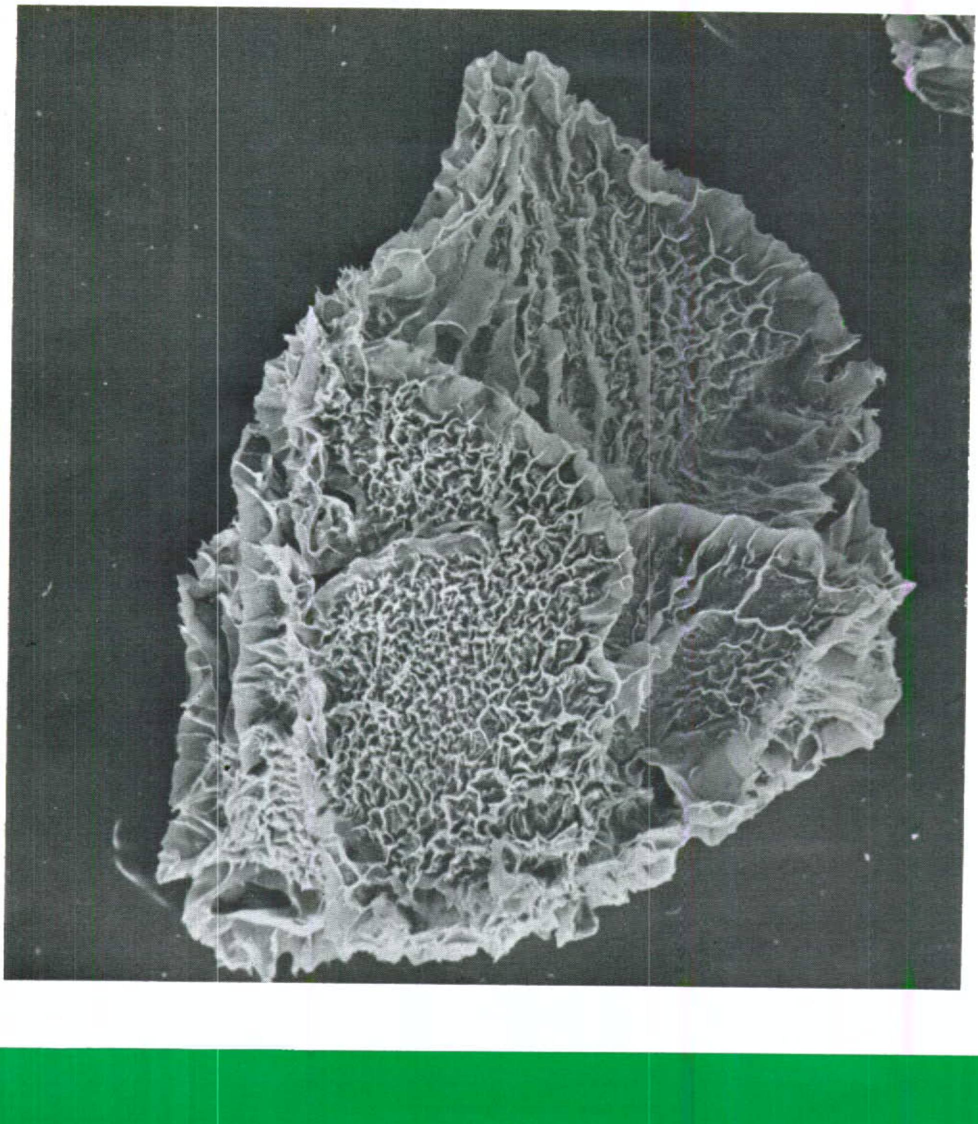
chemistry
in new zealand



President
and
Officers
1976-77

Ion Exchange
Celluloses

Horse Doping

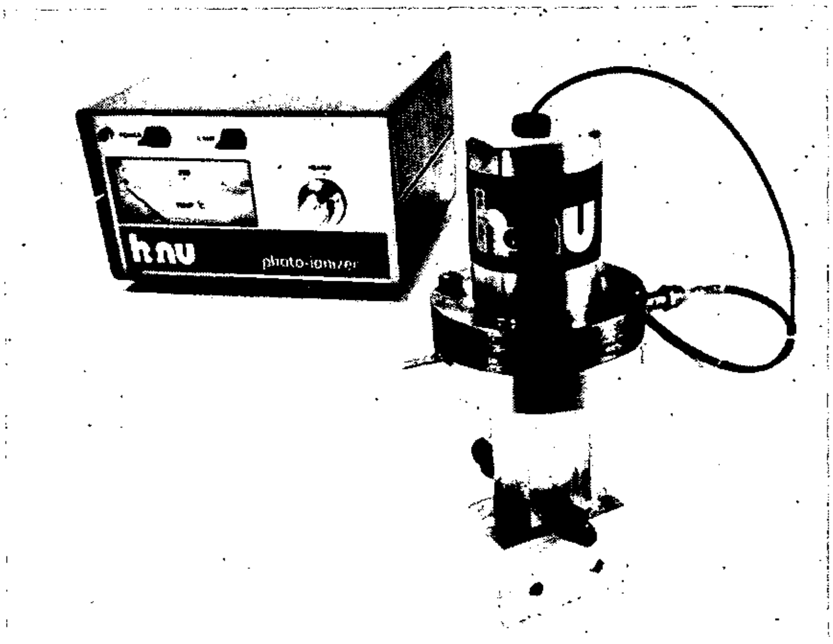
Toxic Wastes

TCDD

VOLUME 41
NUMBER 1
MARCH 1977

Journal of the New Zealand Institute of Chemistry

hnu systems inc.
chemical instrumentation



TO: New Product Editor
SUBJECT: Model PI51
Photoionization Detector
for Gas Chromatography

A unique design photoionization detector (PID) for gas chromatography has just been developed which provides 10 times to 50 times greater sensitivities than flame ionization detectors (FID's). The new photoionization detector employs a sealed ultraviolet lamp adjacent to an ionization detector and uses ultraviolet photon energy for ionization of the species. The new detector has a wide dynamic range ($>10^7$) and is extremely versatile, responding to most organics including aromatics, chlorinated hydrocarbons, amines, organic sulfurs, ketones, high molecular weight compounds such as pesticides, and some inorganics including hydrogen sulfide, hydrogen selenide, organometallics, ammonia, iodine and phosphine. The detector does not respond to several commonly used solvents such as methanol, or extraction solvents such as methylene chloride, dichloroethane, carbon tetrachloride or acetonitrile.

The principle of operation is termed photoionization since the absorption of ultraviolet light by a molecule leads to ionization via:

$$R + hv \rightarrow R^+ + e^-$$

where R^+ is the ionized species and h is a photon which has an energy $\geqq$ the ionization potential of the species.

The sensor consists of a sealed ultraviolet light source that emits photons which are energetic enough to ionize many trace species (particularly organics) but do not ionize components such as O_2, N_2, CO, CO_2, H_2O, or He. A chamber adjacent to the ultraviolet source contains a pair of electrodes. When a positive potential is applied to one electrode, the field created drives any ions formed by absorption of the UV light to the collector electrode where the current (proportional to concentration) is measured.

In addition to providing a state-of-the-art improvement in sensitivity, the detector has several other important characteristics. Since the photoionization technique is nondestructive, the sample can be run in series with a destructive or element selective detector. The detector sample can be recovered for further analysis and quantification by mass spectrometry or IR. The detector has been designed with a built in heater that allows operation from abient temperatures to 250°C. The fundamental simplicity of the detector also makes it easy to install and operate. There is only one gas (carrier) required for operation. The photoionization detector is useable on any gas chromatograph.

For further information, contact:

WILTONS


AnalaR
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chemistry in new zealand

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EDITOR
Dr L. K. Creamer
N.Z. Dairy Research Institute
Private Bag
Palmerston North

ADVERTISING MANAGER
R. Turner
P.O. Box 250 Wellington

DISTRIBUTION
D. J. Hogan
P.O. Box 1926 Christchurch

BRANCH EDITORS
Auckland
Dr K. R. Bedford
Chemistry Division
DSIR
Box 2224
Auckland

Waikato
Dr P. C. Molan
N.Z. Dairy Board
No. 4 R.D.
Hamilton

Manawatu
Dr G. R. Hedwig
Chemistry, Biochemistry and
Biophysics Department
Massey University

Wellington
Dr B. Halton
Chemistry Department
Victoria University of Wellington

Otago
S. D. Gray
Fletcher Industries Ltd
Box 973
Dunedin

ACTING GENERAL SECRETARY
G. J. Fletcher
Applied Research Office
Auckland University

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TWELVE YEARS OF EDITORSHIP
A Tribute to Miss Joan Mattingly

In 40 years there have been seven editors of the Institute's Journal – Keys, Parton, Brooker, Wallace, McGillivray, Clare, and Mattingley; and with 12 years in this office Joan Mattingley has carried the responsibility far longer than any of her predecessors. These have been years of considerable activity and development in the Institute, and hence, inevitably, in the Journal. Now as she hands over the editorial pencil to Dr Creamer the Institute pays tribute to Joan for her assiduous but unobtrusive work in producing some 70 issues regularly and at a high standard in style and content.

In the year before Joan took over the Journal it became apparent that publishing arrangements must be reorganised if issues were to appear regularly and on time – the writer recalls the anxiety whether August issues, containing Conference Abstracts and AGM matter, would reach members in time for the Conference. Hence the new editor almost immediately faced a change of printer. Then in 1966 Joan submitted to Council a comprehensive report on the status of the Journal with recommendations for a new format and features giving a better service to members. While production costs would be higher, the more attractive format was expected to increase advertising revenue. These recommendations were accepted and the more contemporary "standard size" journal started with Volume 31, 1967. The new look included the large double-column page and an individual cover for each issue with illustration related to the contents. At the same time the title was changed to *Chemistry in New Zealand* with the old form, *Journal of the New Zealand Institute of Chemistry,* as sub-title. In 1974 the page was further increased to its present size. Examination of the balance sheets indicates that in the six years after 1967 the net cost of the Journal to the Institute, as a proportion of total expenditure, averaged the same (24%) as in the six years before 1967. However over the last four years the percentage climbed steadily, to 35% in 1974-75. Finally, after further appraisal of the functions and activity of the Journal, the domestic purposes were allocated to a newsletter-style Bulletin and the Journal reduced to three issues per year.

These developments have been summarized in some detail in a tribute to the retiring Editor because they give some indication of the problems faced, the investigations needed, and the decisions necessary by the Editor during her stewardship.

The Editor of a journal serving an Institute covering such a wide field as "chemistry" must maintain a balance of articles published; between branches, and sub-branches, of the subject; between "pure" chemistry and a diversity of applications; between general and specialist approaches; and between universal chemistry and topics with mainly local relevance. The Journal is an archive for the history of chemists and chemistry in New Zealand. It is our spokesman to kindred bodies abroad and through the exchange system has been the means of building up a substantial library. A primary function, until recently, has been to maintain contact between a scattered membership and between Branches, keeping them informed on Institute affairs, the actions of Council, and developments affecting the profession. An editor's selection is often further complicated by a sometimes plethora and a sometimes dearth of suitable material. Joan Mattingley maintained a clear concept of the purposes of the Journal, held a good balance between the diverse interests of members, and kept a faith in the importance of the Journal to the Institute when others of more pragmatic mind have doubted it.

In addition to her control of the Journal, Joan has served the Institute well, as Wellington Branch Chairman, as Council Delegate, as a member of the Professional Status Committee, and as representative on the Member Bodies Committee of the Royal Society. Next to the Secretary and Registrar the Editor probably has more direct contact with a large section of the membership than any other officer, and although attendance at Council meetings is primarily as a reporter with no voice in decisions, unofficially, Joan's long acquaintance with Institute business was often valuable. All members of our Institute have good reason to be grateful to Joan Mattingley for her thorough devotion to the Editorship for so long, over a critical period in the Institute's growth.

From the new Editor, Dr L. K. Creamer, already familiar through his production of the *Bulletin,* we confidently anticipate the continuance of a high quality Journal.

– N.T.C.

President 1976-77

The new President of the Institute is Professor G. N. Malcolm, Professor of Physical Chemistry at Massey University.

Professor Malcolm graduated from Canterbury University with an M.Sc. degree with First Class Honours in Chemistry in 1953, and was appointed as a Junior Lecturer for 1954. He specialised in the study of electrolyte solution chemistry with Professor H. N. Parton. During 1954 he was awarded the 1851 Exhibition Science Research Scholarship for New Zealand, and proceeded to Manchester University to study the physical chemistry of polymer solutions for his Ph.D. degree. He was appointed to the staff of Manchester University Chemistry Department in 1956, and returned to New Zealand to a lectureship in physical chemistry at Otago University in 1957. He was awarded a Nuffield Fellowship in 1964 and spent a year at Imperial College in London studying the applications of the theory of branching processes to polymer network systems. He moved to his present position in 1969.

Professor Malcolm was elected to membership of the Institute of Chemistry in 1960 and to Fellowship in 1966. He served as Chairman of the Otago branch in 1968, as Dunedin Conference Secretary in 1965 and as Conference Chairman at Palmerston North in 1970.

Professor Malcolm is subject convenor for chemistry for the Universities Entrance Board and is a member of the Research Committee of the University Grants Committee.

John Packer gained his B.Sc. and M.Sc. at Canterbury University College and then joined the N.Z. Defence Science Corps working at University College, London, for his Ph.D., the Low Temperature Research Station, Cambridge and the Institute of Nuclear Sciences, Lower Hutt during the tenure of his commission. In 1962 he joined the staff of the Chemistry Department at the University of Auckland where he is now Senior Lecturer.

His main research interests lie in the field of radiation chemistry and the kinetics of free radical chain reactions. He spent 1969 at the University of Manchester furthering his work which was based on a Co-60 source using the technique of pulse radiolysis.

Dr Packer has also been active in student welfare and chemical education. He was warden of O'Rorke Hall for five years, is co-author of a guide-book on 6th and 7th form chemistry, co-author of the Education Department's handbook on SI Units in School Chemistry and is currently chairman of the Chemical Education Group of the Institute, his main activity in this latter capacity being working towards an NZIC publication on Chemical Processes in New Zealand.

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After 4 years war service with the R.A.F., Dr Lester studied for 3 years at Medway Technical College, England, from which Institution he passed the appropriate examination to become an Associate of the Royal Institute of Chemistry. After two years as a research chemist with Pest Control Ltd of Cambridge where he worked on herbicides and organophosphorus pesticides, Dr Lester turned to educational matters and taught successively at Queen Elizabeth Grammar School, Wimbourne, Widnes College for Further Education and Poole Technical College. He resigned his position as Head of Department of Science at latter college in 1966 in order to take up an appointment at the Technical Correspondence Institute in Wellington, and in 1967, he moved to Hamilton Teachers College. In 1969 he found it necessary to return to England and he took this as an opportunity to become a student again at Bristol University where he carried out research on trace metal analysis that led to the award of a Ph.D. degree. He returned to New Zealand in 1972 and is at present Head of Department of Science at Tuakau College.

Dr Lester was elected a Fellow of the Royal Institute of Chemistry in 1963 and a Fellow of the New Zealand Institute of Chemistry in 1966.

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Branch

Graeme Russell graduated B.Sc. (Hons) in chemistry from Canterbury in 1960 and went on to complete his Ph.D. in 1963. From there he joined the Plant Chemistry Division of DSIR where he studied the implication of plant glycolipids in the bloat syndrome of cattle. In 1965 he was awarded a Post-doctoral Fellowship from a U.S. National Institute of Health contract to work at the Division of Applied Chemistry, CSIRO, Melbourne, Australia on the isolation, identification and chemistry of anti-tumour active compounds from New Guinea plants. On his return to Applies Biochemistry Division in 1967 he continued his interests in naturally occurring compounds with biological activity, turning his attention to compounds affecting insect development in the native flora. This research resulted in the isolation of a number of ecdysones – insect moulting hormones, from native podocarps and led to the study of the activity of a number of related synthetic ecdysteroids. In 1972 he was awarded a Royal Society Commonwealth Fellowship to work under Professor A. W. Johnson at the Insect Chemistry and Physiology Unit, University of Sussex on ecdysone metabolism in the blowfly. After returning to New Zealand his current research is concerned with the chemistry of plant-insect interactions, which attempts to define an ecological role for many natural compounds of high insect activity. Of particular importance is the work on the isolation of grass-grub feeding deterrents from pasture plants that will help define and develop insect resistant pastures.

Michael Kingsford is a graduate from the University of Auckland where he studied plant anthroquinones for a Masters Degree and built and applied a gas chromatograph to essential oils for a doctorate. In 1961 he moved to Petone to become the Foundation Tutor in Pharmaceutical Chemistry, at the N.Z. School of Pharmacy. Five years later he joined the Chemistry Division of D.S.I.R. and shortly afterwards became leader of its food and drug section where he was responsible for supervising quality investigations of food and waters and initiating studies of drug quality. Since that time, the section has grown and been divided into three parts and he has remained with the pharmaceuticals section.

Current research interests include pharmacokinetics and bioavailability of drugs and their decomposition chemistry. He is a member of the Drug Assessment Advisory Committee of the Health Department and of committees of the Testing Laboratory Registration Council, the Standards Association and the Australasian Society of Clinical and Experimental Pharmacologists.

His extramural interests include singing and model railways and has long associations with Church music.

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Officers 1976-77

Glen Metcalf is a Career Fellow of the Medical Research Council of New Zealand who works in the Medical Unit at Princess Margaret Hospital, Christchurch. She gained her M.Sc. in Chemistry at Wellington in 1948, then worked briefly as a chemist in the Soil Bureau before succumbing to a common hazard of the female sex and retiring for 13 years. In 1961 she joined the staff of the Medical Unit under Dr D. W. Beaven and was involved in the introduction of steroid hormone measurements as a service for the endocrinologists at the hospital. Progress in this field led to a Ph.D. in Medicine from the University of Otago in 1972, and the award of a Career Fellowship the following year.

Additional interests are Walter Metcalf, hill walking and music making.

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Peter Grant joined the Dunedin Branch of Dominion Laboratory (now Chemistry Division) as a cadet in 1949 and at the same time attended the University of Otago, graduating B.Sc. in 1951 and M.Sc. in 1953. In 1955 he took up a N.Z. University Travelling Scholarship in Science at Cambridge University where, working with Professor A. W. Johnson, he graduated Ph.D. in 1957. After a short post-doctoral period at the University of Nottingham he rejoined the organic chemistry section of Chemistry Division in Wellington. In 1962 he took up an appointment in the chemistry department of the University of Otago where he is now Associate Professor.

Dr Grant's research interests are in the field of natural products, originally in structure determination but more recently in synthesis directed towards the utilisation of N.Z. natural products. In 1965 he spent sabbatical leave with Professor Franz Sondheimer at Cambridge University. He was Secretary to the 1969 N.Z.I.C. Conference and more recently was Secretary to the 10th I.U.P.A.C. Symposium on the Chemistry of Natural Products.

Otago Branch Officers

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CELLULOSE ION EXCHANGERS — NEW ZEALAND MADE

G. S. McNAUGHTON
Physics and Engineering Laboratory, DSIR, Lower Hutt

INTRODUCTION

Late in 1967 a group of scientists from the Physics and Engineering Laboratory of DSIR (PEL) toured the Gear Meat Company's Petone works as part of a programme to find ways for DSIR scientists to help the Meat Industry. The party included Dr Roy Grant, a visiting research Fellow, who suggested that the ion exchange resins that he had been developing before coming to New Zealand might recover much of the potentially valuable protein which was going down the drains. In this way a useful by-product might be recovered at the same time as pollution was being reduced. From this beginning developments took place which have resulted in a small New Zealand Company manufacturing a modern ion exchange resin which competes with the products from such giants as Pharmacia Fine Chemicals, Whatmans and the Viscose Group. The purpose of this article is to record the history of these developments which are of general interest, and to discuss briefly present and future applications of these resins.

CHRONOLOGICAL DEVELOPMENTS

Since Grant's initial suggestion several groups within New Zealand have become involved with the manufacture and the application of the resin. Our laboratory (PEL) began work in 1968 and soon reported on the possibility of using the resin in the treatment of meatworks effluent [4]. Tasman Vaccine Laboratory (TVL) acquired rights to Grant's New Zealand patent for making an ion exchange material based on viscose [10] and also rights to the overseas promotion of a PEL patent (administered by the Inventions Development Authority, IDA) in which the resin is used for the treatment of proteinaceous wastes [11]. The meatworks application was sufficiently promising to take to a pilot plant scale so the next step was the formation of a Meatworks Treatment Consortium in 1969 to finance a plant at the Gear Meat Company. Besides TVL, PEL and IDA, six Meat Companies (Borthwicks, Hellabys, the Canterbury Frozen Meat Co., the Southland Frozen Meat Co., the N.Z. Refrigerating Co. and the Gear Meat Co.) took part in the development. This pilot plant operated in 1971 and 1972.

Meanwhile Dalgety, who backed Tasman Vaccine Laboratory in New Zealand, were supporting further resin development and effluent treatment work by Dr Roy Grant in the U.K. In late 1973 TVL formed a separate division called Ecotech Systems, which operated from Wingate, Lower Hutt and in 1974 a U.K. subsidiary was set up in Poole, Dorset.

In order that resin manufacture and development could be more adequately exploited in New Zealand, TVL had from the start encouraged the involvement of University groups to give a more solid scientific foundation for future expansion. Those who embarked on resin research programmes about 1971 were members of the staffs of the Dept. of Biochemistry at Massey University, and the Chemical Engineering Dept. at Canterbury University. Somewhat later the Cawthron Institute, and the N.Z. Co-op. Rennet Co. Ltd. at Eltham developed processes which used the resin.

Eventually in 1975 Dalgety closed down Ecotech Systems (U.K.) Ltd., and in the following year its N.Z. parent also. Fortunately, most of the expertise in this Fortunately, most of the expertise in this field has been retained and several of the N.Z. staff are now employed by a Wellington firm of Consulting Engineers (Morrison, Cooper and Partners) and are still concerned with effluent treatment. With TVL no longer involved, the newly re-organised Development Finance Corporation (DFC) now owns the patents and the right to their development. The DFC is currently investigating the licensing of a new Company, appropriately called the Phoenix Resin Co. Ltd., to ensure the continuing supply of resin in New Zealand.

GRAEME McNAUGHTON graduated M.Sc. from Otago University in 1952 and Ph.D. from Leeds in 1956 as a member of the Defence Science Corps. Later he joined what is now the Institute of Nuclear Sciences and worked on radioactive fallout and radiation chemistry. After two years working on a U.K. Atomic Energy Agency Fellowship he returned for further work at I.N.S. Transferring in 1970 to P.E.L. to work on plant growth he soon became involved with work on the Grant resin and is at present in the Biophysics Division of P.E.L.

RESIN MANUFACTURE

In July 1968 Grant applied for a N.Z. patent for an ion exchange material made from regenerated cellulose. Resin manufacture was further developed at PEL and in one approach to the reduction of costs the production of resins based on sawdust rather than on viscose was investigated, but this investigation was not taken very far.

Scanning electron micrograph of a DEAE ion-exchange cellulose made, after milling, from viscose obtained from the Viscose Development Corporation. The laminar structure of the flake viscose is preserved in exchanger. Magnification 33x.

Resin manufacture was later taken over by TVL assisted from 1971 by Dr John Ayers. TVL built a pilot plant to make 20 kg batches of resin and later this was stepped up by Ecotech Systems at Wingate where in 1975 production could be carried out at the rate of 1 tonne/week if required.

Chromatographic grade resin, described in TVL's brochure [14] was marketed under the name PROTION in two forms, DEAE and CM resins, and from two size ranges of dry sieved viscose (50-100μm and 250-420 μm). Many other types have been made experimentally. Industrial grades were marketed as GRANTEX resins and were tailor-made for specific applications. Besides the most common DEAE form it is possible to produce resin with CM, sulphur-propyl or many other groups on the cellulose backbone.

Scanning electron micrograph of a DEAE ion-exchange cellulose made, after milling, from milled viscose rayon monofilaments of large dernier obtained from Courtaulds. Magnifucation 33x.

COVER PHOTO
Electron micrograph of 'Protion' DEAE ion-exchange cellulose modified at Massey University to give a greater capacity for larger proteins such as catalase. This exchanger was used in the continuous fluidised bed extraction apparatus. Magnification 200x.

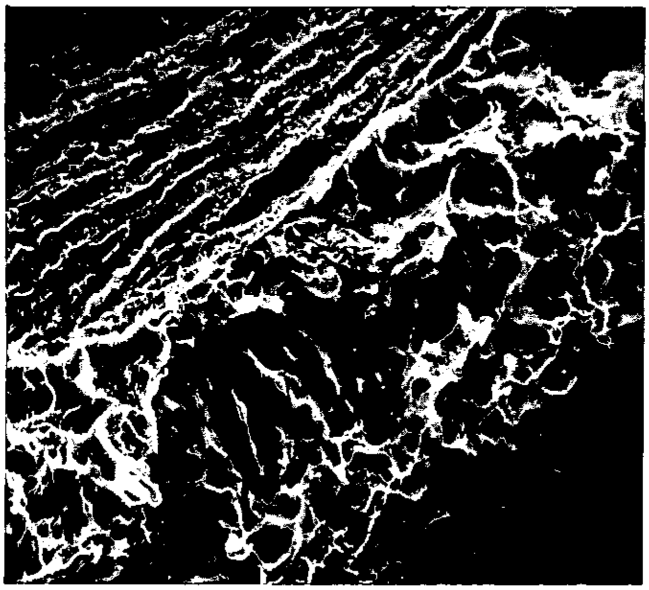
SPECIAL RESIN PROPERTIES

PROTION is an ion exchange medium for the adsorption of certain types of macromolecules, and we should consider how it compares with alternative methods. Macromolecule separations may, of course, be carried out by widely differing techniques such as fractional precipitation and ultra-filtration. They may be carried out on a wide range of sorbents which includes porous inorganic spheroids [9] as well as controlled pore-size gels and cellulose-based ion exchangers. The PROTION brochure [14] claims that the product exhibits the same order of capacity for macromolecules as fibrous cellulose ion exchangers, while possessing the excellent hydraulic properties and physical stability associated with resins commonly used for the separation of small ions. High flow rates can be used with gravity feed, while the build-up of back-pressure is small. Suspended solids trapped in the resin bed can be removed by back-washing.

Scanning electron micrograph of a DEAE ion-exchange cellulose made, after milling, from milled viscose rayon monofilaments of large dernier obtained from the Asaki Company in Japan. The rough and smoother fracture surfaces are similar to those across and along the grain in wood samples. The preferred alignment in the viscose may be due to the manufacturing extrusion process. Magnification 175x.

In our experience it is certainly possible to use the resin in continuous fluidised bed equipment which is an even more demanding test than its use in agitated beds as suggested in a Cawthron Institute patent for albumin preparation [12]. Besides Dr Grant in the U.K., the Massey University Biochemistry Dept. group have probably had the most experience in comparing the overall performance of columns of PROTION with columns of other protein sorbents.

It is clear that the best solution to any separation problem can be found only by experimentation with the



Grain structure of an ion-exchanger made from Asaki viscose monofilament at 850x magnification.

actual material to be treated, since pH, molecular weight, liquid volume, presence of suspended solids and other parameters, can all be critical. Although it is not possible to generalise too far in comparing resin properties, PROTION does seem able to withstand mechanical handling better than early large-pore and ion exchange gels, although the newer cellulose and Sephadex cross-linked gels should be more rugged. These seem to be available so far only as small particles, 40-160 μm diameter when hydrated.

There are many ways in which PROTION could be developed—for instance, the original patent [10] suggests that it could be produced as filaments, flakes, sponge, beads or in other forms. If the resin is to be considered as a potential export further research and development seems essential to obtain much more information about its properties. However, its choice by the N.Z. Rennet Company for its enzyme process demonstrates that even in its present form it can compete successfully with its overseas rivals.

APPLICATIONS OF PROTION

(1) Effluent Treatment

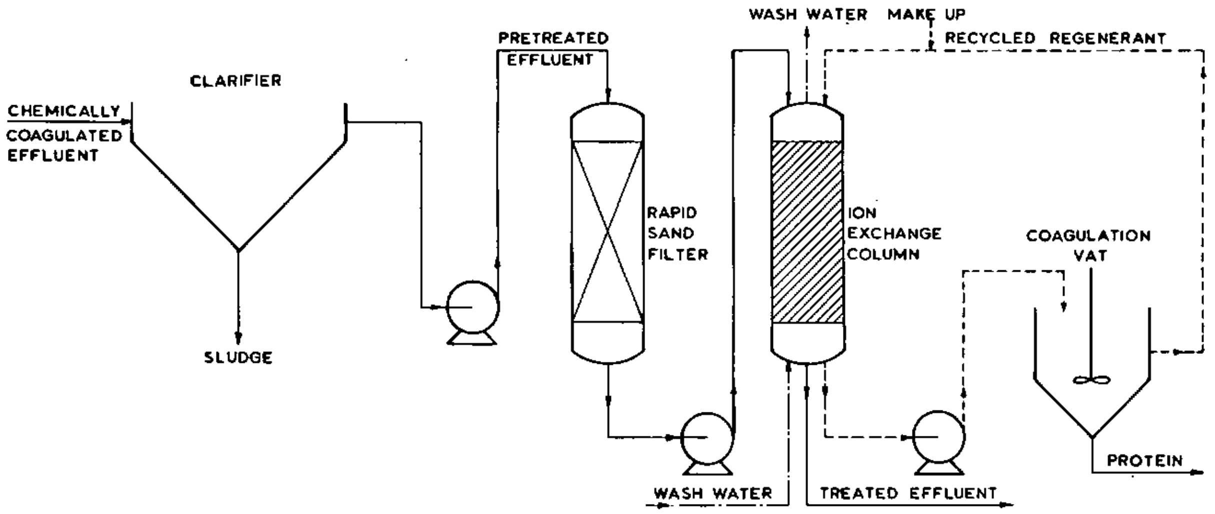
The most extensive investigations have been the meatworks studies begun at PEL in 1968. In early experiments the potential of the resin for treating raw effluent was studied but subsequently, following a suggestion from Mr Denmead of the Meat Industry Research Institute, a preliminary chemical flocculation stage was investigated.

This removed much of the soluble protein and suspended solids and it became possible to use finer grade resins and obtain water of a more nearly re-usable quality from the resin stage. Resin life tests were carried out in 1971 and 1972 at the Petone Meatworks using treated slaughterhouse effluent from the Consortium's 3000 litre pilot plant. Several different resin types were subject to life tests in five 4 litre columns. Some aspects of this work have been reported [6, 8]. It was concluded that the resin process found a niche between a preliminary physico-chemical stage and a final treatment to produce potable water. In a meatworks output from the resin stage could be used for some non-potable applications such as skin wash or in the fellmongery.

When the Consortium was wound up in 1973, TVL and later Ecotech Systems continued to work on a complete treatment system. This was demonstrated on a pilot plant scale at the Aotearoa Meatworks, Cambridge, in July 1974. Although most of the emphasis was on the preliminary treatment there was also a following resin stage. Fig. 1 is a sketch of the treatment process. In England use of the resin for gelatine removal from meatworks wastes and for the treatment of chicken processing wastes was being considered, and as St. Ives a full scale chemical pre-treatment plant for the latter purpose was installed in 1975. A pilot plant resin stage was scheduled for later operation [13].

Experience indicates that the conditions most favourable for use of the resin in effluent treatment are when:—

(i) bulk protein and suspended matter are removed by a preliminary process,



Schematic diagram of pilot-scale plant for protein removal from meat works effluent. Demonstrated at Aotearoa Meat Works.

(ii) the resulting waste stream is predominantly protein since other organics may not be adsorbed,

(iii) the object of the treatment is either
  - re-use of water in areas where water costs are high, or else
  - to reduce pollution to conform with local or national regulations.

At present, the wastes that seem most likely to be treated by PROTION resin are those from meatworks or from fish processing. However, further progress with resin treatment processes is unlikely until these industries have preliminary treatment processes installed and working.

(2) Edible Protein Extraction

When the protein recovered from wastes is used for fertiliser or for animal consumption, flocculation processes are generally cheaper and preferable to ion exchange processes. However, when hygiene and other conditions allow the protein to be used for human consumption, or if the recovered product can find a clinical or laboratory use, then the increased value may allow the use of ion exchange extraction methods. As one example, the patent for 'improvements in or relating to the preparation of albumin' granted to the Cawthron Institute [12] describes a preparation of albumin from blood or blood plasma. In this method the blood proteins are removed from the plasma, a preferred resin being PROTION.

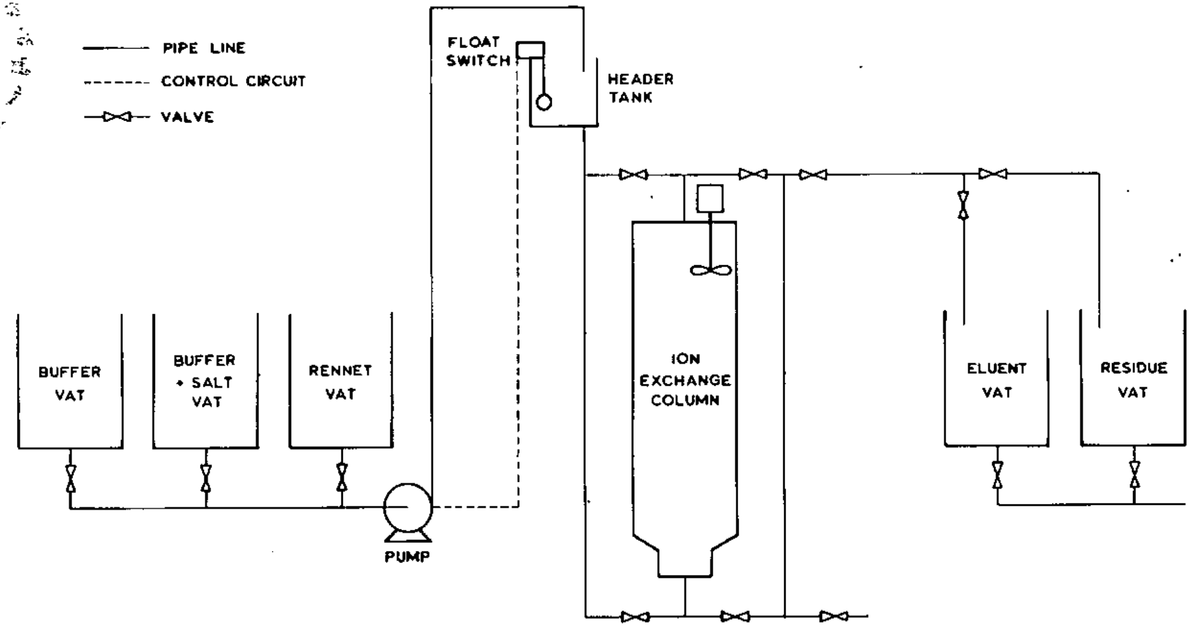
(3) Extraction of Fine Chemicals

This is probably the most straightforward application of PROTION and already at least two processes have been used commercially. Tasman Vaccine Laboratory used the resin for separating toxins for veterinary anaerobe vaccine production and improved potencies of vaccines were obtained. In particular, the E toxin of *Clostridium welchii* Type D was purified; the contaminating proteins were adsorbed on the resin while the toxin was not. The other successful application has been by the N.Z. Co-op. Rennet Company Ltd., Eltham, based on work done by Dr Neil Clarke at the Food Technology Dept. of Massey University. Clarke has described the use of PROTION, which adsorbs rennet enzymes from rennet extract while mucoproteins, which cause cloudiness in the rennet preparation, remain unadsorbed [1-3]. A sketch of the process equipment is shown in Fig. 2. Rennet purified in this way is claimed to be the highest commercial quality rennet available anywhere in the world.

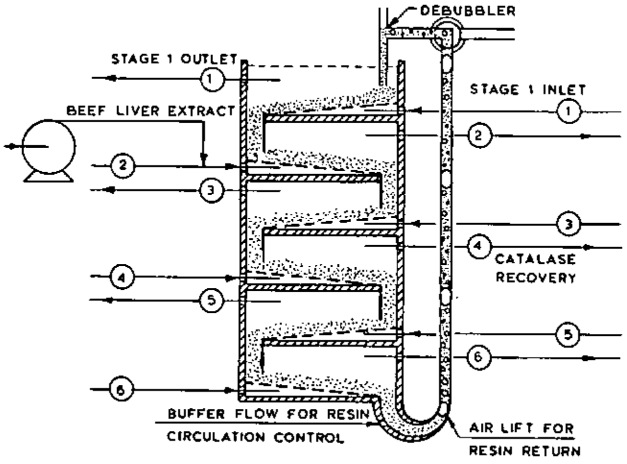
A considerable effort has been expended by the Massey University Biochemistry Dept. to evaluate and use PROTION resins for the purification of biochemicals, particularly enzymes. With patents pending, publication of this work has been delayed, but it seems that in New Zealand it is marketing problems rather than technological ones which may inhibit further developments along these lines.

(4) Miscellaneous Investigations

One of the main advantages of PROTION over early cellulose-based and porous gel protein sorbents was the possibility of using it in fluidised beds without significant damage to the resin. In order to exploit this advantage, and also because fine suspended solids had caused column blockage of downflow columns in the resin life tests and thus emphasised the potential of fluidised bed techniques, it was decided to work on a fluidised bed system at PEL. Since fluidised beds can be readily adapted to continuous processing, it was decided to develop a continuous process for the extraction of enzymes from protein broths, and to work with a model system – the extraction of catalase from a beef liver extract. A 50% catalase recovery of a product in which the specific activity of the enzyme had



Schematic diagram of a commercial ion-exchange plant for rennet purification. Redrawn, with permission from reference 2.



Sketch of bench-scale continuous ion-exchange column for preliminary enzyme extraction. Resin is circulated down the column which consists of 6 stages – from the top: 1, wash; 2, sorption; 3, wash; 4, enzyme desorption; 5, regeneration; 6, wash. Resin is returned to the top of the column by an air-lift. Resin on the gauze tray at each stage is fluidized by a pumped buffer/salt inlet flow, the hydraulic balance at each stage being maintained by a pumped outlet flow.

been increased by a factor of 3-4 in a bench-top scale apparatus was achieved [7]. There are still a number of technical problems to be solved, but further work has been delayed until there is a need to apply the technique to a real, rather than a model, system. A sketch of the experimental column is given in Fig. 3.

The Chemical Engineering Dept. at Canterbury University have for several years been studying sorption rates and equilibria as well as the physical properties of fixed and fluidised beds and their relation to equipment design. This work, which has largely been with serum albumin, has been described in several B.E. (Chem.) project reports. Graham and Gilmour [5] have fitted this data to a composite 'film diffusion' and 'particle diffusion' model. Current work is directed towards predicting breakthrough curves for column operation from batch equilibration experiments.

A number of potential applications considered by Ecotech Systems included decoloration of raw sugar solutions, removal of humic acids from power station water supplies, removal of organics from distillery condensates and, in a non-aqueous system, the removal of fatty acids from palm oil. At Massey University work continues on the development of specialised resins,

CONCLUSIONS

PROTION is an ion exchanger which has been manufactured and promoted in New Zealand and used commercially for the production of at least two biochemicals. Although less is generally known about its properties than about those of overseas-made alternatives, its special features are its ability to be used in fluidised beds and stirred tank reactors and the good flow rates available when it is used in columns. It can be produced in a wide variety of forms and may be used for protein purification, effluent and impurity removal. There are several research groups in New Zealand which have had experience with PROTION and could provide useful back-up for any licensed manufacturer.

By tracing some of the historical background to the development of PROTION in New Zealand and describing some of its possible uses, I hope to have helped make PROTION more widely known and promote further this interesting innovation in New Zealand industry.

ACKNOWLEDGEMENTS

The author is grateful to the groups mentioned in this paper for their assistance with preparing the text.

All the electron micrographs shown, including the cover picture, were supplied by the Electron Microscopy group at PEL.

REFERENCES

1 Clarke, N. H. (1974), Perspectives in Protein Chemistry, Proc. Symp. by N.Z. Inst. Chem. (Manawatu Branch), N.Z. Biochem. Soc., Massey University, 36

2 Clarke, N. H. (1976), N.Z.I.E. Proc. Technical Groups Vo. 2, Issue 1, 27

3 Clarke, N. H. (1976), N.Z. J. Dairy Sci. & Tech., 11, A52

4 DSIR Information Service (1968), Science and Industry, Vol. 18 Development in Biotechnology, Massey University, 6

5 Graham, E.E. and Gilmour, I. A. (1973), Proc. Symp. Process

6 Grant, R. A. (1974), Process Biochemistry Feb./March, 11

7 McNaughton, G. S. Robins, J. C. and Zwaaneveld, C. H. (1976)
(a) Physics & Eng. Lab. Report No. 530
(b) 10th Int. I.U.P.A.C. Symp. Chem. of Natural Products, Dunedin, N.Z. Paper F1

8 McNaughton, G. S. and Wakelin, W. S. (1973), Proc. Pollution Res. Conf. Wairakei N.Z. June 1973, DSIR Information Series No. 97, 245

9 Miles, B. J. and Thomson, A. R. (1974), Process Biochemistry, May

10 N.Z. Patent 153 128; U.K. Patent 1 226 448; U.S. Patent 3 537 227

11 N.Z. Patent 153 129

12 N.Z. Patent 171 343

13 Processing (October 1975), 7

14 Tasman Vaccine Laboratory, Whakatiki St, Upper Hutt (1972), PROTION Information Bulletin

ACTS, CHEMISTS AND UNIONS

Members of the New Zealand Institute must meet vigorous professional standards, they must agree to abide by the Institute's Ethics and Rules. All this notwithstanding, the Institute has no legal monopoly of the abbreviation M.N.Z.I.C. and anyone who wishes may call himself a chemist, anyone who wishes may practise the profession of chemistry.

Some professions and trades do have standards and practises which are prescribed by statute. Various Acts of Parliament set forth the requirements for practitioner registration; they provide for legal action against persons who falsely represent themselves to be registered; they define activities which may only be performed by persons registered under the Act. Only a registered drainlayer may open drains, only a registered medical practitioner may open people.

Rightly or wrongly, some consider that legally proscribed professions enjoy a higher status than those which have no legal obligations. It has been suggested that this form of esteem by lay persons has deeper, more subtle origins. Lawyers, dentists and medical practitioners all provide an immediate personal service; their clients are in peril of ruin, pain or death if the services are not forthcoming. Few chemists have such close relations with the public, few project such an aura of personal power. Even when the fate of an individual hangs upon a chemical determination such as blood alcohol, the analyst is closeted deep in the anonymity of the civil service.

In some Commonwealth countries certain professional organisations have been granted Royal Charters. Only members of these organisations may style themselves "chartered" and the term is only of significance in a country which legally recognises the charter. John Smith, a chartered dentist, may sound more impressive than John Smith, a member of the New Zealand Institute of Chemistry; certainly it carries the implication that the qualification has Royal approval.

In practice, the charters are conferred by the Privy Council after a rigorous examination of the qualifying body's standards and rules. This is a mixed blessing because a chartered institution must seek Privy Council approval whenever it wishes to alter any rule.

To apply for a Royal Charter an organisation must have the support of the government of the country concerned. It is for this reason that neither the New Zealand Institute of Chemistry nor the Institution of Engineers has ever got beyond the preliminary consideration of a Royal Charter. Successive Governments have declined to support an application. It is believed that the prime reason is a refusal to permit a New Zealand organisation to become subject to control by the Privy Council.

It seems improbable that the Institute could gain the right to style its members chartered chemists.

In this context it should be noted that N.Z. chartered accountants are not chartered at all; they have legal sanction to use the word "chartered" in lieu of "registered". No other registered body in New Zealand has succeeded in so warping the accepted use of the word "chartered".

In New Zealand the various registration Acts confine certain practices to approved persons. This brings greater legal status than a Royal Charter since there is nothing so exclusive as being one of a band who may do things that others may not. Whatever the trade or profession, registration has a common denominator in the protection of the public from malpractice, be it physical, fiscal or moral.

Registration was one of the original aims of the embryo Institute, but it was not pursued. Today it is hard to make a case for seeking to protect the public from the malpractice of persons calling themselves chemists. With few exceptions chemists are employed by others, and generally the prime responsibility is carried by the employer. Even where malpractice could have dire consequences, the chemist in New Zealand is overseen by licensing and inspecting agencies acting under various Acts such as Food and Drugs, Dangerous Goods, Health. A prudent employer would ensure that his chemical employees were properly qualified, but an Institute qualification is not a legal prerequisite for any chemical post that I know of in New Zealand.

The legal status of the professional engineer in New Zealand provides interesting parallels and contrasts. Like the chemist, any person may call himself an engineer and paractice engineering. Like the Institute, the Institution of Engineers has no exclusive right to the abbreviation M.N.Z.I.E. There is however an Engineers Registration Act administered by the Engineers Registration Board. The Board has no legal connection with the Institution but it accepts for registration the standard of experience and education currently required by the N.Z.I.E. for admission to corporate membership. Because of this common standard most young engineers are able to become registered as soon as they have qualified for admission to corporate membership of the N.Z.I.E. Because of this common standard there is often a misconception that the N.Z.I.E. is a registering body and that all engineers have to be registered.

The close association has sometimes led to the suggestion that the N.Z.I.E. should take over the administration of the Registration Act by becoming incorporated by statute. This would give legal right to the abbreviation M.N.Z.I.E. but it could well lead to a loss of autonomy. Rules would become subject to the Parliamentary law draftsmen, outside organisations who have an interest in registered engineers would have a claim to be represented on the Council. For these and other reasons the N.Z.I.E. has been strongly advised not to seek statutory protection of its status.

If for any reason members of the Institute felt that it was desirable to register chemists and a convincing case could be put to Parliament, it would seem undesirable to seek Institute administration of the appropriate Registration Act.

The main proscription of the Engineers Registration Act is a requirement that local bodies spending more than $70,000 a year on engineering works must employ a registered engineer as supervisor. There are some other activities which require attestation by a registered engineer but even these combined needs involve relatively few registered persons. The chief reason young graduates seek registration is the fact that long ago both government and local bodies agreed that above certain salary levels they would employ only registered engineers.

Even if a case could be made for registering chemists in the public interest, I cannot see government departments and the research associations agreeing to salary bars for all unregistered chemists any more than they have required corporate membership of the Institute for upper salary posts.

Without financial or administrative recognition registration for a chemist would not hold much interest since the numbers that would be directly responsible for public safety would be very few indeed.

Late last year the right to practise and the salary bar took on new importance. During the last Labour administration many engineers became alarmed at the growing pressures for compulsory unionism for employed persons, professional or otherwise. To avoid being absorbed into non-professional trade unions there was serious discussion about the formation of an industrial union of professional engineers. This concern receded with the return of a National government. As a precaution, both the N.Z.I.E. and the N.Z.I.C. requested the new Minister of Labour to consider the case of their professional members in the event of any legislation being introduced for compulsory unionism. The subsequent events are detailed in the accompanying articles.

As things now stand, the proposed Bill allows for specific groups of persons to be exempted from union membership by Order-in-Council. At present the Minister's rationale for exemption is membership of a self-disciplining society which has the power in certain circumstances to deprive any member of his livelihood.

Both the N.Z.I.E. and the N.Z.I.C. meet the self-disciplinary requirement but not the power to deprive of livelihood. Because most N.Z.I.E. members happen to be registered engineers, the rationale is of less concern to the N.Z.I.E. From the beginning registered engineers were an exempted group.

The Council has yet to gauge the extent to which industrial chemists are concerned about the impending legislation on compulsory unionism. Much as I did in my address to the Branches, this article has attempted to fill in the background to registration and the current developments on unionism.

John Pollard

INDUSTRIAL RELATIONS AMENDMENT (No. 3)

17. Miscellaneous exemptions — The principal Act is hereby amended by inserting, after section 112, the following section:—

"112A. (1) Notwithstanding anything in this Act or in any unqualified preference provision within the meaning of section 98 of this Act, no person shall be obliged for the purposes of any employment in respect of which an award or collective agreement is in force to become or remain a member of any industrial union if—

"(a) His earnings by way of commission in that employment amount, over any year of employment or proposed employment, to more than one half of his earnings in that employment; or

"(b) He is, and his duties in that employment require him to be,—

"(i) The holder of a practising certificate under the Law Practitioners Act 1955:

(ii) Registered or conditionally registered as a medical practitioner under the Medical Practitioners Act 1968:

"(iii) The holder of a provisional certificate issued under section 32 of the Medical Practitioners Act 1968:

"(iv) The holder of a certificate of temporary registration issued under section 33 of the Medical Practitioners Act 1968:

"(v) A chartered accountant:

"(vi) Registered as an engineer under the Engineers Registration Act 1924:

"(vii) Registered as a valuer under the Valuers Act 1948:

"(viii) Registered as a veterinary surgeon under the Veterinary Surgeons Act 1956:

"(ix) A registered surveyor within the meaning of the Surveyors Act 1966:

"(x) Registered as an optician under the Opticians Act 1928:

"(xi) Registered as an architect under the Architects Act 1963:

"(xii) A registered dentist within the meaning of the Dental Act 1963."

INDUSTRIAL CHEMISTS AND THE INDUSTRIAL RELATIONS AMENDMENT (No. 3) BILL 1976

On October 1st 1976 Government introduced into Parliament the Industrial Relations Amendment (No. 3) Bill which dealt mainly with the controversial matters of strike penalties, non-political strikes and ballots on compulsory union membership. These were of no direct concern to Institute members. But Clause 17 of the Bill, which is set out below, dealt with exemptions from union membership for certain classes of professional people. Presumably these were persons whose relationship with their employers involved a high degree of responsibility and judgement, and for whom there could be conflict of interest if they were obliged to follow the dictates of a union in dealing with their employer.

There was no mention of industrial chemists in this clause, in spite of the fact that many major industries in New Zealand employ chemists in key positions. For this reason a submission was made to the Labour Select Committee which considered this Bill, requesting that the list of persons to be exempted from compulsory union membership should be extended to include "an industrial chemist who is a Member or a Fellow of the New Zealand Institute of Chemistry Inc." The full text of the submission is as follows:

To the Chairman and Members of *14 October 1976*
The Labour Committee:

INTRODUCTION – THE INSTITUTE

1.1 This submission is presented by the New Zealand Institute of Chemistry Inc., representing over 1300 members. The Institute is a professional body whose objects include the promotion and protection of professional standards in the practice of chemistry. (See Appendix I).

1.2 The requirements for admission to the Institute as members or fellows are stringent, being based upon both high standards of academic qualifications and professional experience. (See Appendix II).

1.3 The Institute has also laid down in its rules a detailed code of ethics which are designed to ensure that "Every member of the New Zealand Institute of Chemistry is under an obligation to advance the science and art of chemistry, to guard and uphold its high standard of honour, and to conform to the principles of professional conduct." (See Appendix III). If any member fails to comply with the Code of Ethics, the rules of the Institute provide for disciplinary action to be taken by the Institute against the member concerned. (See Appendix IV).

1.4 The Institute operates as a professional regulatory body in much the same manner as other professional organisations, such as the New Zealand Institute of Engineers.

1.5 Approximately one half of the Institute's membership are employed as Industrial Chemists in a wide variety of industries, such as the pulp and paper industry, the freezing industry, wool and textile industries, food processing industry, fertiliser industry, building materials industry and many others. Industrial Chemists are employed at various levels within these industries from work on the shop floor in their early years of employment, through to positions of considerable professional and managerial responsibility. It is on behalf of these members of the Institute that it is presenting this submission.

THE SUBMISSION ON CLAUSE 17–MISCELLANEOUS EXEMPTIONS

2.1 The Institute's submission relates to clause 17 of the Bill, which provides that "... no person shall be obliged for the purposes of any employment in respect of which an award or collective agreement is in force to become or remain a member of any industrial union if ..." they are members of the classes of person specified in section 112A (1) (b).

2.2 It is the submission of the Institute that an addition should be made to section 112A (1) (b) in the following terms:

> *"(xiii) An industrial chemist who is a member or fellow of the New Zealand Institute of Chemistry Inc."*

This submission is based upon the following grounds:

2.3 (a) Industrial chemists who are members or fellows of the New Zealand Institute of Chemistry are a similar class of professional persons already specified in clause 17 of the Bill. Although registration of industrial chemists is not required in exactly the same manner as many groups referred to in clause 17, the Institute does note that the class of chartered accountants does not require registration under an Act of Parliament specified in the clause. The Institute also wishes to draw the Commitee's attention to the fact that industrial chemists are primarily in an employment situation and do not usually act as private consultants. This fact means provision for an in-

demnity fund to recompense the public for professional misconduct is not necessary as it is with many other professional groups.

2.4 *(b) Several of our members have found that when approached about joining a union that they have a conflict of interest because of the nature of their professional work. Our members have expressed their concern to the Institute on this matter. The Institute has been unable to assist these people in the past because of the presence of an unqualified preference provision in the relevant award or collective agreement. The present Bill however would provide relief to these members by allowing them an exemption from union membership, if they feel union membership makes it difficult for them to fulfil their professional obligations in their employment situation.*

2.5 *(c) The Institute also submits that it appears that the rationale behind the present Bill is to enable people to have a freer choice as to whether or not they wish to become or remain union members. The Bill also through clause 17 recognises the particular difficulty professional people encounter when faced with the prospect of having to join a union. The Institute supports the attempt to give these people a greater freedom of choice in this matter,and therefore submits that industrial chemists be included in the list of specified professional classes that are exempt from union membership under clause 17 of the Bill.*

ALTERNATIVE PROPOSAL

3.1 The Institute further submits that if the Commitee feels unable to specially include industrial chemists who are members or fellows of the New Zealand Institute of Chemistry to the classes of professional bodies referred to in clause 17, the committee give favourable consideration to the addition of a further provision in clause 17 that would permit any professional body, with the approval of the Registrar, to apply for coverage under clause 17. It may also be necessary in such an instance to provide for a right of appeal to the Industrial Court.

3.2 The Institute submits that such a provision may be of benefit to many professional bodies whose members face similar difficulties as our own members. Such a provision would also enable complete coverage of all professional bodies, whose members feel they require the protection provided by clause 17.

CONCLUSION

4.1 The Institute trusts the Committee will give consideration to its submission and the problems facing its members, who presently find themselves in a very vulnerable position on the question of union membership, and feel they require the protection afforded by clause 17 to professional persons.

LIST OF APPENDICES

I Rule 3 Objects of the Institute
II Rule 11 Conditions for Election as Member
Rule 12 Conditions for Election as Fellow
III Code of Ethics
IV Rule 7 Cessation of Membership

After the Bill had been passed by Parliament the following information was received in a letter from the Honourable J. B. Gordon, Minister of Labour:

> "The submission made by your institute has been noted by the Labour Select Committee, as have others on the same clause. The Commitee has decided that the qualifications specified in clause 17 will be transferred to a separate schedule of the Act and will therefore be alterable by Order in Council. Once the Bill is enacted I will be in a position to consider the merits or otherwise of amending the schedule. I should point out, however, that the common feature of the qualifications specified in clause 17 is that those who hold them belong to a self-disciplinary society which has the power, in certain circumstances, to deprive any member of his livelihood. This is the rationale for exempting these groups from union membership and it will also be the criteria for adding other groups to the schedule."

At the November meeting of the Council of the Institute it was resolved that all possible steps should be taken to have industrial chemists who are Members or Fellows of the Institute added to the groups already included in the Schedule to clause 17 of the Act. Council invites all those members of the Institute who have particular knowledge and experience relating to this matter to write urgently to the General Secretary giving evidence, information or advice which could help Council in the preparation of a case for presentation to the Minister.

Note: The address of the Acting General Secretary, Mr J. G. Fletcher, is The Applied Research Office, University of Auckland, Private Bag, Auckland.

G. N. Malcolm
President

INSTITUTE PRIZES

Entries for the following Institute prizes must be received by the Registrar, Box 1926, Christchurch, by April 30, 1977, or the Acting General Secretary, Mr J. G. Fletcher, Applied Research Office, Auckland University, Auckland, as stated below.

1. THE I.C.I. PRIZE

This prize of $100.00 and a medallion has been donated by I.C.I. (New Zealand) Ltd. The conditions of the award are as follows:

1. The prize shall be awarded to a member of the Institute who, in the opinion of the Council, has made some contribution to some branch of chemical science, the contribution to be judged by research work published or accepted for publication during the five years immediately preceding 30 April in the year of the award.
2. Applications by members, or nominations, which may be submitted by Branch Committees or by individual members, must be accompanied by copies of papers presented in support of the entry. The Council itself may nominate candidates for the award.
3. A nomination or application, once made, shall stand for five years, but material which fails to satisfy clause 1 shall automatically be deleted, and additional material may be presented at any time.
4. If in the opinion of the Council there is no candidate of sufficient merit, the Council may refrain from making the award.
5. The prize shall be presented at the annual conference of the Institute or at a meeting of the Branch to which the prizewinner belongs.
6. A member to whom the prize has been awarded shall not be eligible for re-nomination.

2. THE CHEMICAL ESSAY PRIZE

The New Zealand Institute of Chemistry shall offer annually a prize for an essay or review on a chemical topic. The conditions of the award are as follows:

1. The prize shall be open to anyone who has not attained the age of 25 years before April 30 in the year of the contest, whether a member of the Institute or not.
   (Note: Entries from students will be welcomed.)
2. The entry shall be not longer than 5,000 words.;
3. The entry shall be in a form suitable for publication and the Institute shall have the right to publish the winning entry.
4. Applications, in completed form, must be received by the General Secretary not later than April 30 in the year of the contest.
5. The entries shall be judged by a Committee of examiners set up by Council for the purpose. The President of the Institute and the Editor of the Journal shall be ex officio members of this Committee.
6. The award shall be made by the Council after consideration of the report of the Committee of examiners, and the presentation of the prize shall be made, whenever possible, at the annual conference of the Institute.
7. No award shall be made if, in the opinion of the Committee of examiners, there is no entry of a sufficiently high standard of merit.
8. The value of the prize shall be such sum as the Council may from time to time determine, and the prize shall be spent on books or instruments to the satisfaction of the Council.
   (Note: The value of the prize is at present $50.)

TVL PRIZES

The conditions for these prizes will be announced at a later date.

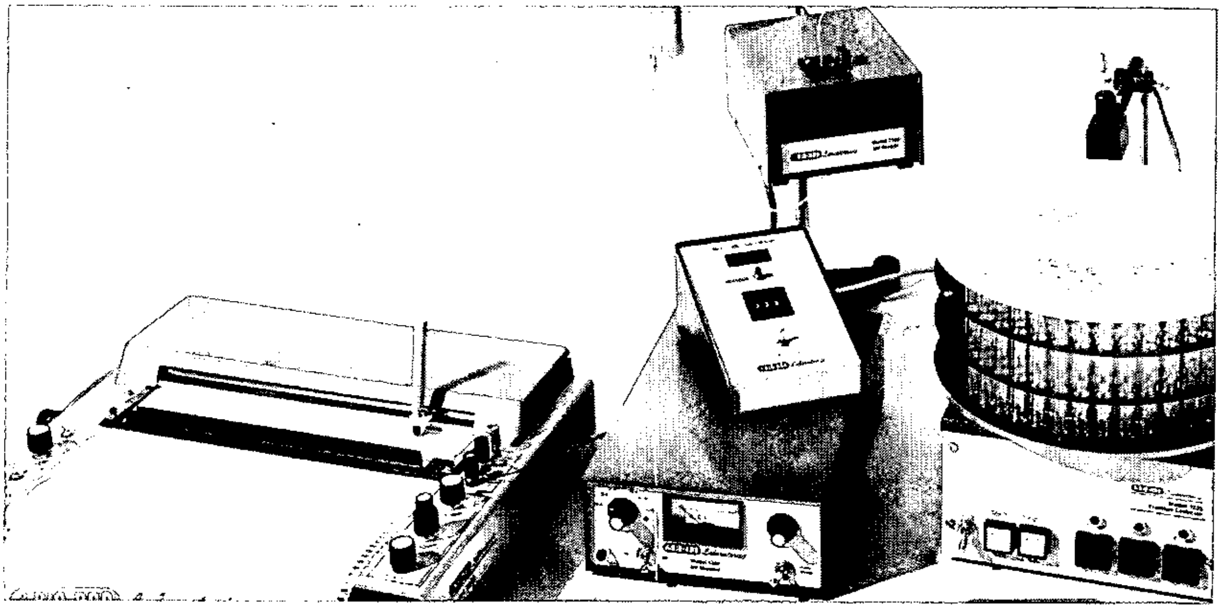
EASTERFIELD AWARD (next award 1978)

(1) The medal shall be awarded to chemists within New Zealand in recognition of the quality and originality of their research work.
(2) Candidates must be under the age of 35 years at the 30th April, 1977.
(3) The award will be open to all chemists whether or not they are members of the Royal Institute of Chemistry or the New Zealand Institute of Chemistry.
(4) The major portion of the candidate's research work submitted must have been carried out in New Zealand.
(5) No person may be awarded the Easterfield Medal more than once.
(6) The successful candidate will be required to deliver a lecture on the subject of his research at the Annual Conference of the N.Z. Institute of Chemistry, or on some other suitable occasion.
(7) The medal shall be awarded biennially and presented to the successful candidate on the occasion of his lecture.
(8) The Selection Committee reserves the right to make no award in any year if the standard of work submitted is not of sufficient merit.
(9) Expenses necessarily incurred by the Medallist in connection with the delivery of his lecture will be defrayed.
(10) Applications by or on behalf of candidates for the award must be in the hands of the General Secretary of the N.Z. Institute of Chemistry not later than 15th April 1977 and must be fully supported by all rrelevant papers (either published or unpublished).

1976 ICI PRIZE-WINNER

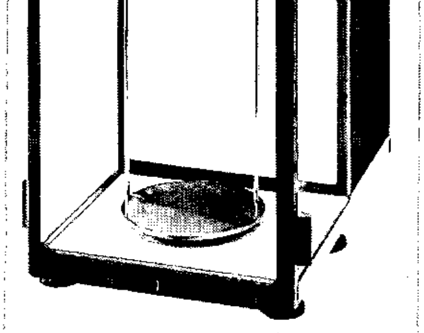
Dr Powell, who is a senior lecturer at the University of Canterbury, took his Masters and Doctoral degrees at Victoria University working with Professor N. F. Curtis. His research work has centred on energy changes in reactions between metals and organic reagents and in the analytical application of these reactions. During 1970-71 he worked with Professor G. H. Nancollas at State University of N.Y. in Buffalo studying reactions between molecular oxygen and oxygen-carrying complexes. Current research interests are in the chemistry of oxime reagents and in trace element deficiencies on 'pakihi' soils.

NEW PRODUCTS



Bio-Rad have introduced a U.V. Monitor, a Strip Chart Recorder and a Fraction Collector as adjuncts to their column chromatography range.
The U.V. monitor has a low pressure mercury lamp, with a phosphor for 280 nm., in a double beam configuration. There is a range of cells and of sensitivities, with meter readout and 0-10 mV output for a recorder.
The 10 inch recorder has 16 input ranges from 0-1 mV to 0-300 V, uses a felt tip pen and has 12 chart speeds from 0.5 inches/hour to 20 inches/min.
The fraction collector operates on the spiral cassette principle with 135 x 13 mm test tubes, 50 x 25 mm test tubes, etc. The cable-connected controller counts up to 999 drops, seconds or minutes.
All of these instruments operate on 220 V 50 Hz and in the range 2°-40°C.

M.S.E. have announced the PREPSPIN 50, a 50,000 rpm, 347,000 x g preparative ultracentrifuge. Temperatures in the range 0-40°C can be controlled to within 1.5°C using an infra-red rotor temperature sensor. Several novel features include a brush wear indicator and a variable acceleration/deceleration control.



Mettler has introduced a new easy-to-use balance, the H80. It weighs to 160 g with a readability of 0.1 mg and it is unnecessary to arrest the pan at any time during the weighing operation.

DISPOSAL OF TOXIC WASTES

T. H. BIERRE
P.O. Box 51-202, Pakuranga, Auckland 6.

Wastes are materials which are superfluous, no longer serving a useful purpose, or left over after use, and require disposal.

The disposal of wastes is a broad field which can be divided into two main categories: disposal of (a) obnoxious wastes, (b) toxic wastes.

Disposal, in the case of obnoxious wastes, is mainly for aesthetic reasons. The disposal of toxic wastes is an important matter as they may, in the course of handling, transportation and even after 'disposal' become a danger to life and health. These toxic substances when swallowed, inhaled or otherwise absorbed may destroy life or be injurious to health.

MODE OF ABSORPTION

Skin contact is of primary importance in the number of medical cases occurring. From the point of view of seriousness of the medical condition resulting from exposure to toxic wastes and also the facility for creating annoyance or widespread community effects, inhalation is of major importance; oral intake, perhaps except in the case of young children or the mentally deranged is of minor importance. There may be multiple routes of entry.

Skin Contact

Skin is normally an effective barrier. Toxic wastes can cause irritation or penetrate the skin and enter the blood stream and widespread effects on the functioning of major body organs can then occur.

Serious poisonings can occur from short exposure of small skin areas with organic-phosphate agricultural chemicals, hydrocyanic acid and phenols. Death with the latter has resulted from absorption of concentrated material through a skin area of 64 square inches, i.e. following complete coverage of one hand and forearm [5].

DR TREVOR H. BIERRE, an Otago Medical Graduate, is a Specialist in Occupational Medicine who is retained as a consultant by several large industrial undertakings. Formerly with the New Zealand Department of Health, he has had extensive first hand experience with the disposal of toxic wastes. He has both the Diploma in Public Health and Industrial Health from Otago University. Presently President of the New Zealand branch of The Australian and New Zealand Society of Occupational Medicine, and consultant to the Waterfront Training Organisation.

Inhalation

The most important means by which injurious substances enter the body is by inhalation. Internal damage usually occurs because these substances pass from the lungs to the bloodstream and thence to major organs such as the liver or the kidneys.

Permissible Limits

The permissible limits for concentrations of toxic substances in the air are given by the Threshold Limit Values (1976) (T.V.L.) adopted by the American Conference of Governmental Industrial Hygienists and the M.A.C. U.S.S.R. ceiling fixed by the Soviet Ministry of Public Health. These values are subject to periodic adjustment and should not be observed over-rigidly. The limits are intended for use in the practice of industrial hygiene and should be interpreted and applied only by a person trained in this discipline. They are not intended for use, or for modification for use.

(1) As a relative index of hazard or toxicity.
(2) In the evaluation or control of community air pollution or air pollution nuisances.
(3) For adoption by countries whose working conditions differ markedly from those in the country of origin.

Threshold limit values refer to air-borne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. They refer to time weighted concentrations for a 7-8 hour day and 40 hour work week. They are of no value in assessing the risks to health of air-borne toxic substances when exposure is transitory.

CLASSIFICATION OF EFFECTS OF TOXIC SUBSTANCES

If toxic wastes produce odour, dust, mist, fume or gas, the main effect will be on the respiratory system, but other materials may have their main effect through the skin – the two routes may be combined.

1. Industrial Organic Solvent Vapours

(e.g. benzene, xylene, alcohol, acetone, trichloroethylene.) These have a narcotic effect on the central nervous system and act in a similar way to an aesthetic, producing excitement first and then sleep. Benzene also has a toxic effect on bone marrow.

2. Upper Respiratory Tract Irritants

(e.g. ammonia, acetic acid, sulphur dioxide.)
These are irritating to the eyes and upper respiratory tract – ample warning is given and those exposed may escape before more serious effects develop.

3. Pulmonary Lung Irritants

(e.g. chlorine, phosgene, and toluene di-isocyanate.)
There is little irritant effect upon the upper respiratory tract and the warning properties of these gases are slight. With phosgene, which has a pleasant smell of hay, acute exposure produces slight irritation to the eyes and throat, but there may be no immediate warning that dangerous concentrations are being breathed. Pulmonary oedema after 2-24 hours occurs, with death after 36 hours. Phosgene is produced when chlorinated hydrocarbons such as trichloroethylene are decomposed by heat.

4. Chemical Asphyxiants

(e.g. carbon monoxide, hydrocyanic acid.)
Carbon monoxide competes with oxygen for haemoglobin in red blood cells and usually wins. Hydrocyanic acid and the cyanides are true protoplasmic poisons combining in the tissue with enzymes associated with cellular oxidation. They render oxygen unavailable to the tissues and cause death by asphyxia.

5. Simple Asphyxiants

(e.g. nitrogen, carbon dioxide, methane.)
These displace the oxygen in the air, so that it is no longer available to support life.

6. Agricultural Pesticides

(e.g. organic phosphates such as parathion, and carbamates such as carbaryl.)
These are reversible inhibitors of cholinesterase and they may be inhaled, ingested or absorbed through the skin.

Any of the materials I have mentioned may be encountered as toxic wastes – there are many more, too numerous to mention.

SOURCE OF WASTE

Toxic wastes are commonly generated as a result of increased industrial activity, disasters such as fires involving storage areas, warehouses and manufacturing plants. Accidents occuring during the transportation of hazardous chemicals have been of continuing concern to many countries, and we are all much more familiar now with the effects on populations of chemical spillages.

The Food and Drug Administration (F.D.A.) in the U.S.A. is responsible for the monitoring of foods and has been concerned with the large number of incidents occurring during transportation. Pesticides have been mentioned most frequently as contaminating agents, but there have also been cases of oatmeal being contaminated with phenol, animal feed with arsenic, potatoes with lead paint pigment, and nuts with timber preservative such as pentachlorophenol.

Industrial Wastes

With diversification of manufacturing processes, a wide range of toxic chemicals is being used. The larger well-established industries tend to deal responsibly with their inevitable wastes, but this has not always been the case. For many years now Health Legislation has dealt with only the more toxic processes and the offensive trades. The clamour of the environmentalists has been necessary to catch the ear of the industrialists and this has produced a more responsible attitude to the less toxic but nonetheless harmful materials not covered by legislation.

The mercury and cadmium disasters in Japan, the experiences with lead and asbestos in many countries, have led to a more responsible attitude. Firms which spend annually large sums of money on advertising their products, cannot now afford to waste hard-won goodwill, with the adverse public reaction to the inevitable publicity when man or wildlife suffers from the careless disposal of toxic wastes.

Unfortunately, the smaller undertakings, the backyard manufacturers are less amenable to public pressure and control.

The generation of wastes is inevitable from manufacturing processes, contamination of essential ingredients with incompatible materials such as water occurs, or aging may render a material unusable. Accidents may occur, and often quite large volumes of chemicals require disposal as they may no longer be used in the process for which they were originally destined.

Chemical Spillages

The increasingly large amounts of basic manufacturing chemicals being manufactured in, or imported into New Zealand for a variety of processes (to name a few: agriculture, forestry, plastics manufacture, food manufacture) means there are many opportunities for incidents during handling and transportation. Incidents are relatively few in manufacturing plants due to careful worker selection and the interests of economy. However, once the product is in transit anything can happen, from deliberate sabotage to genuine accidents. Damage from storms at sea to deck cargo, dropped drums on wharves, accidents with fork-lifts and insecurely fastened loads on trucks, both road and rail, produce "orphaned" materials which may become a public health hazard.

Chemical spillages may be in the nature of an acute emergency or as a result of normal day to day activity.

In dealing with spillages there are several basic rules to follow:

(a) Notification

Since the Parnell Emergency Report [3] chemical spillages have been "news", and the media always swing into action, often producing a distorted picture of the likely hazards to health. This over-reaction often encourages a corresponding reaction from the emergency services causing unnecessary inconvenience to many members of the public. Since the establishment of Hazardous Chemicals Technical Liaison Committees consisting of representatives of the major Government departments and emergency services, co-operation has improved and the roles of the various agencies have been better defined. As a result whenever the situation arises where there is a threat to the health of the public directly or indirectly from the presence of a toxic material in the neighbourhood, or where injudicious disposal might also have this effect, the Department of Health (that is, the Medical Officer of Health) should be notified as soon as possible. **It must be remembered that**

the local fire service have the prime responsibility as the agency of first contact in all chemical emergencies.

(b) Containment

The use of sand, soil or gravel is invaluable. Materials on wharves and roadways can be placed in 44 gallon drums and jumbo bins lined with polythene, bearing in mind of course, that ultimately safe disposal will be necessary. At this stage containment measures should facilitate later disposal.

(c) Identification

After initial containment, it is most essential that the chemical and its attendant hazards be identified before proceeding further.

(d) Decontamination

When toxic wastes require disposal and when chemical spillages occur, if there is any doubt at all as to the correct procedures to be followed, either at the site or in relation to disposal, the Medical Officer of Health who is District Registrar of Poisons should be consulted. Section 31 of the Poisons Act 1960 gives the Police and the Medical Officer of Health special responsibilities in relation to poisons and toxic substances. Fire Brigades should always notify the Medical Officer of Health of incidents, particularly if the health of the public is involved.

Measures to be taken in practice are usually agreed on in consultation between Fire Prevention Officers, Chemists from the Department of Scientific and Industrial Research and the Medical Officer of Health.

Disposal

Every endeavour to prevent the contamination of streams and watercourses, not only because of the adverse effect on the ecology, but also the possibility of contamination of human water supplies, should be borne in mind.

The direct disposal of spilled toxic materials into watercourses or the sea should not be considered, and the burial of chemicals in adjacent situations where underground seepage may in the long term have as a serious an effect, is out of the question.

Satisfactory disposal may be by recycling, incineration, pyrolysis or deposition in landfills following inactivation or chemical neutralisation.

Recycling

The material may still be used for its original purpose. In the case of chemical spillages we always try to find out who owns the spilled material, as technical officers from these firms very often have considerable information and experience in dealing with the substance and this is of considerable assistance in deciding what action should be taken.

Quality control is often a problem and many firms prefer to claim on the insurance company, thinking that will be the end of an unpleasant incident and that others will now take over the responsibility for disposal. This is not the case and my policy is always that firms with this attitude should be told that they have a responsibility to the end, and I see that they carry out this function.

Sometimes a new use may be found for a product but this is not very practical.

Pyrolysis and Incineration

The process best suited to the disposal of special toxic and liquid refuse appears to be pyrolysis. The Auckland Regional Authority is investigating this means of waste disposal, but said in March 1974 in the Report on Refuse Disposal for Metropolitan Auckland, that it will be three years before a pyrolysis plant is operating. In the meantime investigations are being made for interim land disposal sites for special toxic and liquid refuse.

Landfill

Biodegradability is important and must always be considered when working out where to dump materials. The organo-phosphorus pesticides are readily degradable, but some materials such as D.D.T. are not, and are extremely persistent. As I have already indicated, the disposal of diluent containing toxic materials, in particular particles say from liquid spillages or following the use of water for washing down contaminated surfaces, is very important and care must be taken not to contaminate watercourses, the sea or ground water supplies. With pesticides of short half-life washings can sometimes be trapped and held for an appropriate period before release; otherwise they can be disposed of in pits in extreme dilution. Special sites are often necessary; after a chemical warehouse fire in Auckland when large quantities of agricultural chemicals were partly burned and damaged, finding a suitable site took several days.

Very often a toxic material (an example is toluene di-isocyanate) may be rendered quite harmless by appropriate chemical treatment, and the end product (in this case urea) may be quite safely deposited in a landfill.

Problems often arise with containers. Those constructed of metal should be decontaminated, crushed and buried deeply and not re-used, because polythene liners and even the metal may have been weakened or damaged by the original contents. Cardboard containers are sometimes better burned.

Chemical Safety Data Sheets

These publications by the Manufacturing Chemists' Association cover in detail chemical properties, engineering control of hazards, safety, fire fighting, handling, storage, waste disposal, and medical management of a whole range of materials. There is a complete booklet for each substance and there is an ideal, detailed reference source.

Manufacturers' Data Sheets

Most manufacturers have Data Sheets of properties, medical effects and precautions to be taken in the safe handling of specific toxic chemicals and wastes.

CONCLUSIONS

In the long run for the satisfactory disposal of all toxic wastes generated in metropolitan areas, a total operation must be set up ideally organised on a regional basis with compulsory participation. This is a local authority or community responsibility and the pooling of expert knowledge and experience is necessary to deal safely with the great variety of toxic materials.

Such an operation requires adequate legislation to ensure complete community participation and safe operation. Financial arrangements must be adequate and should be shared by Government, the industries concerned and the public. Complete disposal of toxic wastes at collection points should ensure minimum handling and opportunities for human contact, and safe disposal of innocuous low bulk materials.

The chemical challenge to man and his environment is real and it is only by forward planning, sound administration and the application of well known toxicological techniques in a spirit of universal co-operation and good sense, that man will face up to this challenge.

REFERENCES

1 Chemical Safety Data Sheet, Manufacturing Chemists Assn, 1825 Connecticut Avenue, N.W., Washington, D.C. 20009, U.S.A.
2 Poisons Act (1960) Amendment (1969), p. 21, Government Printer, Wellington
3 Report of Commission of Enquiry into Parnell Civil Defence Emergency (1973), Government Printer, Wellington
4 Report on Refuse Disposal for Metropolitan Auckland (1974), section 5.4, Auckland Regional Authority
5 Sax, N.I. (1975), Dangerous Properties of Industrial Materials, p. 1008, 4th Ed., Van Nostrand, Reinold, New York
6 Threshold Limit Values (1976), pp. 1-4, Department of Health, Government Printer, Wellington

FIRST AID IN A TOXIC EMERGENCY

General –

Remove the toxic material from the affected persons by transfer to the fresh air, or by transferring him to the fresh air, or by drenching his skin with copious amounts of clean water. Sustain his life and transfer him to hospital as quickly as possible. If the patient is conscious, ask what happened; if not, then ensure that he can breathe freely. Start artificial respiration if necessary.

Always send as much information as possible to the hospital with the casualty.

Skin Contact –

1. Drench the casualty with copious quantities of clean fresh water in a bath or shower.
2. Apply a stream of water onto the skin whilst removing all of the contaminated clothing.
3. Cleanse skin with soap and water.
4. DO NOT attempt to use chemical antidotes.
5. Remove the casualty to hospital urgently.

Inhalation –

1. Carry the victim to fresh air: loosen any tight clothing.
2. Ensure that the rescuers are properly protected and that they have self-contained breathing apparatus and lifelines. There should be more than one rescuer.
3. Clear the air passages and apply artificial respiration and/or oxygen.
4. Conserve the victims body warmth and remove urgently to hospital.

References

Dreisbach, R. H. (1974), Handbook of Poisoning, 8th Ed., Lange Medical Publications, Calif., U.S.A.

First Aid – the Authorised Manual of St John Ambulance Association and Brigade, 3rd Ed., 1972

A NEW APPROACH TO TESTING FOR 'DOPING' IN RACE HORSES

G. J. DOUGHERTY
43 Sheridan Terrace, Wellington 4.

In 1972, a worldwide total of more than 240,000 specimens from racehorses were tested for 'doping' [1]. Chemical tests for the doping of racehorses traditionally have followed a time consuming extraction and identification approach, but this is now becoming expensive as the routine use of expensive techniques (such as gas chromatography and mass spectroscopy) has become necessary to satisfactorily identify the wide range of drugs which is now available for veterinary use. For this reason, a test procedure based on an entirely different approach may have considerable potential.

The basic behavioural difference between normal persons and persons intoxicated by drugs which was observed by Doctors Arieff and Wetzal [3] may well have a use in the dope testing of racehorses. In the test devised by Doctors Arieff and Wetzal, the human subject is blindfolded and stands on one leg with his arms extended. Normal subjects with no injury to their central nervous systems or inner ears are able to maintain this position without loss of equilibrium and with little noticeable movement, while subjects intoxicated by drugs (or alcoholics) start to rotate around a vertical axis, and begin a distinctive motion in an effort to maintain balance.

If this procedure were applied to testing for drugs in animals, the test animal would be blindfolded and required to stand on a number of limbs which would be less than the total number of available limbs. Its behaviour in this stance would then be observed by trained personnel.

A general case for the leg arrangement of an animal in this posture is easily derived. If the animal has X legs, Y of which are in contact with the supporting surface, the number of possible combinations is:

$$\frac{X!}{(X-Y)!\,Y!}$$

MR GAVIN DOUGHERTY graduated M.Sc. in Chemistry from the University of Canterbury in 1970. For the next three years he worked for Chemical Services Laboratories in Johnsonville, Wellington. This company is the official analyst for the New Zealand Racing Conference.

He is currently employed as a scientist in the Applied Chemistry Section of Chemistry Division, DSIR at Gracefield.

where X ! is the total number of permutations of all the animal's legs, Y ! is the number of permutations of legs on the supporting surface, and (X − Y) ! is the number of permutations of the legs not resting on the supporting surface. It should be noted that the legs comprising the permutations of Y and (X − Y) are members of discrete subsets of the total set of legs, X.

The resulting total number of combinations is then:

$$2^X$$

This includes the situations where all the feet of the animal are on the supporting surface (Y = X) and where all the feet are clear of the surface (Y = 0). If these situations are deducted, the number of possible combinations is:

$$(2^X - 2)$$

This situation may be simply demonstrated by the use of a human example (as in the original experiments of Arieff and Wetzal). For most humans, the total number of available legs (X) is 2. Therefore

$$2^X = 4$$

combinations are possible. On deducting the two combinations which are not applicable to the test (the combinations in which both legs rest on the supporting surface, or remain clear of the surface which is then non-supporting), only two situations remain and the subject has the option of standing on either the left or right foot. This should be considered if it is ever necessary to undertake the Arieff-Wetzal test. A similar situation would apply if the test is applied to other two-legged animals, such as ostriches, for example.

Horses and other quadrupeds possess

$$2^4 - 2 = 14$$

possible combinations of leg arrangements, four of which involve standing on only one leg, six involve standing on two legs, and four involve standing on three legs.

Figure 1 and Table 1 show typical arrangements of legs on horses. Table 2 shows the combinations of legs which may be used in the Arieff-Wetzal test.

It is clear that quadrupedal animals, including horses, should not be allowed to stand on three feet during the test because of the inherent stability of this tripedal pose. In particular, dogs should not be tested in this pose as they have considerable experience in balancing in this position. To prevent the test subject assuming such postures of stable equilibrium, not more than 50% of available legs

TABLE 1 – *Typical Arrangement of Legs on Horses (or other quadrupeds)*

	Head	
Left foreleg (LF)		Right foreleg (RF)
Left hindleg (LH)		Right hindleg (RH)
	Tail	

should be permissably utilized during testing procedures. This recommended ratio is obtained by analogy with human subjects and may require revision after evaluation of the test procedure on the appropriate species.

Two exceptions to this proposal would be the cases where one of the supporting legs is considerably shorter than the other two, or where the centre of mass of the animal lies outside the triangle formed by the tripedal posture. However, further consideration shows that attempting to race horses or other animals possessing either of these configurations would pose considerable difficulties and these situations may therefore be neglected.

In six-legged animals, the use of 50% of available legs leads to stable tripedal configurations in 90% of the possible combinations. It is therefore suggested that appropriate alterations to cover this situation should be formulated when the extent of racing of six-legged animal species merits tests for doping.

In the case where the species under test has an uneven number of limbs for ground support purposes (such as kangaroos and wallabies, which also use their tails) it is recommended that further investigation be carried out if kangaroo racing becomes a commercial proposition.

Several technical difficulties are to be expected in applying the Arieff-Wetzal test to racehorses. Two major problems involve the testing procedures and the effectiveness of the test.

It will be necessary to train all racehorses to stand on two legs in the appropriate posture while blindfolded. However, experience with circus elephants indicates that this training will be easily achieved [2], although it may take some time to successfully train the approximately 6,000 horses in the New Zealand racing industry.

It is obvious that extensive field testing with horses in racing condition will be required to determine the range and levels of drugs detected by this method before the test

TABLE 2 – *Combinations of Legs which are Suitable for the Test*

(1) Standing on one leg:
    LF; RF; LH; RH.
(2) Standing on two legs:
    LF, RF; LF, LH; LF, RH;
    RF, LH; RF, RH; LH, RH.
(3) Standing on three legs:
    LF, RF, LH; LF, RF, RH; LF, LH, RH;
    RF, LH, RH.

The permutations (such as RF, LF, or RF, LF, LH) are, of course, included in these basic combinations.

A HORSE, showing a typical arrangement of legs.

AN ELEPHANT. The testing of elephants may be a health hazard.

procedure can be adopted generally. This test will also provide standard data with which to compare the actual test subjects.

If these trials prove satisfactory, the test will have several major advantages over present methods. The test may be (and in fact should be) performed immediately before or after the race, which thus eliminates the considerable delay involved in chemical analysis at a central laboratory. Unlike chemical analysis, the apparatus requirements are modest; only suitable blindfolds and a suitable testing area are required. It also seems likely that the personnel requirements of the test will be modest; depending on the distinctiveness of a positive response in the subjects, it may only be necessary to employ observers rather than qualified scientists.

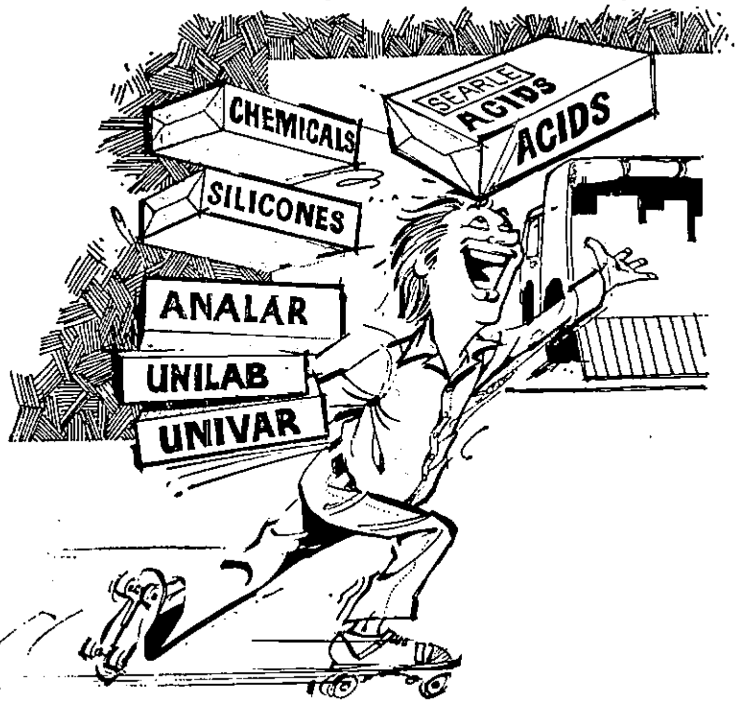
Even if the Arieff-Wetzal test is not entirely suitable as a replacement for present methods, it may serve well as a preliminary screening test to indicate those racehorses which warrant further investigation. Use of the test in this way could achieve outstanding economies; of the 240,000 specimens analysed in 1972, only 0.14% were found to contain drugs of any kind.

The major advantage of the Arieff-Wetzal test is its broad range of application. Not only may it work on horses and dogs which are both regularly raced in New Zealand, it may also apply to elephants, camels, giraffes and ostriches although these are not raced in this country at the present (although testing these species may introduce peculiar problems: a blindfolded elephant standing on two legs could be a significant health hazard to the observers). Of course, the test is not limited to animals; it may also be applied to the riders, as Doctors Arieff and Wetzal described originally.

These possibly major advantages of economy and speed in testing may be very simply achieved by training every animal used in racing to stand blindfolded on half of its available legs, and then observing its response to this situation. Surely this is a concept which warrants further investigation.

REFERENCES

1 Association of Official Racing Chemists, Proceedings of the 27th meeting, Bal Harbour, Florida, January 1973 (strictly confidential to members)
2 Miss J. Goggin, personal communication
3 Review: Readers Digest, page 176, November 1970.



CENTENNIAL CELEBRATIONS OF THE AMERICAN CHEMICAL SOCIETY

A Ceremonial Session was held in New York on April 5th, 1976, to mark the centennary of the American Chemical Society. A scroll was prepared to convey to the American Chemical Society the greetings and congratulations of the New Zealand Institute of Chemistry. This scroll was presented at the Ceremonial Session by Professor J. Vaughan who was in North America at the time of the ceremony and was invited by Council to act as our representative.

The scroll contained the following wording:

> *The Council, Fellows and Members of the N.Z.I.C. extend to the Officers and Fellows of the American Chemical Society, fraternal greetings, congratulations, and best wishes for the future, on the occasion of the Society's centennial celebrations in April 1976.*

The following letter from the President of the American Chemical Society, Glen T. Seaborg, was received by Professor Vaughan in November 1976.

The Centennial Year of the American Chemical Society is drawing to a close, and we have reached the point where we can discern some of the long-range benefits that will accrue to chemistry from our anniversary celebration.

For example, our Centennial Meetings in New York last spring and in San Francisco in late summer have been remarkably productive of new information which will be of value to our science and profession for many years.

The Centennial ceremonies at these meetings not only made the meetings exceptionally interesting for our own members and guests but attracted an unusual degree of public attention to our work. We believe this will lead to increased public understanding of the meaning and importance of chemical progress.

As we look back over the many special Centennial events, we realise that none was more inspiring than the colourful Ceremonial Session in New York on April 5. Your participation there, along with that of delegates from more than 100 other societies, provided encouraging evidence of the strong ties existing among scientists and engineers of all nations and of all disciplines. The warm greetings presented to our Society by your organisation added greatly to the fraternal spirit of the occasion.

No doubt you recall that the attractive scrolls and other congratulatory messages were displayed at the banquet in New York on April 6, the exact anniversary of the founding of the Society. Subsequently they were shown at the Society's headquarters and also at the San Francisco meeting. In all three places they were much admired. We plan to arrange a permanent exhibit of these cherished mementos at ACS headquarters.

Scores of leading scientists from other countries presented papers at our Centennial Meetings, and twenty-five ACS Centennial Foreign Fellows were honoured in New York, in San Francisco, or in their homelands.

The enthusiastic co-operation of so many distinguished chemists from so many countries in our anniversary observance strengthens the hope I have expressed several times this year that before long we can form an international chemical society which will facilitate the dissemination of the benefits of chemistry to all the peoples of the world.

In any event, I am confident that the American Chemical Society, as it enters its second century, will continue to do its best to promote the utilisation of chemistry for the benefit and well-being of mankind.

With best regards,

Cordially,
Glen T. Seaborg.

BOOK REVIEW

Treatise on Solid State Chemistry. Volumes 6A (Surfaces I) and 6B (Surfaces II) – edited by N. B. Hannay. Plenum Press, New York-London 1976. Pp 491 (6A) and 418 (6B). Price $54 each.

These volumes are the most recent addition to the *Treatise* series and deal with the study of solid surfaces in terms of their properties and reactivity towards extraneous species (gases, ions) which are adsorbed or deposited on such surfaces. The characterisation of surface phenomena has been considerably aided by the development in recent years of new and sophisticated electron diffraction and spectroscopic techniques. The long and tongue-twisting names of many of these methods have necessitated the use of a series of abbreviations such as AES, FEED, FES, ILEED, INS, UPS and XPS. A glossary of these terms at the beginning or the end of the books would perhaps be helpful.

The scope of the books may best be indicated by listing the heading and number of pages of each chapter: The structure and thermodynamics of clean surfaces, 55 pp; Surface structure – experimental methods, 106 pp; Evaporation from solids, 75 pp; Molecular beam deposition of solids on surfaces – ultrathin films, 101 pp; Adsorption of gases on solids, 144 pp; Cataysis by solid surfaces, 124 pp; Ion implantation and channeling, 76 pp; Semiconductor surfaces, 61 pp; The role of the solid in electrochemical phenomena, 76 pp; Polymer surfaces, 69 pp.

The text is clearly printed on good quality paper; the figures and tables reproduce well in keeping with the high standard of the publishers. In a multi-author work of this kind, a slight overlap between chapters is inevitable but the style of writing is remarkably even and readable. Equally surprising is the lack of typographical errors, reflecting the meticulous editing and proof reading that have gone into it. Each chapter contains a balanced blend of theory and experiment, concluding with a valuable list of up-to-date references to the relevant literature. Regrettably, the title to the citations has been omitted from many of the chapters. Also lacking is an author index although the subject index seems adequately comprehensive.

As stated in the foreword, the *Treatise* is intended for advanced workers. However, the non-specialist who wishes to get quickly acquainted with the recent advances and developments in the field covered by the various reviews, will benefit from reading these volumes. Although we are probably used to seeing price tags of between $30 and $50 for a reference text in these days of high inflation, few research workers would be able to afford their own copy. These volumes can be recommended to institutional and university libraries.

B. K. G. Theng

N.Z.I.C. CONFERENCE 1977

The 1977 Conference will be held at the University of Waikato, Hamilton, from 22 to 25 August 1977. Dr K. M. Mackay is Chairman of the Conference Committee and Dr A. G. Langdon is Secretary.

This year the theme of the Conference is "The Future of Chemistry in New Zealand" and plenary lectures will reflect this theme in the general areas of Education, Law, Government, Energy, Industry and the role of the Institute. Overseas speakers will include Professor R. D. Brown from Monash University and Dr J. R. E. Wells from University of Adelaide.

In addition there will be the traditional specialist sessions incorporating student papers, current research papers, review lectures and meetings of the specialist groups. As usual, the Conference will form a joint meeting with the the N.Z. Biochemical Society. A Teacher Refresher Course and a Trace Elements in Health Symposium are planned to be held in conjunction with the Conference and the Association of Clinical Biochemists are scheduled to hold their Conference in Hamilton during the same week.

Social functions will include an informal get-together on Monday 22, a Social Evening, a Theatre Evening and the Conference Dinner.

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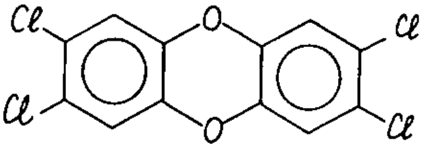
TCDD

A Deadly Molecule

Gordon W. Gribble
Dartmouth College
Hanover, N.H. 03755

TCDD is incredibly toxic. The lethal dose is less than one millionth of a gram for guinea pigs. In man, a single exposure to a few micrograms of TCDD may cause a severe skin disease. TCDD has also been responsible for the death of millions of chicks. TCDD is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.



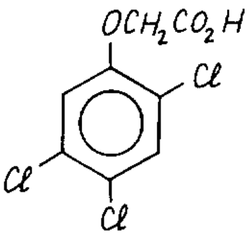
TCDD

In 1899 a German physician, G. Herxheimer, described a severe skin disease contracted by workers involved in the electrolytic production of chlorine gas using carbon electrodes. He incorrectly attributed the disease to free chlorine. Subsequent reports of chloracne continued through 1964, when 60 Dow Chemical Co. workers developed the disease. Chloracne, a generalized dermatitis composed of comedones (blackheads) and papules with inflammation so severe it may cause permanent scarring, is morphologically similar to teenage acne. Although face, neck, and arms are the most common sites, areas covered by clothing also may be affected.

Chloracne is a hazard for industrial workers producing chlorinated hydrocarbons such as polychloronaphthalenes (Halowax), polychlorobiphenyls (Arochlor), and polychlorophenols. In 1957, TCDD was isolated from 2,4,5-trichlorophenol and found to be the cause of chloracne.

Teratogenicity of TCDD

In 1969, the teratogenicity (birth abnormality) of pesticides was studied at the Bionetics Research Laboratories under contract to the National Cancer Institute. Laboratory animals fed samples of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) were observed to have given birth to offspring having fetal defects such as lack of heads



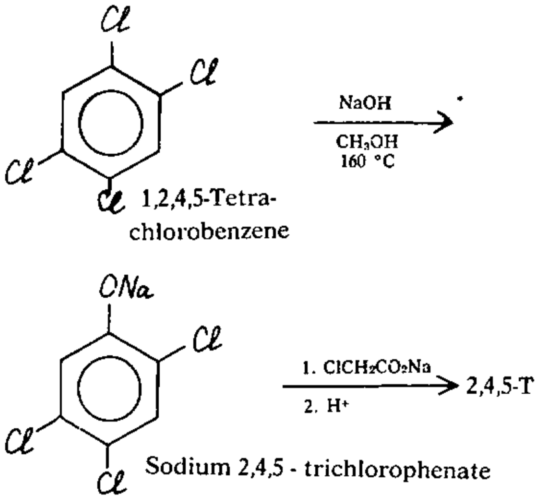
2,4,5-T

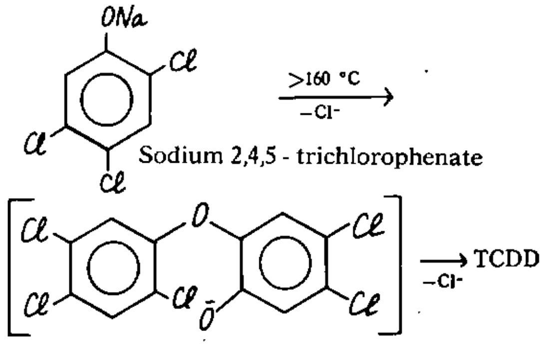
and eyes, cystic kidneys, cleft palates, abnormal livers, or other biological abnormalities. This study was widely quoted by the lay press and caused public concern since 2,4,5-T and a related herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), had been widely used domestically for weed control and in South Vietnam as a jungle defoliant.

Later it was learned that the study sample of 2,4,5-T was contaminated with 30 ppm of TCDD. Further, other studies of TCDD revealed it to be so powerful a teratogen that it could completely account for any birth malformations observed in the Bionetics study. Purified 2,4,5-T, containing less than 1 ppm TCDD, was found not teratogenic. Unfortunately, the lay press in discussing the herbicides 2,4,5-T and 2,4-D continues to overlook the fact that it is the TCDD impurity that is responsible for fetal abnormalities.

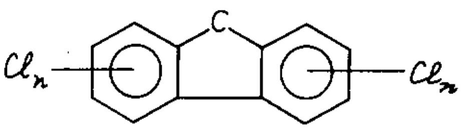
Preparation of TCDD

1,2,4,5-Tetrachlorobenzene and sodium hydroxide in methanol are heated under pressure; then the intermediate sodium 2,4,5-trichlorophenate is treated first with sodium chloroacetate and second with acid to yield 2,4,5-T. The temperature for the sodium hydroxide reaction is crucial. If it is not carefully maintained at 160 °C the intermediate can condense with itself to form TCDD.

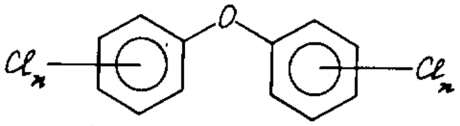




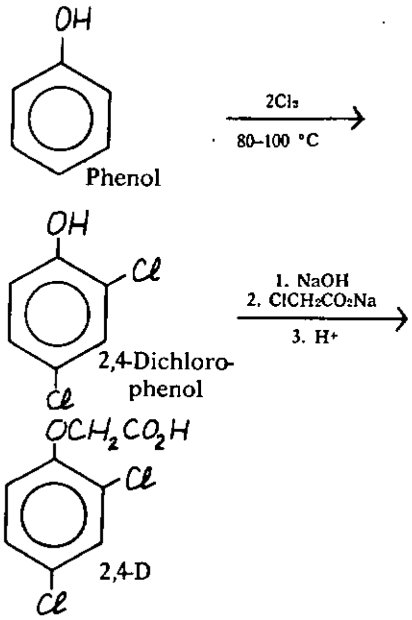
At temperatures above 160 °C polychlorodibenzofuran and polychlorodiphenyl ether, much less toxic than TCDD, may also be produced. Control experiments demonstrate that TCDD is formed when pure 2,4,5-trichlorophenate is heated 350–400 °C. The related herbicide, 2,4-D, is not usually contaminated with chlorodioxins since it is prepared at lower reaction temperatures by chlorination of phenol as shown in the following equation:



Polychlorodibenzofuran

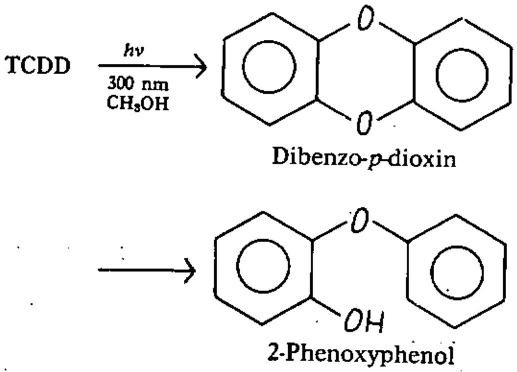


Polychlorodiphenylether



Chemical Properties of TCDD

TCDD is a chemically stable water-insoluble, white solid having a melting point of about 300 °C. Thermal decomposition begins at 700 °C and is complete at 800 °C. TCDD does not react with strong acids and is inert to most reagents. It slowly photodechlorinates in methanol to give dibenzo-*p*-dioxin and, eventually, 2-phenoxy phenol.



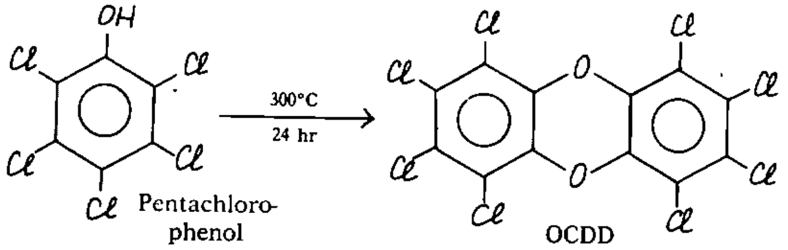
Other Chlorinated Dibenzo-*p*-dioxins

Other chlorinated dibenzo-*p*-dioxins can be formed in reactions involving chlorinated phenols. Isomeric tetrachlorophenols and pentachlorophenol are prepared at high temperatures by exhaustive chlorination of phenol or hydroxide displacement of chlorine from polychlorobenzenes. Consequently, production of chlorinated dibenzo-*p*-dioxins may be thermally promoted. For example, heating pentachlorophenol to 300 °C gives octachlorodibenzo-*p*-dioxin (OCDD) in 4% yield.

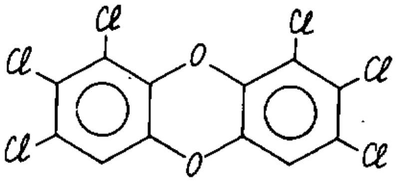
Table I. Relative Toxicity of TCDD

Compound	LD$_{50}$ mg/kg[a] Guinea pig	Rat	Mouse	Dog
TCDD[b]	0.0006	0.04	0.001	0.1
2,4,5-T[c]	470	375	370	100
2,4-D[c]	380	500	390	100
Strychnine		5	0.5	
Tetraodotoxin			0.008	
Sarin (nerve agent)	0.05		0.2	
Rotenone		130		
NaCN			10	
NaF			23	20
Parathion		10		

[a] The dose required to kill 50% of the animals. [b] Reference 2. [c] Reference *10*.



Another dioxin, 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (HCDD), has been identified as a toxic factor in chick edema disease.



HCDD

This compound presumably arises from polychlorophenols used to preserve animal hides which are subjected to hydrolysis and heating during fatty acid manufacture. The fatty acid component of chicken feed becomes contaminated with toxic polychlorinated dibenzo-*p*-dioxins and leads to flock mortality as high as 90% with disastrous results to the chicken broiler industry.

Chick edema factor or disease periodically kills millions of young chicks in the U.S. It causes a buildup of fluid in heart sac and lungs. HCDD was identified in the toxic fat of feeds responsible for the disease

Toxicity of TCDD

TCDD is acnegenic, teratogenic, and deadly toxic. Guinea pigs are particularly vulnerable —the lethal dose for an average size guinea pig is about 5×10^{-7} gram! Table I compares the amazing toxicity of TCDD with other poisons.

nm = nanometre = 10^{-9} metre

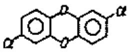
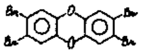
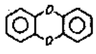
The mechanism of the systemic toxic action of TCDD is unknown. It is known, however, that TCDD concentrates mainly in the liver and to a lesser extent in the brain and fatty tissues of laboratory animals. Oral administration of TCDD to laboratory animals has caused edema and hemorrhaging in their subcutaneous tissues, intestine, and brain ventricles, and general liver injury. Death occurs anytime from one to seven weeks after treatment with TCDD.

A solution of TCDD applied daily in microgram amounts to the inner surface of a rabbit's ear causes severe acne characterized by papules, comedones, and cysts. The chloracne response is judged by the formation of comedones. Microscopically, the skin shows marked plugging of hair follicles from an abnormal increase in skin keratin (hyperkeratosis), also the basic pathological defect in human chloracne.

Structure-Activity Relationships

The extraordinary biological activity of TCDD is almost unique to its particular ar-

Table II. Activity of TCDD and Related Compounds[a]

Compound	LD_{50} (mg/kg), rats	Chloracne response	Terato-genic response	Chick edema response
TCDD	0.04	Strongly positive	Strongly positive	Strongly positive
	$>1000^b$	Negative	Negative	—
HCDD (mixture of two isomers)	$>10^b$	Positive	Positive	Positive
OCDD	$>1000^b$	Negative	Negative	Negative
	—	Strongly positive	—	—
	—	Negative	—	—

[a] Reference 3.
[b] Largest dose fed at which there were no deaths.

rangement of halogens. Other chlorinated dibenzo-*p*-dioxins are much less active or inactive (Table II). In addition, the 2,8-dichloro-, the 2,3-dichloro-, the 1,2,4-trichloro-, and the 1,2,3,4-tetrachlorodibenzo-*p*-dioxins are not acnegenic and probably not teratogenic.

Environmental Studies of TCDD

Although the use of herbicides 2,4,5-T and 2,4-D has been partially banned, mainly because of the Bionetics study, the major concern should be with TCDD and other dioxin contaminants. Fortunately, the supplier of most of the highly contaminated 2,4,5-T (≅30 ppm TCDD) no longer manufactures it.

The U. S. Department of Agriculture and other agencies have subjected TCDD to environmental scrutiny and have learned that in soil TCDD is not readily degraded, photochemically or otherwise; or biosynthesized or photosynthesized from 2,4,5-trichlorophenol; or absorbed into plants; or mobile in the soil. TCDD applied to leaves is not translocated within the plant. The most important of these facts as far as the environment is concerned is that the soil is an unreactive storage container for TCDD.

GORDON W. GRIBBLE, assistant professor of chemistry at Dartmouth since 1968, has research interests in natural product synthesis and nuclear magnetic resonance spectroscopy.

The USDA recently tested 129 samples of 17 pesticides prepared from polychlorophenols and also 20 samples of polychlorophenols for dioxin contamination. Most of the pesticide samples analyzed (76%) contained from no TCDD to less than 0.1 ppm, 15% contained 0.1 to 10 ppm TCDD, and 9% contained more than 10 ppm TCDD. 2,4,5-T samples were shown to contain most of the TCDD and only one other pesticide, silvex, contained more than 0.5 ppm TCDD. Analyses of chlorophenol samples showed more than 0.5 ppm TCDD. Higher chlorinated dioxins were present in many of the chlorophenol samples. For example, analysis of pentachlorophenol samples showed 30% contained more than 100 ppm OCDD. 2,4,5-T currently produced by Dow Chemical Co. contains fewer than 0.5 ppm TCDD.

Human Health and TCDD

A direct relationship between TCDD and chloracne is clear. TCDD's effect on laboratory animals has been established. But no relationship between 2,4,5-T and/or TCDD and human birth abnormalities has been found, despite studies of the 5 million acres of South Vietnam sprayed from 1962 to 1969 with 60,000 tons of 2,4,5-T.

Research is needed to determine the effects of 2,4,5-T TCDD, and related compounds on human health. As future studies unfold, decisions can be made regarding the proper role of these chemicals in our society. Ω

Suggested Reading

(1) Aaronson, T., *Environment*, **1971**, 13 (7), 21.
(2) Abstracts, Chlorodioxin Symposium, 162nd National American Chemical Society Meeting, Washington, D.C., Sept. 17, 1971, Pesticide Division.
(3) Collins, T. F. X., Williams, C. H., *Bull. Environ. Contam. Toxicol.* **1971**, 6, 559.
(4) Courtney, K. D., Gaylor, D. W., Hogan, M. D., Falk, H. J., Bates, R. R., Mitchell, I., *Science*, **1970**, 168, 864.
(5) Friedman, L., Firestone, D., Horwitz, W., Banes, D., Anstead, M., Shue, G., *J. Ass. Offic. Anal. Chem.*, **1959**, 42, 129.
(6) Kearney, P. C., presentation before the Council on Environmental Quality and President's Cabinet Committee on the Environment Working Group in Pesticides, Washington, D.C., Nov. 5, 1970.
(7) Pohland, A. E., Yang, G. C., *J. Agr. Food Chem.*, **1972**, 20, 1093.
(8) Poland, A. P., Smith, D., Metter, G., Possick, P., *Arch. Environ. Health*, **1971**, 22, 316.
(9) "Report of the Secretary's Commission on Pesticides and Their Relationship to Environmental Health," **1969**, pp. 665–674. U.S. Department of Health, Education, and Welfare, Washington, D.C.
(10) Rowe, V. K., Hymas, T. A., *Am. J. Vet. Res.*, **1954**, 15, 622.
(11) Sparschu, G. L., Dunn, F. L., Rowe, V. K., *Fd. Cosmet. Toxicol*, **1971**, 9, 405.
(12) Whiteside, T., "Defoliation," **1970**, Ballantine, New York, N.Y.
(13) Woolson, E. A., Thomas, R. F., Ensor, P. D. J., *J. Agr. Food Chem.*, **1972**, 20, 351.

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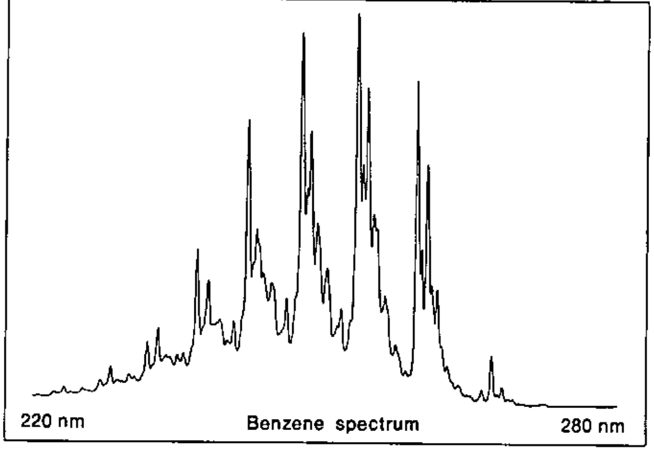

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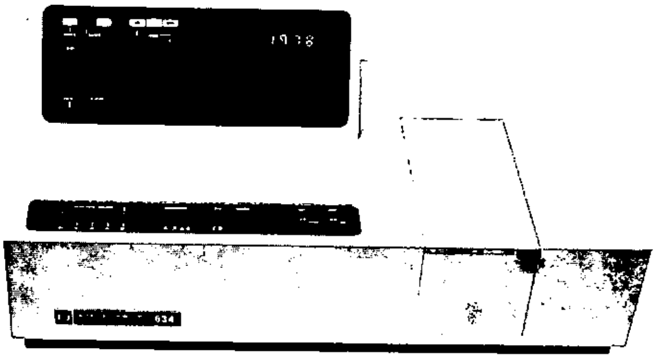

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