Sc. by the University of Auckland, and to Mr K. Hunter of the University of Auckland, who has been offered a Rutherford Scholarship by the Royal Society, London.

Waikato

Waikato Technical Institute Prize

The Waikato Branch book prize for the best Chemistry student at the Waikato Technical Institute was awarded to Michael Howell from the Research Unit, N.Z. Cooperative Dairy Co., Matangi.

J. E. Allan Memorial Prize in Chemistry

The first J. E. Allan Memorial Prize in Chemistry was awarded to Pierre Bonny. This prize was established in 1973 by the Waikato Branch in memory of James Eric Allan, M.Sc., F.N.Z.I.C., who gained an international reputation as one of New Zealand's foremost scientists through his outstanding contributions to the development of atomic absorption spectroscopy. The book prize is awarded to a second year undergraduate student majoring in Chemistry at the University of Waikato.

University of Waikato

Dr K. M. Mackay has returned from study leave spent in the Department of Chemistry, University of Edinburgh, where he worked in association with Professor E. A. V. Elsworth on silicon-metal compounds.

Manawatu

The May meeting of the branch was addressed by the President of the Institute, Dr P. K. Foster on "Management of Production and Research".

Dairy Research Institute

Dr M. W. Taylor of the Milkfat and Butter Section has been awarded a Ph.D. from Massey University. Dr Taylor's thesis was concerned with

Dr P. J. Morris has returned from study leave spent in the Research School of Chemistry at the Australian National University, Canberra, where he worked in association with Dr D. A. Buckingham and Professor A. M. Sargeson on intramolecular reactions of some nitrite ligands coordinated to Co (III).

Branch Meetings

The May meeting was held in the laboratories of New Zealand Forest Products Ltd. at Kinleith at the invitation of Dr A. F. Wilson. 39 members and friends travelled by coach from Hamilton, and were joined at Kinleith by members from other centres in the Waikato district. A very acceptable meal was provided after which there was a conducted tour of the pulp and paper plant, followed by several short talks by staff members on aspects of the work at New Zealand Forest Products. The visit was enjoyed by all.

The June meeting was addressed by Mr A. Twomey, Superintendent of the Waikato Dairy Laboratory. He gave an entertaining lecture on "Our Surface-Active Life", in which he discussed aspects of surface-active agents and their uses in modern society.

aspects of the triglyceride structure of milkfat.

Mrs L. B. Collins (nee Stewart) has resigned from the Institute and has left for Port Moresby with her husband.

Professor W. E. Sandine from the University of Oregon is spending one year at the Institute on sabbatical leave. He is working on streptococcal bacteriophages.

Massey University

Professor B. W. Matthews, Professor of Physics and Research Fellow in the Institute of Molecular Biology, University of Oregon, spent a day in the Department of Chemistry, Biochemistry and Biophysics. He gave a talk entitled "Aspects of the Structure and Function of Thermolysin and T₄ Phage Lysozyme".

Other visitors to the department have included Professor P. B. Garland, Department of Biochemistry, University of Dundee and Dr R. Colton, Department of Inorganic Chemistry, University of Melbourne.

Professor G. N. Malcolm and Dr I. D. Watson attended the Symposium on the Chemistry and Physics of Liquid and Liquid Mixtures held in Canberra.

Dr R. R. Brooks has returned from leave spent at the University of New South Wales.

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

Professor E. Epstein from the Department of Soils and Plant Nutrition,

University of California, Davis, has been awarded a Fulbright Research Scholarship and as from July 1974 will be spending 12 months at the DSIR, Palmerston North on a joint collaboration with Applied Biochemistry Division and Grasslands Division. He will be working mainly with Dr J. Dunlop of Grasslands Division on the genetic control of mineral absorption and transport in plants.

Professor W. D. Loomis, a distinguished visitor from the Department of Biophysics and Biochemistry, Oregon State University, Corvallis, is on a National Research Fellowship at Applied Biochemistry Division, Palmerston North, studying plant phenolics in relation to horseradish peroxidase in collaboration with Drs J. W. Lyttleton and E. Wong.

Dr M. J. Boland left Applied Biochemistry Division, DSIR, Palmerston North at the end of May on study leave to work with Dr H. Gutfreund at the University of Bristol. He will be working on fast enzyme reactions.

Wellington

DSIR — Institute of Nuclear Sciences

Dr H. C. Sutton is overseas visiting various centres concerned with radiation chemistry studies, and will attend a conference on the western seaboard of the United States.

A new D/H VG-Micromass 602C has arrived and been installed.

A solid source VG-Micromass 30B has been ordered. This will be used, among other things, for study of strontium isotopes and geochronology.

A successful symposium on mass spectrometry was held in May at the Institute.

In June a party from the accelerator group visited the research campus around Massey to advertise their techniques in trace analysis and their ability to produce unusual shortlived tracers.

DSIR — Chemistry Division

In June Mr I. R. C. McDonald visited the U.S.A. as a member of a Government Housing Evaluation team. While there he visited a number of laboratories and some instrument manufacturers.

Mr B. J. Judd, B.Sc. (Hons) Sheffield, has joined the Chemical Engineering Section. Mr Judd has in fact been associated with the Section for a number of years as a representative of Carpentaria Exploration Company in the Joint Carpentaria-DSIR illumenite project.

Dr V. R. Gray, Ph.D. Cambridge, has commenced work in the Forensic Section. He has had considerable experience in the field of building and fire research.

Dr K. R. Markham left in August on a three month trip to visit phytochemical laboratories in U.S.A., England, France and Germany.

Dr T. D. R. Manning left in August

to spend fifteen months working in the field of organic photochemistry with Professor P. J. Kropp at the University of Chapel Hill, North Carolina.

Mr D. K. W. Smith of the Chemical Engineering Section leaves for Britain in September. He will be carrying out studies for his Ph.D. at the Mineral Technology Department of Imperial College, London.

Mr M. Hutchison of the Geochemistry Section has resigned, to leave for Canada where he will undertake a Ph.D. at the University of Toronto.

Dr I. M. Morice retired on 13 June. She has been associated with DSIR for many years, formerly with the now defunct Fats Laboratory and recently with the Organic Section of Chemistry Division. Dr Morice is well known for her work in elucidating the fatty acid constituents of seed oils. Dr Morice was farewelled at a staff function at which both Dr F. B. Shorland and Dr A. J. Ellis spoke of her work with the Department.

DSIR — Soil Bureau

Mr N. Wells is paying several visits to Singapore this year to advise the Singapore Government on the useful disposal of sewage sludge. While overseas he will also visit other cities with major sludge disposal problems and attend the International Society of Soil Science 10th Congress in Moscow in August.

Mr J. M. Bailey has left the Bureau and returned to the U.K.

Dr R. B. Miller will attend the International Society of Soil Science 10th Congress in Moscow in August.

Dr Ken Birrell retired from Soil Bureau in April after over 39 years in soil research. Dr Birrell has made many contributions in the fields of soil physics and soil chemistry including

the study of allophanic soils; his detailed knowledge will be missed at Soil Bureau.

**Victoria University of Wellington —
Chemistry Department**

Professor J. F. Duncan has returned

Canterbury

On May 20th the Branch held a Dinner Meeting to mark the retirement of Sir Malcolm Burns as Principal of Lincoln College. At the meeting Mr John Pollard announced that Sir Malcolm had been elected an Honorary Fellow of the Institute. Following the presentation Sir Malcolm addressed the meeting on the subject of "The Role of the Chemist in the Next Half Century".

Dr R. W. Carrell of the Clinical Biochemistry Department spoke to the branch on June 17th on the topic of "Haemoglobin".

Dr M. F. Barnes of the Biochemistry Department at Lincoln College addressed members of the Christchurch Biochemical Society on June 10th on the changes in pectin enzymes which occur in strawberries during ripening.

On July 8th Dr D. C. Reaney talked to the society on his recent proposals for a possible solution to the question of the origin of the genetic code.

During the University May vacation a Quantitative Biology Symposium was held at 11 a.m. Among the subjects presented were papers on haemoglobin, synthetic models for haemoglobin, radioimmunoassay techniques and a description of C^{13} nmr spectroscopy.

Otago

The May meeting was held in conjunction with the N.Z. Institution of Engineers. Mr J. W. Ridley (M.P., Taupo) gave an address on 'Energy Resources in New Zealand'.

A seminar on 'Technical Aspects of Pollution' was held in June. A panel comprising Mr D. Higgins (Kempthorne Prosser) and Mr T. Douglas (Health Department) chaired by Professor A. D. Campbell discussed legal, industrial and related matters concerning air pollution.

Chemistry Department

Drs D. Jones and D. Fenby attended and presented papers at the Royal Australian Institute of Chemistry 5th National Convention in Canberra on May 20-24th.

Professor E. Wenkert, E.D. Butcher Professor of Chemistry, Rice University, Houston, Texas, U.S.A., has arrived to take up the position of Mellor Visiting Professor for 1974. His research interests in organic chemistry

from Madrid after attending a Conference on "Anomalous Scattering".

Professor W. E. Harvey is attending a course in England in connection with the Department purchase of a Micro-mass Fragmentation Mass Spectrometer.

Christchurch Hospital

Mr Harvey Taylor, assistant analyst at the hospital, returned recently from overseas. He visited hospital laboratories in England investigating computer installations and automated equipment. In addition to attending a number of conferences, he visited Cambridge with support from the Canterbury Branch of the Royal Society as a consequence of his research interest in population genetics.

Mr D. Munster has taken up a research position in the Clinical Biochemistry Department to study blood lipid analysis.

Dr J. D. Evans has joined the Department of Obstetrics and Gynaecology at the Clinical School where he will study hormone analysis in blood.

The Clinical Biochemistry Department is setting up a series of vitamin assays to assist in a geriatric nutritional assessment survey being undertaken by Professor D. W. Beavan and Miss A. Ward.

Lincoln College

Mr G. Grant has joined the Department of Biochemistry as a Demonstrator.

University of Canterbury

Dr J. Coxon will visit Monash University from the end of July as an exchange lecturer for two months.

are wide but specifically cover ^{13}C NMR and synthesis of natural products. He has already given a number of lectures on these topics to the department.

Dr F. J. B. Aggett from Auckland University visited the department in early June and gave a seminar on 'Non-Flame Atomisation in Atomic Absorption Spectroscopy'.

Dr D. B. Hubbard has received a U.G.C. grant for the purchase of a spectrofluorometer.

Biochemistry Department

Professor P. Garland from Dundee University visited the department and gave seminars on 'Mechanisms of Oxidative Phosphorylation' and 'Modern Audio-Visual Teaching Techniques'.

Professor C. A. Thomas, a world authority on chromosome structure from Harvard University, visited recently and lectured on "endonucleases and eucaryotic DNA as a tool to understanding chromosome structure".

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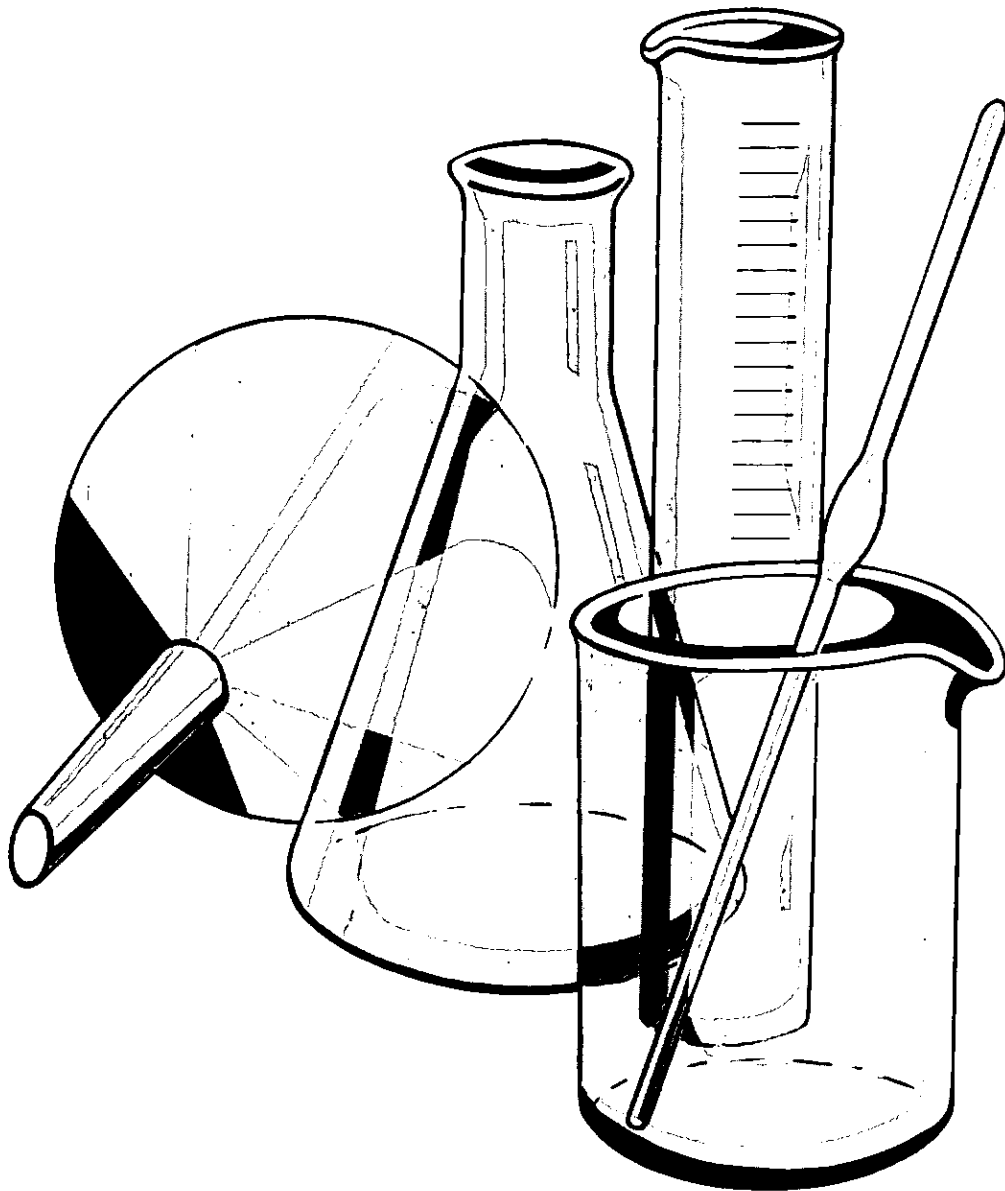


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