

# Personal Reminiscences of Forty Years of Mass Spectrometry in Australia

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If antiquity is any measure of respectability, we as mass spectrometrists belong to perhaps the world's second oldest profession, though certainly the most eminently respectable, in that the measurement of mass was probably the earliest scientific technique applied by mankind. The development of the whole of scientific knowledge since has come about due more than anything else to progressive refinements in mass measurement.

Dalton's atomic weights, Prout's hypothesis that all atoms were built of hydrogen, the masterly recognition by Mendeleev that chemical properties were periodic in mass, not long after the experiments of J. J. Thomson on the behaviour of charged atoms and molecules in electric and magnetic fields, all these are milestones in the development of our field. J. J. Thomson certainly foresaw the tremendous potentialities for chemistry in his book published in 1913 entitled *Rays of Positive Electricity and their Application to Chemical Analysis*.

Thomson's young associates, Aston and Dempster, went on, the first to build mass spectrographs, to measure isotopic masses and to discover packing fractions, leading to the knowledge of nuclear binding forces and to the exploitation of atomic energy; the second to build the mass spectrometers which were the predecessors of all our present machines.

A very early Australian involvement with mass spectrometry was made by my old chief in CSIRO, Ian Wark. As a PhD student in 1922, he wrote to Aston seeking advice on building a mass spectrograph to measure molecular ionization potentials. Aston's reply was enough to persuade him that mass spectrometry was not practicable for a chemist at that time. The letter is interesting, however, in that Aston has been given a reputation for secretiveness and unhelpfulness to others and this is sometimes quoted as a reason for the loss of interest in Britain in mass spectrometry after his time. This letter shows at least that this reputation is not wholly justified (Figure 1).

It was really only with the tremendous technological advances of World War 2 that a practical mass spectrometer was created that was suitable for chemical analysis on a routine basis. This was the Consolidated Engineering Company's CEC 21101, designed for the quantitative analysis of petroleum products.

Ian Wark had become chief of the new Division of Industrial Chemistry of the Council for Scientific and Industrial Research, CSIR, later CSIRO, at the beginning of the War (1939), and in 1944 had appointed Lloyd Rees as head of a section to be concerned with applying physical techniques to chemistry (Figure 2).

I think it must have been Ian's earlier interest in mass spectrometry which alerted him to the possibilities of this technique. It was decided in about 1946 to purchase a CEC mass spectrometer, but this proved at that time not to be a simple matter. With the beginning of the 'cold war,' the US government had embargoed the export of anything to do with isotopes and atom bombs. Clearly mass spectrometers fell into this category and it was only after an interchange at the very highest level between Prime Minister Chifley and President Truman that an exemption was made for Australia, on the grounds, as it was put: 'In the light of our nations' successful collaboration in the recent war.' A CEC 21102 mass spectrometer was brought to Melbourne from Pasadena by Graham Hercus (Figure 3). This machine was not cheap, costing around £15 000 at a time when a new PhD's salary was £600 p.a., i.e. a ratio of 25:1. It is interesting to compare this ratio with the corresponding figure today.

In 1947, Ian Wark had paid a visit to Glasgow University, where I was a PhD student completing a degree in x-ray crystallography. Ian painted a glowing picture of his new laboratory at Fishermans Bend, a picture reinforced for me by Geoff Badger, a young Australian ICI Fellow working in the Organic Chemistry department at Glasgow, who showed me a book of photographs of sunlit Australian beaches. I applied for a job, was accepted, and set sail for Australia in 1948. Before I left, I was sent to visit a physicist at the National Physical Laboratory, Teddington, a Dr Barnard, I think one of the very few men in Britain at that time who had built his own mass spectrometer. It was a depressing visit. His machine was in bits, he told me that mass spectrometers were usually in this state, and strongly advised me to repent, and turn back before it was too late and I had embarked on a lifetime of disasters and despair. I think, looking back on it, that I caught him on a bad day. Mass spectrometrists sometimes do feel like that, but fortunately not quite all the time.

My coming to Australia was, I think, fore-ordained, in that on the back of my birth certificate, issued in Glasgow in 1924, it stated that 'any attempt to alter the document rendered the person so doing liable to up to 7 years' transportation.' I swear I didn't do it, but I am now just completing my 6th term. The Scots are an economical race, I guess that pile of forms they used for me must have been printed in 1830.

My brief, as a new young research officer of the Commonwealth, aged 24, was to see whether a mass spectrometer could be of any use in chemistry. In 1949, mass spectrometers had not been used for qualitative

TRINITY COLLEGE  
CAMBRIDGE  
Jan 27<sup>th</sup>/22

Dear Mr Wark

In answer to your letter of yesterday I think that a 12" coil will be ample for your purpose 50,000 volts should not strain it severely even with one pole earthed. I never used more than 50,000 volts generally less than 40,000. It is quite possible to get good mass spectra with 20,000. The essential pump is a Gaede rotating mercury pump. To get the 'fore-vacuum' for this a filter pump will do though a oil pump is better. You evidently misunderstood me as regards magnetic field. The highest I ever used is the figure you mention 15,000 gauss with circular pole pieces 4 cms radius and 3 mm apart. This is for a deflection of  $\phi = \frac{1}{3}$ " and is not enough for atomic weights  $> 200$  unless the potential is low say 25,000 volts. If you cannot put H up you will have to be content with a smaller  $\phi$  as you want to work with heavy particles. You can work out the quantities quite easily from the simple  $=^{ns}$  of motion if you put in the values of the constants for Kay and Laby. A lot of information will soon be available in a paper by Fowler and myself to appear in the Phil. Mag. and my book on 'Isotopes' coming out in March (Edward Arnold).

I should think dry cells will do if they are kept at constant temp. during the exposure. You will want 200-500 volts about.

Wishing you every success

Yours sincerely

F. W. Aston

Trinity College  
Jan. 27th/22

Figure 1. Letter from F. W. Aston to Ian Wark (original in the archives of the Australian Academy of Science):

analysis, only almost exclusively for quantitative analysis of hydrocarbons in refinery samples.

It was beginning to be evident that the mass spectra of organic molecules were unique fingerprints, so in collaboration with Adrienne Clark of the CSIR Division of Food Preservation and Transport at Homebush, near Sydney, Graham Hercus and I tried to analyse the vapour given off by apples in cold storage. Apples breathe, and it was suspected that a bad apple infected others in its vicinity by its halitosis. We collected the breath of a Granny Smith in a cold trap, ran its mass spectrum and were able to publish a short note showing that this consisted of a mixture of ten olefins, esters and aldehydes, which we identified.

We also did some quantitative analysis, on the effluent from the new catalytic crackers in the oil refineries just being established at Geelong, near Melbourne, by Mobil and Shell. This was a wearisome task. It involved

evaluating  $8 \times 8$  determinants, each of which took a week to carry out on a desk calculator.

At about the same time, in the early 1950s two very hardy pioneers, Ian Lauder at the University of Queensland and Peter Jeffrey at the University of Western Australia, had almost single handedly embarked on the construction of their own mass spectrometers, Ian with the aim of using oxygen isotopes as tracers in the study of reaction mechanisms and Peter for geological age determination (Figures 4 and 5). It was a truly tremendous achievement then that both were successful. Other machines had been projected, at Melbourne University in the Department of Physics by a Dr Bird, and in Chemistry by a student of Professor Buchanan, but so far as I know neither of these was ever completed.

It perhaps needs to be emphasized that in those days, and for the next 10 years with a very few notable exceptions, in Australia, as in the USA and in the UK, mass

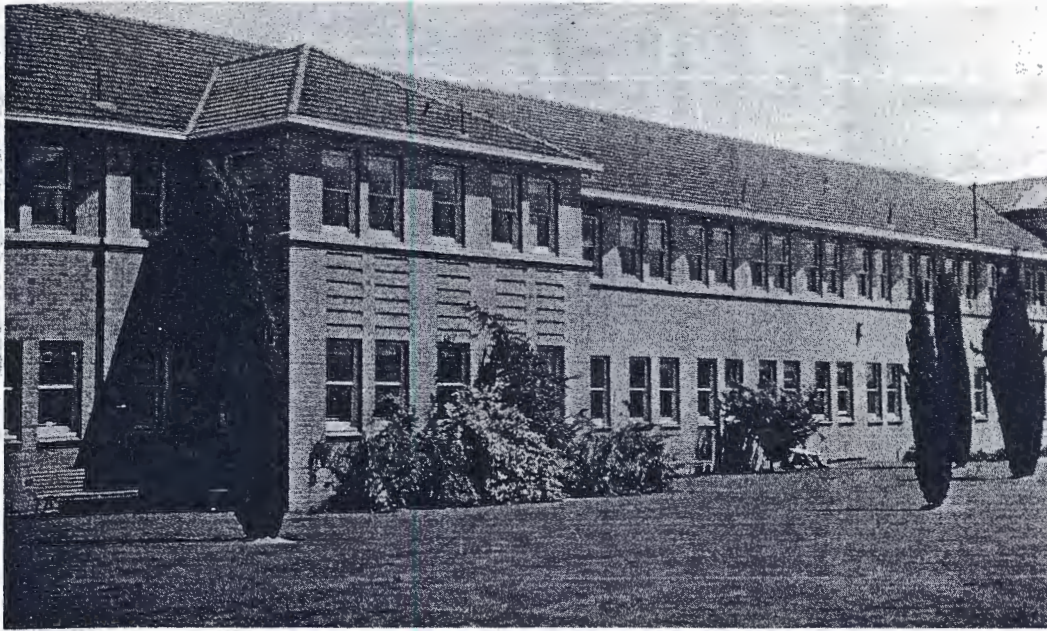


Figure 2. The laboratories of the Division of Industrial Chemistry, CSIR, Fishermans Bend, 1949.

spectrometry was almost totally ignored by university chemists.

Almost at once I had become fascinated by the way molecules fall apart in the mass spectrometer under electron impact to produce a mass spectrum. By varying the energy of this electron bombardment, and determining the threshold energy at which a given fragment appeared, this seemed to offer the possibility of directly measuring chemical bond strengths. It was soon apparent, however, that the bond energies measured in this way were both inconsistent with each other and in serious disagreement with thermochemical values. It

took us quite some time to find reliable ways of interpreting our data, and in the process we learned a lot about the basic mechanisms of energy transfer from electrons, later also from photons, to molecules.

In 1952, Graham Hercus having left to become a cryophysicist, I was joined by Dr A. J. C. (Tony) Nicholson, a physical chemist whose background in photochemistry and reaction kinetics was invaluable in the interpretations we were seeking to make.

Getting data from a mass spectrometer called for better and better signal-to-noise ratios, and in 1953 I built what was certainly the world's first electronic mass

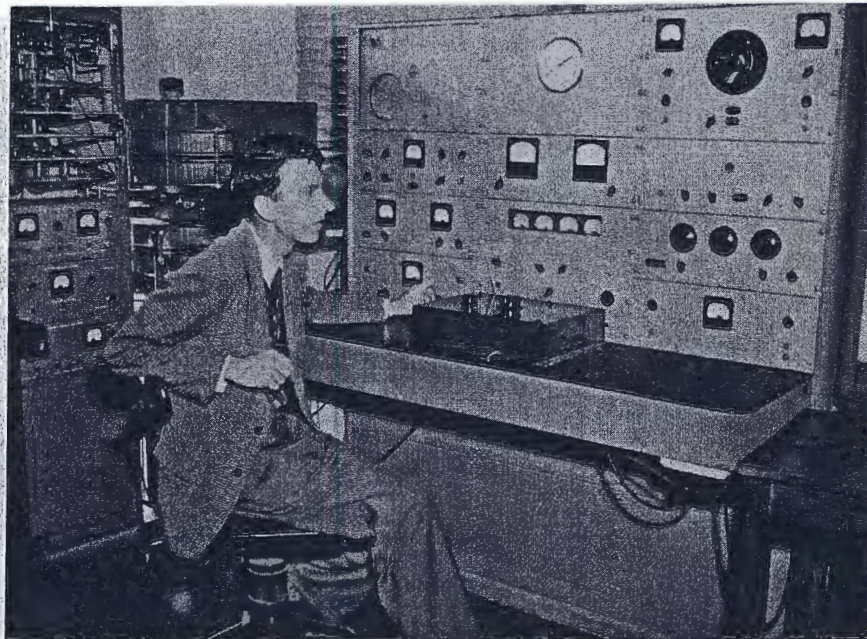


Figure 3. The CSIR CEC 21102 mass spectrometer with the author, 1949.

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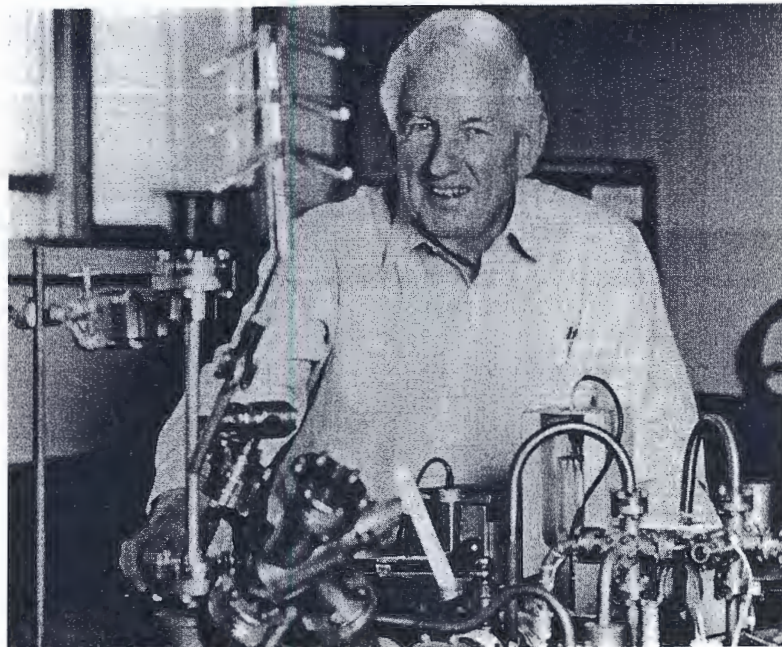


Figure 4. The late Dr Peter Jeffrey, University of Western Australia.

spectral digitizer. It consisted of an A/D converter, using thyratrons and flip-flops to form a sawtooth generator, a comparator, gating a pulse generator into a counter, feeding a string of neon bulbs which were photographed by a moving film camera. It produced a six-bit binary number every one-third of a second. It worked fairly well, but unfortunately there were no computers then to make any use of our data, and reading binary numbers by eye from 35-mm film was just too tedious (Figure 6).

I remember it particularly also because the only way we could get it to work was by wiring the library in-basket into the circuit. In those days, we had the luxury

that charming young ladies from the library brought around to each laboratory the latest journals for circulation every morning. I was called up before the chief librarian, who seemed then a ferocious elderly dragon (I think now she was probably about 48 years of age) to ask me what my intentions were in shocking one of her young ladies.

The manual for the CEC 21102 recommended that a dime be placed on the magnet as an offering to the gods, before switching on the mass spectrometer, in the pious hope that the source temperature controller should not burst into flames at an inopportune moment. The filament regulator emitted a 1000-cycle

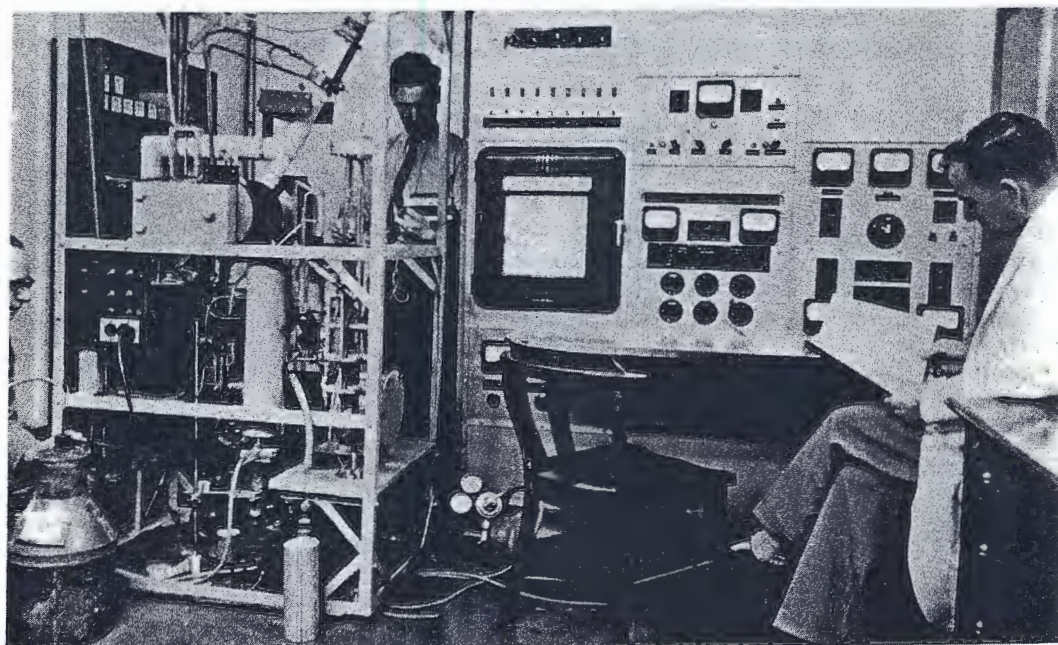


Figure 5. Right foreground, Dr Ian Lauder, University of Queensland, ca. 1950.

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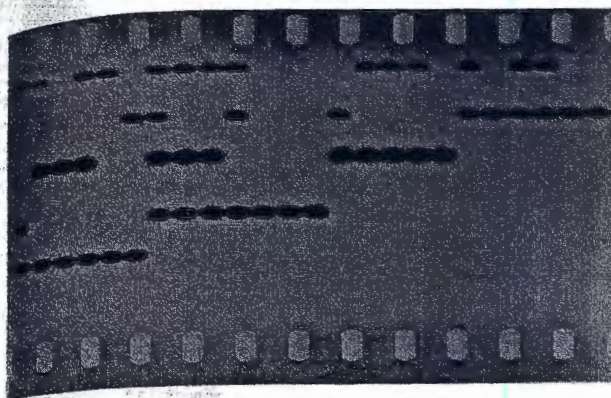


Figure 6. Output of the first primitive all-electronic signal digitizer recording a segment of an ionization efficiency curve, 1953.

whine to which one became very sensitive. The slightest change in its note implied a change in the filament's health, and replacing a filament was a major and nerve-racking task. New filaments had to be conditioned with a magic treatment using butene and butane, lest they became 'gas sensitive'. Almost at once, we had to disconnect the protective interlock on the cabinet doors, which prevented them from being opened when the high voltages were turned on. I think sometimes we spent more time inside the cabinet than outside it. Yet another hazard was that the glass vacuum envelope for the CEC 21102 had one end sealed off with a metal plate which was stuck on with black wax, and we lived in dread on hot days of this melting and sucking in.

Ions were detected with a selected 38 tube energized by a trickle-charged car battery and had a signal detection threshold of  $10^{-13}$  A. This situation improved slightly in 1953, with the arrival of the Applied Physics vibrating reed electrometer, lowering the detection threshold to  $10^{-16}$  A. Research was a constant struggle to improve signal-to-noise ratios. I built many analogue signal-averaging devices using the then newly introduced low-leakage polystyrene capacitors and acquired a keen interest in Information Theory.

I had acquired another colleague by this time, Dr Fred Dorman. Fred suffered from deafness, and used a hearing aid, but neglected to keep its batteries in good condition, so that communication was sometimes not always as reliable as one might wish. I well remember on one occasion being inside the back of the mass spectrometer cabinet, and asking Fred, who was at the console, 'Is the HT off?' On his replying, 'yes', I was surprised to see bright sparks jump on to the tip of my soldering iron. Going round to the front, I found the ion accelerating volts on, and Fred happily trying to find the water ion at mass 18.

In 1956, I was very fortunate to be awarded a Commonwealth Fund Fellowship, which took me for a year to the University of Chicago. Here, I encountered a remarkable man, to whom I want to give particular credit. The contribution of Professor Mark Inghram to the development of the whole field of mass spectrometry has been much underrated, and almost forgotten today.

The mass spectrometers of the early 1950s in general were temperamental, either fragile creations of glass and black wax, or rather messy affairs of copper and brass tubing and greasy rubber gaskets. Diffusion pumps used

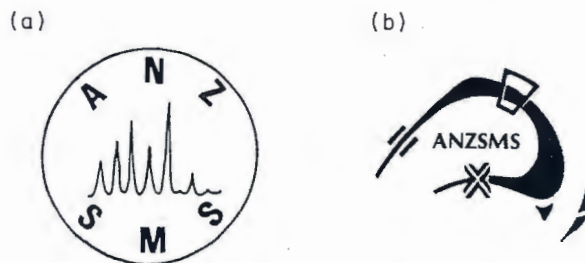


Figure 7. Left, the first logo of the Australian and New Zealand Society for Mass Spectrometry, devised by A. J. C. Nicholson, 1971; right, the present logo, designed by L. P. Johnson, 1988.

usually mercury as a working fluid, and had a speed of about  $10 \text{ l s}^{-1}$ . Liquid air, a pale blue liquid liable to explode if any organic solvent fell into it, had to be used to trap the mercury vapour. Q-compound, a kind of black plasticine, was used to seal leaks. I expect that few young mass spectrometrists of today would recognize the original logo of ANZSMS, the mass spectrum of the mercury isotopes. This was always present in every mass spectrum at  $m/z$  values around 102 and 204, and not only confirmed that one's instrument was working, but also gave useful mass markers (Figure 7).

In 1956, Inghram was the supreme mass spectrometer builder. In the same way that Augustus came to Rome, finding it a village of wooden house band unmade muddy streets, and left it with magnificent marble buildings and temples and splendidly paved roads, Mark came to a mass spectrometry of glass, black wax, rubber gaskets, silicone varnish and Q-compound, and dubious vacua of  $10^{-6}$  Torr, and left it with argon-arc welded inconel vacuum chambers, gold gaskets, glass to metal seals and single ion detection, at a routine working pressure of  $10^{-9}$  Torr (1 Torr = 133.3 Pa).

Mark was a great do-it-yourselfer. We had decided to build a photoionization mass spectrometer, and when the time came to connect the cooling water, there was no outlet from the water supply in the laboratory, nor any convenient way to turn it off at a main. We discovered, however, that if we went into the nearby lavatory on that floor and turned on all the taps, and kept flushing everything repeatedly, the pressure could be reduced sufficiently for Mark to cut the pipes with a hacksaw, and install a T-junction and outlet. Unfortunately, while I was in action, flushing madely, Robert Mulliken came into the men's room wishing to use the facilities and it took quite a bit of explaining later to convince him that I had not finally found America a bit too much for me.

I believe that the laboratory I was given at Chicago had been in fact Dempster's old laboratory, and I very nearly achieved another kind of distinction. On a table near the window was a heap of brass plates, stuck together with black wax, a few wires and a roughly made electromagnet. I decided I needed more room, so had loaded this on to a trolley to be collected as garbage. Luckily Mark saw it, and pointed out in some distress that this was Dempster's original mass spectrometer. I believe it is now in the Smithsonian for safer keeping.

People nowadays talk proudly about the sensitivity of their mass analysers and their ability to run femto-



Figure 8. A visit to some hardy American pioneers in the application of mass spectrometry to coal research, US Bureau of Mines, Pittsburgh, 1957 (left to right: A. G. Sharkey, R. A. Friedel, J. L. Shultz and the author).

gram samples, but in fact in 1956, Hans Hurzeler and I had achieved a mass spectrometric identification of a single molecule. Inghram was one of the very first to use electron multipliers as ion detectors—we made them ourselves from a specially prepared alloy of 2% magnesium in silver and they required a most elaborate activation. They did allow the detection of single ions, with background counting rates as low as 1 in 10 min. Hans and I found that if we connected the output of the multiplier and its amplifier to an audio amplifier, hence to a small loudspeaker placed in a tin bucket, standing on a brick, and we then focused on the mass 79 peak, a mixture of bromine and pyridine in the inlet gave a sound like 'bing, bing, boing', etc. The 'bing' sounds were the bromine ions, the 'boings' were the pyridines, as we proved by turning one of the samples off. There is in fact a good scientific reason for this—polyatomic ions produce significantly more secondary electrons than monatomic ones do.

This stay in the USA was for me the beginning of long-standing friendships with very many mass spectrometrists, those who attended the meetings of what was then called the ASTM Committee E14, but which subsequently became the American Society for Mass Spectrometry, also the beginning of a connection with the University of Utah which has continued to this day (Figure 8).

On returning to Australia in 1957, I immediately embarked on building another Inghram-type machine. The Broken Hill Proprietary (BHP) steel company were able to make a very pure magnet iron for me. There was a minor drawback in that I had to take it in 5-tonne ingots, because they could not make less than a full crucible. We sawed it into 1-tonne blocks, and had it machined to form the magnet yoke pieces in the Victorian Railways' workshops, the only place with lathes and shapers large enough to handle the pieces. The pieces of iron left over we buried at the back of the laboratories at Fishermans' Bend. I having read some-

where that the magnetic properties of iron improved by keeping it in this way. Regrettably we forgot later just where we buried them (Figure 9).

Our group in Chemical Physics had begun a very happy collaboration with the Dairy Section of CSIRO,

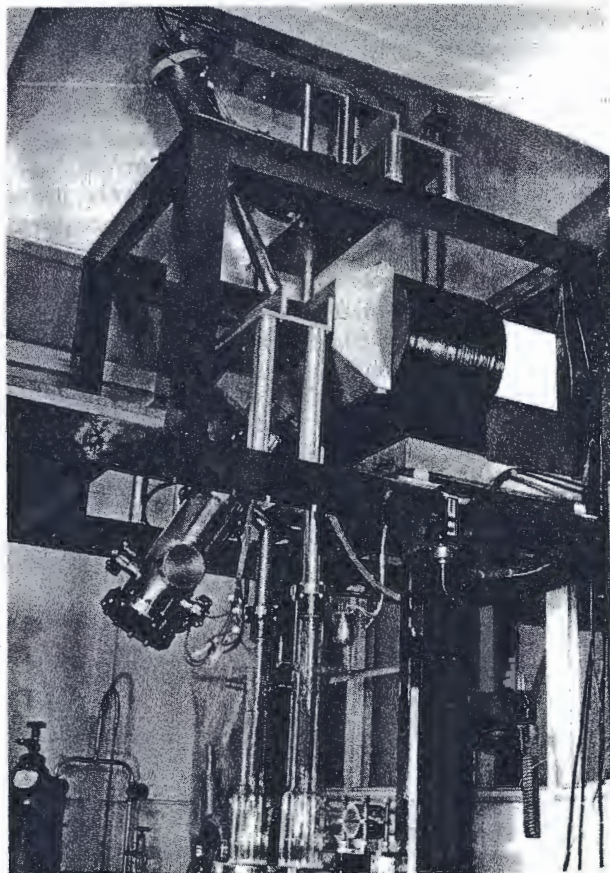


Figure 9. Inghram-type mass spectrometer constructed in Melbourne, 1957-58.

David Forss, B. Ramsdell, and Inghram-type machine section built for this work.

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In 1962, Occolowicz Laboratories an excellent mass spectrometry chemists in Occolowicz 1963, and I in the USA. University of Boulder and (days, with them to think I can I needs.

Keith Morrison section at CH4, which interfaced using a Whitten Atomic I. This time I think an the Dept. National lead isotope acquired Compton embark fromete and ma. In 1961 Should originate by the the air and g

David Forss, Bill Stark, Gerda Urbach and Eric Ramshaw, and in 1959 we built a second similar Inghram-type machine for them. Later Bill Fock of that same section built a monopole also in our laboratory for this work.

It was only in 1959 and the early 1960s that commercial mass spectrometers began to appear in any variety, and users in Australia had been convinced to buy them. These were the Metropolitan Vickers series MS2, MS3 and MS10 and also the Atlas CH4. The first, an MS2, went to the University of New South Wales in 1959, and was shared by Jim Green and Jack Garnett, for work in radiation chemistry. This machine was long kept going by a most unusual personality, Lt Commander Jim Mason, ex-Royal Navy. About the same time Jim Shannon at the CSIRO Coal Research section acquired a CH4, a most impressive machine looking from the front somewhat like the controls of a submarine. I believe that the Atlas company was in fact set up by some ex-submariners. Jim subsequently took this machine with him when he went to the CSIRO Division of Entomology, Canberra. Apart from his work on coals, Jim and his colleagues made outstanding advances in understanding the mass spectra of coordination compounds.

In 1962, Dick Gillis, Geoff White and John Occolowitz installed a CH4 in the Defence Standards Laboratories at Maribyrnong in Melbourne. They were an excellent combination and did much to popularize mass spectrometry by helping many other organic chemists in the country with their problems. John Occolowitz went on the Klaus Biemann's laboratory in 1963, and later ended up with the Eli Lilly Company in the USA. Another CH4 was installed in the University of Queensland at St Lucia, operated by Ian Lauder and Geoff Woods, jointly for Physical Chemistry and Geology. It was a common mistake in those days, with the high cost of the instruments, to expect them to cover a wide range of different tasks, and I think Ian had a difficult job reconciling these conflicting needs.

Keith Murray had joined CSIRO Food Research section at North Ryde at that time, and also acquired a CH4, which he with Frank Whitfield subsequently interfaced to a gas chromatograph in the late 1960s using a spiral separator of their own design. Neil Whitten and Harold Woodward at the Australian Atomic Energy Commission at Lucas Heights had by this time acquired a number of machines, an MS5 and I think an MS7, for solid sample work. John Richards in the Department of Geophysics in the Australian National University long operated an MS2, measuring lead isotope ratios in lead tetramethyls, and later they acquired a Nuclide Inghram-type machine, run by Bill Compston, a student of Peter Jeffrey. Bill later embarked on the construction of a very large mass spectrometer, which is now the basis of an ion microprobe, and may be marketed commercially in the near future.

In 1962, I was fortunate on a visit to meet Ken Shoulders at Stanford Research Institute, Ken being the originator of the EAI quadrupole. I was very impressed by the simplicity of quadrupoles and on my return, with the aid of my colleague Don Swingler, we had built one and got it working ourselves in about 2 weeks. The



Figure 10. Monoenergetic electron impact ion source used in the Melbourne machine, 1958.

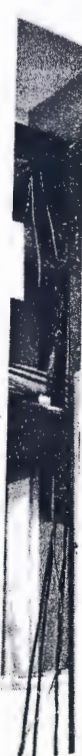
speed of mass scanning possible with this allowed us to record repetitive mass spectra at the rate of 50 spectra per second on magnetic audio tape. Harry Bloom at Tasmania, after sending his student John Hastie to try out a Knudsen cell molten salt ion source on our machines, a little later acquired an EAI 300 quadrupole mass spectrometer, and used it very successfully for this type of work.

In my own work, I had been trying for years to obtain monoenergetic electrons, to study ionization efficiencies (Figure 10). In 1959 I conceived the idea of removing the effect of the energy spread from our data analytically, and with my x-ray background developed a Fourier method which I called 'deconvolution'. My first attempts were carried out using Beavers Lipson strips, a simple paper device used in those days by crystallographers to carry out Fourier summations with the aid of a desk calculator. Luckily, almost at once I discovered CSIRAC, one of the very first computers in Australia, an all-electronic valve machine built by CSIRO in 1950, and which had been transferred to the Physics Department at Melbourne University. This computer possessed all of 1K of mercury column delay line memory and was programmed in binary code. I will never forget the pleasure with which a calculation taking hours by hand could be done in 5 min. The technique of deconvolution worked but, to my surprise, on publishing it, I found that very few would believe that the process was possible. I think it seemed a little bit

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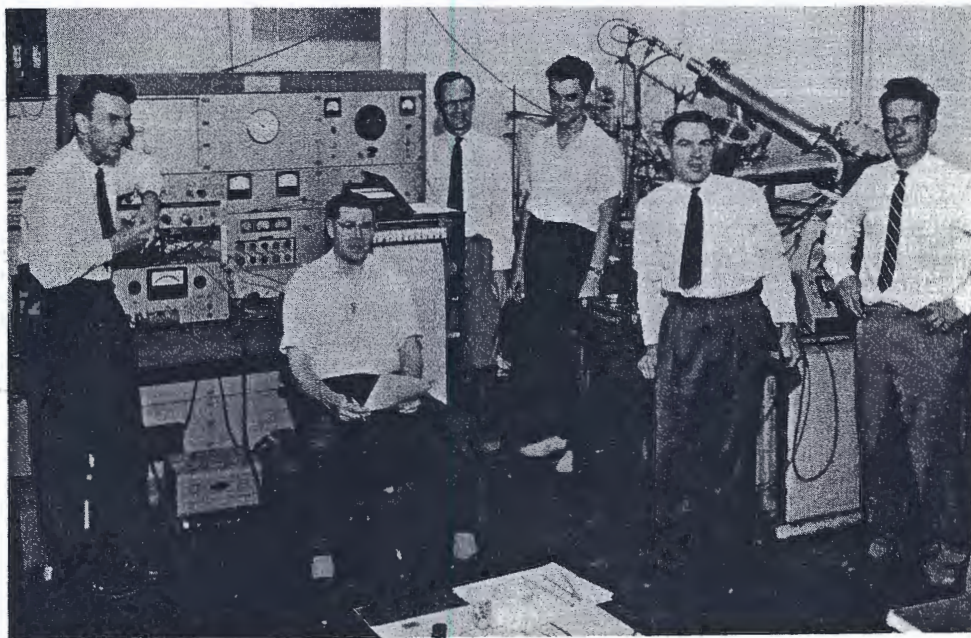


Figure 11. The mass spectrometry group in Melbourne, 1962 (left to right: J. D. Morrison, F. H. Dorman, A. J. C. Nicholson, P. Marmet, D. Swingler and R. Goodchild).

too much like breaking the first law of thermodynamics.

I am happy to say that these days deconvolution is a highly respectable technique, used to enhance resolution in all sorts of ways. Fourier transforms have become fashionable and it has led to the development of the fast Fourier transform routine where today one can even buy a dedicated chip for this purpose. This is not to say that some dreadful crimes of subjectivity are not still being committed in the name of 'deconvolution'.

A little later, in 1961, Paul Marmet from Laval University in Canada spent a year with us, and we successfully built the monoenergetic electron ionization source which he had devised into one of our mass spectrometers (Figure 11).

In the early 1960s computers more like modern ones were just beginning to appear. Fortran was invented and we had first the IBM 1620, with 4K of memory, then an Elliott 503 with 8K, and I with a young colleague, Lindsay Crawford, decided to explore the potentialities of computers for the identification of mass spectral patterns in a catalogue, then for identification of molecular class and finally, using a computer intelligence *ab initio* approach, to determine a molecular structure from a mass spectrum directly. A year at Princeton in 1964 gave me access for the first time to what was then a really large computer—it had 32K of memory. All of these approaches proved surprisingly promising, and became particularly relevant when we were at last able to interface a gas chromatograph with a mass spectrometer. We found that a number of organic mass spectrometrists had published logical interrogation schemes for interpreting spectra, and we turned these into computer subroutines which we labelled with their authors' names. It is nice to think that they thereby attained a kind of immortality. Whenever the computer encounters an aromatic hydrocarbon, it says to itself Call Meyerson, Call Gillis, or for a ketone, Call McLafferty, whereupon they come out of

memory, do what they can, and return their results to the main program.

About this time also, as a result of a bet that we could not do it, we had converted the old CEC 21102 to measure very precise oxygen isotope ratios, and Fred Dorman was able to prove that in the Oligocene period the state of Victoria was 10°C warmer than at present. Fred did not trust electronics, and believed only in batteries. We all treated his highly lethal battery boxes with great respect.

In 1967 I joined La Trobe University as Foundation Professor of Physical Chemistry. My colleague John Smith came with me from CSIRO, and we decided to build an instrument especially dedicated for the analysis of traces of volatiles, a gas chromatograph combined with a mass spectrometer and the whole of which would be computer controlled. To make it easier to access both the ion chamber and the multiplier we decided to change over to a horizontal layout. We had already found that the solid iron magnets which we customarily used could not be made to scan the mass scale rapidly enough owing to eddy currents in the yoke. Rapid scanning was essential when using capillary gas chromatographic columns, so we designed a laminated magnet to overcome this eddy current limitation. This proved very successful and I think we were the first to do this. This magnet, consisting of many interleaving segments, weight about 1.5 ton. We also gave up the idea of using a carrier gas separator, as was common practice at that time, instead putting a very large diffusion pump on the source region which was capable of taking the whole carrier gas flow.

This machine, completed in 1969, was also one of the first anywhere to use a computer, a Digital Equipment Corporation PDP9, both for its control, and for data acquisition and processing. It is still, with many computer updates, happily working away on the Aboriginal Pharmacopoeia project. In 1970, this machine was

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housed in a basement laboratory, and with its computer suffered the ultimate indignity one night of being totally submerged in muddy flood water. By a mammoth effort, and the help of the Royal Australian Air Force (they were experts at dehydrating jet fighters which had ended up in the ocean), it was completely dismantled, cleaned, washed and dried, and then put together again, except that one computer module was left over and we just couldn't see where it ought to have gone. However, on turning on the computer, it seemed to perform just as well as ever. This computer ended up in a DEC museum, and is quoted as an example of the reliability of their products.

By the middle to late 1960s, with the advent of the MS9, the MS12, the MS30, the Perkin-Elmer-Hitachi RMU4 and 6 and a number of quads, many of these machines had become installed in the Australian National University, CSIRO Division of Entomology, Monash University and the Universities of Melbourne, Sydney and New South Wales. They were being applied to a wide variety of tasks by John MacLeod, Jim Shannon, Colin MacDonald and Mike Lacey, Sid Middleton, Quentin Porter, Ken Cavill and Alex Robertson, just to pick out a few. Jim Shannon was appointed as the Australian Editor of Organic Mass Spectrometry. A particularly active group with John de Laeter started also in West Australia at the Waite Institute, now Curtin University, mainly working on geological problems.

At La Trobe University our first horizontal machine having proved very convenient and easy to get at, John

Traeger now built a smaller machine of this type combined with a vacuum UV monochromator and dedicated to photoionization mass spectrometry (Figure 12).

One of my first students, Geoff Dromey, who had greatly extended the earlier work on deconvolution, became so enamoured with the multitude of possible applications of computers to mass spectrometry that he is now Processor of Computing Science at Griffith University.

The 1970s opened with the realization that mass spectrometry was going to become an increasingly powerful tool in tackling biomedical problems. Bert Halpern set up a very successful quadrupole machine for this purpose at the University of Wollongong, and not very long after Alan Duffield established an active group at the University of New South Wales. Another of my students, Les Johnson, after building electron velocity selectors for ion energetics, went on to set up a mass spectrometric service for drug detection at the Royal Brisbane Hospital.

Our workshop in Physical Chemistry at La Trobe had gained by now considerable experience in building mass spectrometers, both magnetic sector instruments and quadrupoles. In 1975, Peter Derrick joined La Trobe University, and he and I embarked on the project to build a large, 1-m magnetic radius, double-focusing, reversed-geometry machine. This machine took some 3 years to build. It had an 8-tonne laminated magnet, and altogether would never have been completed without the dedication and skill of our workshop, particularly of our workshop manager, Mr John Chippindall, and the

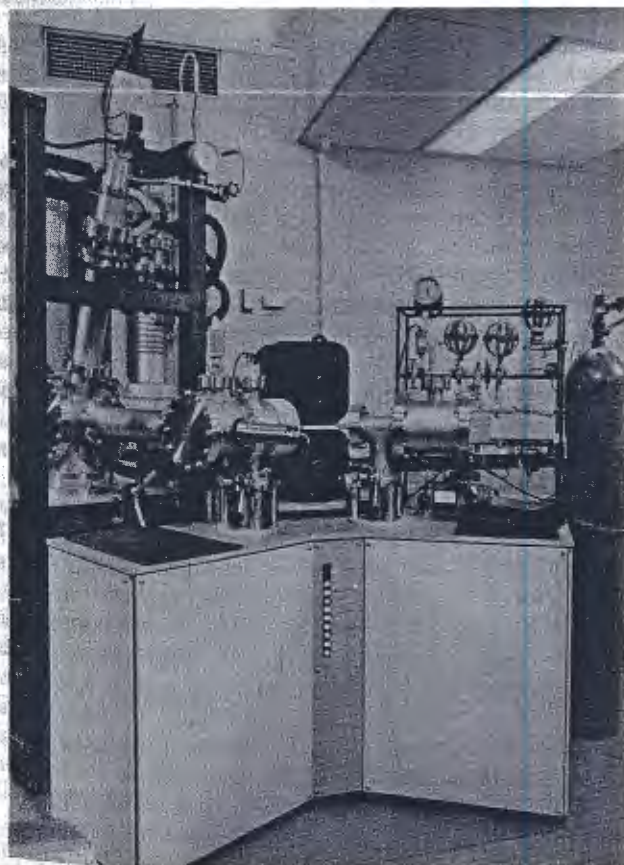


Figure 12. Photoionization mass spectrometer built by J. C. Traeger, La Trobe University, 1974.

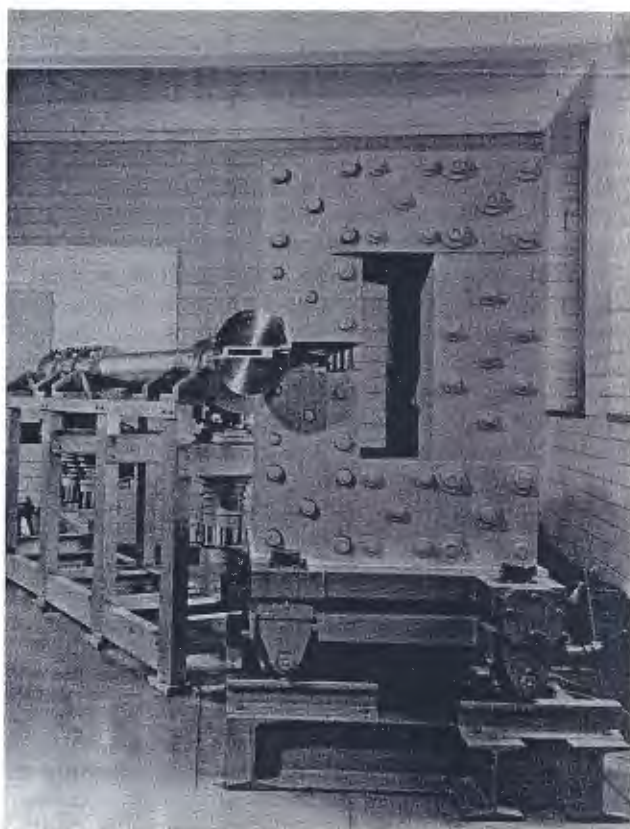


Figure 13. The grand-scale mass spectrometer at an early stage of construction, showing the 8-tonne laminated magnet.

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assistance of the Bendigo Ordnance works and many other workshops in Melbourne (Figure 13).

This machine proved very successful indeed for looking at larger organic ions, particularly using field desorption and fast atom bombardment (FAB)-type ion sources, which were Peter Derrick's special interest and specialty. He took the machine with him when he was appointed to the Chair of Physical Chemistry at the University of New South Wales and it has since gone to Britain with him when he took up the Chair at the University of Warwick. In 1976, a special stimulus to our work came from an extended visit to our laboratory by Fred McLafferty.

A most important development in Australian Mass Spectrometry took place in August 1971 at Macquarie University, with the inaugural meeting of the Australian Society for Mass Spectrometry (ASMS), largely brought about by the enthusiasm of Tony Aspinall, Barry Batts, and Peter Greenhalgh. At this first meeting, on the motion of Jim Shannon, the name was changed at once to ANZMS, to include the mass spectrometrists of New Zealand. The list of participants at this meeting is a veritable 'who's who' in Australian and New Zealand mass spectrometry, and very happily almost all of those who were there then are still active in the field.

ICR machines were not popular in Australia in the 1970s. So far as I know there were only three, one with John Bowie in Adelaide University, doing very nice work on negative ions, one with John MacLeod in Canberra and the other with Trevor McAllister in CSIRO in Melbourne studying reaction kinetics.

Until 1971, we had always designed ion lenses, ion sources, etc., by art rather than by science. Having built a computer graphics set-up by that time, we gradually developed a suite of programs for electrostatic potential and charged-particle trajectory calculations. This was gathered together and greatly improved by a major effort on the part of Don McGilvery, under the name of SIMION. It has proved invaluable to us in the design of electron and ion optical systems, has spread slowly round the world and now finds wide application.

In 1973, I had become very interested in the possibility of examining directly the structure of ions by trying to obtain the spectrum of an ion in the gas phase. All we knew about ion structure up to then was deduced indirectly from cracking patterns. This led us to build a linear triple quadrupole mass spectrometer, combined with a flashlamp-pumped tuneable dye laser, in 1974. In this machine, a given ion could be selected, undergo interaction with photons and any photodissociated fragment ions examined. The signals we obtained from this experiment at the beginning were very small, about one ion per laser flash, but a sophisticated data system and signal averaging gave us very respectable vibration-rotation spectra, resolving rotational structure and ultimately allowed us to make the first direct calculation of an ion structure in a given electronic state in the gas phase.

A chance happy meeting with an old friend from my time at Princeton, Professor Chris Enke, and his then graduate student Rick Yost, at an ASMS meeting in Washington led to Rick's coming to our laboratory in Melbourne, and our proving the special advantages and really unique applicability of the triple quadrupole mass

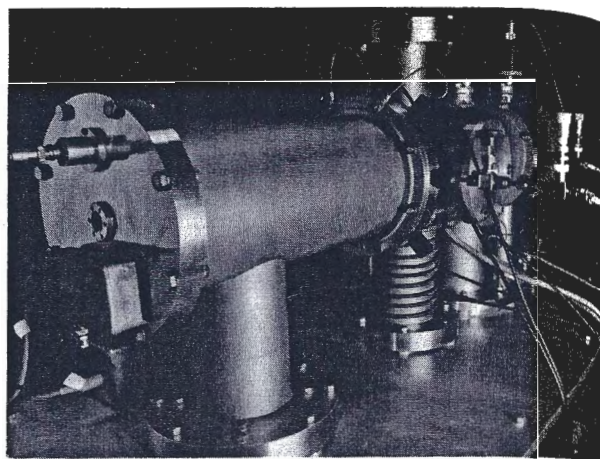


Figure 14. The first triple quadrupole mass spectrometer at La Trobe, built for laser photodissociation of ions, used by Rick Yost to prove its suitability for analytical work, 1977.

spectrometer for the tandem mass spectrometry (MS/MS) technique. This led very soon to its very successful commercial application (Figure 14).

Some 6 months later, Professor John Tedder of St Andrews, spending a sabbatical with us, found that the triple quadrupole mass spectrometer was excellent also for studying organic ion-molecule reaction mechanisms. This collaboration has led to the construction of two quinque-quadrupole mass spectrometers, one in St Andrews and one in Melbourne.

Throughout my whole mass spectrometric life, I would have got nowhere without the enthusiastic help of the men in the mechanical workshops, all real perfectionists, John Colberg at Chicago, Sid Powell and Jock Mills at CSIRO and John Chippindall, Don Balaam and John Reukers at La Trobe, also electronics experts like Don Swingler, and later Georg Haertel.

Over the years there have been some excellent instrumental contributions from Australia which deserve mention. Foremost of all I list Don Swingler, who has a most impressive list of ingenious achievements—slotted quadrupole rods, the leak detector using a Penning ionization source, the aluminium foil electron multiplier which is now marked by ETP and also a lot of clever electronics. John Richards of NSW is noted for the square-wave quadrupole, which it is a great pity has not been exploited. I would also give John Bowie special mention for his efforts in building a number of ingenious ICR cells.

Being known as a builder of mass spectrometers can sometimes get one into trouble in strange ways. In 1967, when I first joined La Trobe University, David Myers, the Vice Chancellor, an electrical engineer and ex-CSIRO man, on this basis asked me to design and build a university residential college. I approached this in exactly the same fashion as building a mass spectrometer, and in 1971, having completed it, thought I was finished with the job. He then however proceeded to put me on the spot by asking me to run it as its Master. While not a mass spectrometer, it worked very well, always full of students and always operating financially in the black. Living actually on the campus did have the great advantage that I could appear in the research laboratories in the small hours of the morning.

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The tremendous sensitivity and analytical power of the gas chromatography/mass spectrometry (GC/MS) computer had always been a source of fascination to me, and over the years led me to many unusual problems. One of these is the smell of things that shouldn't have smells, such as rocks and metals.

It has often been said metaphorically that money smells, but we found at this time that it does so literally as well. I was asked to look into the odour of bank notes, to see whether it was possible to distinguish a forgery from a real note. At that time a 'Mr One by One' as he was being termed by the newspapers, was passing one at a time, very presentable forged \$10 bills. We found, using GC/MS, that the forged notes did smell differently from the real ones, but unfortunately they caught the perpetrator before we could get a mass spectrometer placed into every bank.

A few years ago we were approached by the New South Wales railways. They had been receiving complaints about the smell of their trains travelling from the Blue Mountains to Sydney, but surprisingly not on the return trip. Our first suspicion was the brake blocks. Heating a sample, however, gave nothing that seemed at all reasonable. However, holding the brake material on to a grindstone immediately gave a foul odour. Trapping it on a macroreticular resin, we were able to identify an astonishing collection of isocyanides.

The records of the early settlers in Victoria referred to a fish, the Eastern grayling, which was popularly called

the cucumber fish, because when caught it gave off a smell reminiscent of cucumbers. This fish was thought to be extinct. However, Tim Berra, of the Monash University Department of Zoology, found a healthy colony in the Tambo river in eastern Gippsland. He caught one fish and brought it back to the laboratory but we could find no unusual odour substance present. Finally he took liquid nitrogen in a Dewar vessel down to the stream, caught a fish and froze it at once. A headspace analysis back in the laboratory showed at once that the molecule responsible was identical with that which gives the characteristic odour to the English cucumber. It is only given off for a few seconds, and appears to be a fear or alarm substance which causes other fish in the school to flee the vicinity of the hurt or frightened fish.

I have always had a fascination for dinosaurs ever since a small boy. All the best dinosaurs are found, of course, in the Morrison formation, at the top of the Jurassic, and which has numerous exposures in Utah. In the centre of some newly cut fossil bone specimens one finds a reddish silicified deposit. Careful examination of this material with a heated probe ion source sometimes indicates the presence of small traces of porphyrins and polypeptides. It is interesting to speculate whether in fact these are remnants of dinosaur blood.

Shell middens are found all along the Victorian coastline, each consisting of a heap of shells and charcoal. For millennia before the coming of the white settlers, the various tribes are believed to have visited the beach,

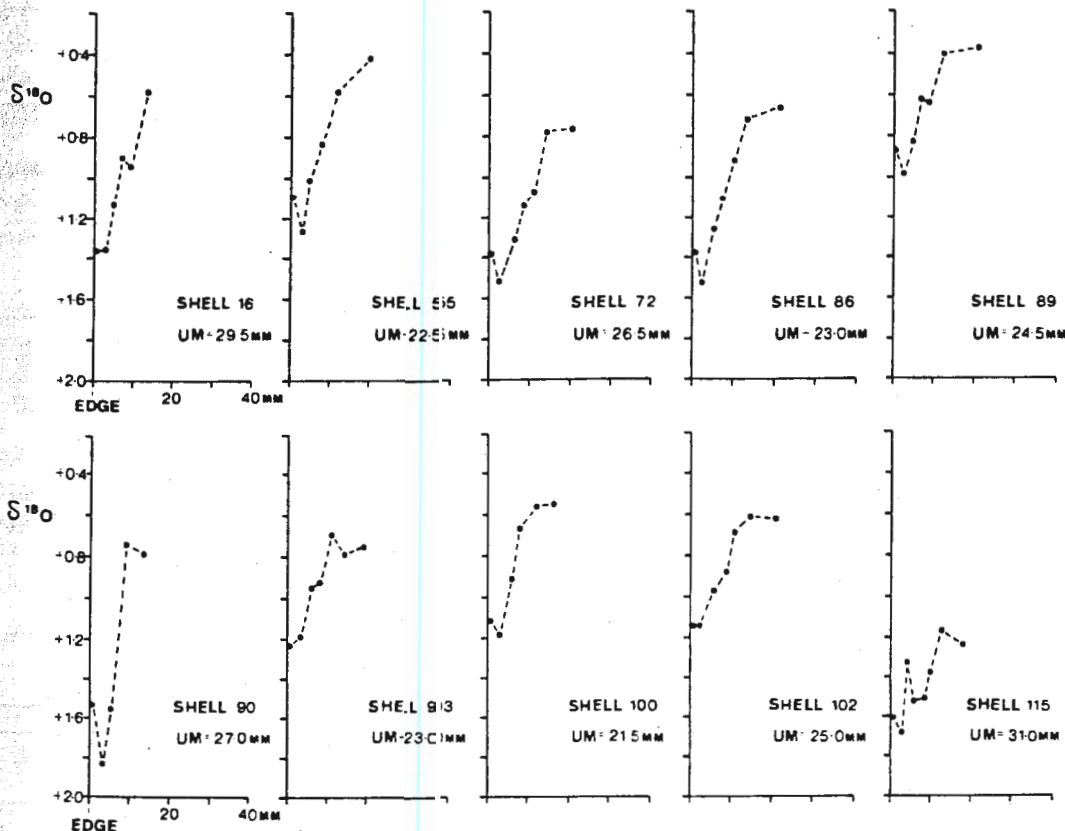


Figure 15. Plots of  $^{18}\text{O}/^{16}\text{O}$  ratio versus distance in from the growing edge for shells gathered on Aboriginal shell middens. The  $^{18}\text{O}/^{16}\text{O}$  ratio in the shell carbonate at any given point correlates with the temperature of the water in which the shell is growing at that time. The temperature at the growing edge just before death indicates that all shells died in late winter or early spring. (Courtesy of *Archeology in Oceania*, 23, 20 (1988).)



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sent the lubras (young women) into the water for shellfish, then over a camp fire eaten the contents of the shells. These middens are sometimes large, and the charcoal yields  $^{14}\text{C}$  dates going back some 40 000 years. Mr Godfrey, my latest PhD student has been examining the  $^{18}\text{O}/^{16}\text{O}$  isotope ratios in these shells. By scraping off layers from the shell very carefully, a variation in isotope ratio is found which indicates a series of summer and winter temperatures of formation, and hence indicates how old is the lifetime of the shell. In this case, to our surprise, the temperature found at the growing edge indicates that every shell, in all the middens, appears to have ceased growth, i.e. died, in the months of July, August or September. Obviously shellfish gathering was a highly seasonal business (Figure 15).

Reverting to the smell of fear, by studying student behaviour in college at examination times, I am convinced that the phenomenon of panic in humans is induced by a chemical message. It is very noticeable that fear in humans can be detected by, among others, horses, dogs and bees. Wright of the Vancouver Police Department maintains that a trained dog can detect a would-be criminal even just thinking about committing a crime. We have been trying for some considerable time to isolate this substance for mass spectral analysis. So far it continues to elude us, but with ever increasing sensitivities of detection I think it is only a matter of time before we find it.

I have been very, very, lucky indeed to have got into the field of mass spectrometry when I did. Throughout

my whole career, it has always been a source of great happiness to me to find how helpful and friendly mass spectrometrists are to each other. Also, far more so than in any other field, the field has always been so exciting. There are constantly new interests, new problems, new applications, new instruments just around the corner. I am just a little sad that there are so few new young machine builders today. Our commercial builders of mass spectrometers are first rate, but they can only meet needs that have already been defined. There has to be a demand before they will endeavour to meet it. We need to be continually finding and establishing new principles and discovering hitherto unimagined new problems.

I confidently expect that in the near future I will see molecules with molecular masses of up to  $10^6$  being analysed,† really portable mass spectrometer gas analyser sniffers about the size of a flashlamp and finally that we will prove Einstein's equation,  $E = mc^2$ , by weighing the excited states of atoms, and the chemical bonds in molecules. After all,  $1 \text{ eV} = 10^{-9}$  Dalton. This last only needs about another 20-fold increase in mass resolution over what can be achieved with the latest FTICR machines. It is time for the young mass spectrometrists to prove how much better they can do all these things than their predecessors were able to.

† I said it was exciting; this has already been surpassed. At the 1990 ASMS meeting John Fenn reported on observing gas-phase ions at masses up to  $5 \times 10^6$ .