

SPECIAL FEATURE: HISTORICAL

A history of mass spectrometry in Australia

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An interest in mass spectrometry in Australia can be traced back to the 1920s with an early correspondence with Francis Aston who first visited these shores a decade earlier. The region has a rich tradition in both the development of the field and its application, from early measurements of ionization and appearance potentials by Jim Morrison at the Council for Scientific and Industrial Research (CSIR) around 1950 to the design and construction of instrumentation including the first use of a triple quadrupole mass spectrometer for tandem mass spectrometry, the first suite of programs to simulate ion optics (SIMION), the development of early TOF/TOF instruments and orthogonal acceleration and the local design and construction of several generations of a sensitive high-resolution ion microprobe (SHRIMP) instrument. Mass spectrometry has been exploited in the study and characterization of the constituents of this nation's unique flora and fauna from Australian apples, honey, tea plant and eucalyptus oil, snake, spider, fish and frog venoms, coal, oil, sediments and shale, environmental studies of groundwater to geochronological dating of limestone and granite, other terrestrial and meteoritic rocks and coral from the Great Barrier Reef. Peter Jeffery's establishment of geochronological dating techniques in Western Australia in the early 1950s led to the establishment of geochronology research both at the Australian National University and at what is now the Curtin Institute of Technology in the 1960s.

This article traces the history of mass spectrometry in its many guises and applications in the island continent of Australia. An article such as this can never be complete. It instead focuses on contributions of scientists who played a major role in the early establishment of mass spectrometry in Australia. In general, those who are presently active in the field, and whose histories are incomplete, have been mentioned at best only briefly despite their important contributions to the field. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: history; mass spectrometry; Australia

INTRODUCTION

To the best of our knowledge, no aberrant behaviour is exhibited by ions within mass spectrometers located 'down under'. The region's significant contributions to the development and practice of mass spectrometry, however, have been recognized and well documented. Australian scientists have been quick to develop, embrace and implement the latest instrumental advances and have applied mass spectrometry to study this continent's unique natural resources. The country has a tradition of innovative discoveries in the

field, from early measurements of ionization potentials^{1,2} and isotope ratios,³ the structural characterization of peptides from natural sources,^{4,5} studies of organic anions important to reaction mechanisms and atmospheric chemistry,⁶ the first use of triple quadrupoles for tandem mass spectrometry,⁷ the development of the first simulated ion trajectory algorithm (SIMION),⁸ the construction of an early TOF/TOF tandem instrument⁹ and implementation of orthogonal acceleration on time-of-flight mass spectrometers.¹⁰ Australia has also forged an enviable reputation in inorganic mass spectrometry in geochronology,¹¹ environmental science, chemical metrology and cosmochemistry and has pioneered a number of instrument innovations including the design and manufacture of a sensitive high-resolution ion microprobe (SHRIMP).¹²

Francis Aston is known as the founder of mass spectrometry. With instruments of his own design, he studied isotopes for some 30 years in the early 1900s, pursued with the aid of

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†An incomplete history of mass spectrometry has been compiled by author Downard and appears on Australia and New Zealand Society for Mass Spectrometry (ANZSMS) web site (<http://www.anzsms.org/>). Contributions from interested persons are welcome.

several mass spectrographs.¹³ During this time, he measured the relative isotope abundances of most of the elements and made the first isotope measurements that enabled the age of a radioactive mineral to be determined by the U–Pb radioactive decay scheme.¹⁴ However, by the 1940s, Aston had predicted the demise of mass spectrometry,¹⁵ an opinion which later events in Australia and elsewhere proved to be unfounded.

It is sometimes argued that Aston left the field without a successor, and certainly the mantle fell to others including Arthur Dempster. But Australia benefited from Aston's influence in at least two ways. The first of these was Aston's advice to Ian Wark (Fig. 1),¹⁶ then a young Ph.D. student, who was contemplating building a mass spectrometer in the early 1920s.

A letter to Aston – early mass spectrometry in Australia

It is difficult to identify Australia's first entry into mass spectrometry, but as reported¹⁶ a communication between the then postgraduate student Ian Wark and Francis Aston is among the earliest documented interest in mass spectrometry. Born in Melbourne in 1899, Wark was a capable student who was offered a scholarship at the Working Men's College (now the Royal Melbourne Institute of Technology University). With a little influence from Professor David Masson, Wark studied chemistry and was awarded an Exhibition of 1851 Postgraduate Research Scholarship. He chose to take up this research at the University College London in 1921 to work with physical chemist Frederick George Donnan in what was described then as mass spectrography. This naturally involved building a mass spectrometer, but disappointingly, essential equipment needed to conduct this research failed to arrive during Wark's tenure at University College.¹⁷ He instead set about studying the chemistry of copper complexes.^{18,19} It is clear though that Wark's interest in mass spectrometry never waned so much so that he penned a letter to Francis Aston, which was received on what is now Australia Day, January 26, 1922. This was the year Aston was awarded the Nobel Prize in Chemistry for his discovery of isotopes of a large number of stable elements by means of the mass spectrograph. Aston replied the next day with advice on constructing a magnetic-sector mass spectrometer and referred to his book on isotopes that was to be published in March of that year.¹⁶ The original letter is retained in the archives of the Australian Academy of Science.

An opportunity for Wark to act on Aston's advice never materialized and he returned to Australia in 1924 accepting a lectureship in chemistry at the University of Sydney. After only a year at Sydney, he returned to Melbourne to work in the industry with the Electrolytic Zinc Company of Australia Limited on the physical and chemical principles associated with the electrodeposition of zinc.

Wark later joined the Council for Scientific and Industrial Research (CSIR; later the Commonwealth Scientific and Industrial Research Organisation, CSIRO) and in 1939 established and headed the Division of Industrial Chemistry. The Chemical Physics section within that division was he



Figure 1. Photograph of Ian Wark. Source: Australian Academy of Science.

asserted to 'have two main functions the first being to apply modern physical methods (and) techniques... including mass spectroscopy and infra-red spectroscopy'.²⁰ To achieve these goals, a Consolidated Engineering Corporation (CEC) model 21102 mass spectrometer was purchased at a cost of UK £15 000, which arrived in 1948. At the time, there were few commercial mass spectrometers on the market. CEC (now CEC Vibration Products Inc.) was formed in 1937 in Pasadena, California, by Herbert Hoover Jr, son of the former US President. The reasons for choosing this instrument over the one manufactured by the Metropolitan-Vickers Company in Manchester, England are recounted by Ian Wark in his documented history of the CSIRO Division.²⁰

The same section also pioneered atomic absorption spectroscopy in the early 1950s, a technology later licensed to Perkin-Elmer. Perkin-Elmer subsequently established a factory in Australia and also manufactured a helium quadrupole mass-spectrometer leak detector developed by Don Swingler, also of CSIRO. Wark is commemorated today by the Ian Wark Laboratories and library at the CSIRO complex in Clayton, Victoria, the Ian Wark Lecture Theatre at the Australian Academy of Sciences in Canberra and the Ian Wark Research Institute at the University of South Australia. At Curtin University, the street on which a number of mass spectrometers are located in the Department of Applied Physics is fittingly named *Wark Avenue*.

The first mass spectra and the other Jim Morrison

Before the arrival of the CSIRO's mass spectrometer, Ian Wark visited the University of Glasgow in 1947. There, with photographs of Australian sunlit beaches, he convinced Jim Morrison, a budding young student just completing his Ph.D., to join CSIR as a Research Officer and to exploit the advantages of mass spectrometry in chemical research. Wark has described the working environment at CSIR as 'utopian. Individual freedom and initiative were not only permitted, they were actively encouraged: a bold failure was more highly regarded than a cautious advance. Red tape and bureaucratic nonsense were totally absent'.²⁰ A photograph of Jim seated at the newly arrived CEC21102 mass spectrometer in 1949 has been published previously.¹⁶

It was around 1950 that some of the first mass spectra were recorded in Australia. In collaboration with Adrienne Thompson of the CSIR Division of Food Preservation and Transport in Homebush (the suburb of Sydney where the 2000 Olympic Games was later staged), Jim Morrison and Graham Hercus analysed the vapour off a Granny Smith apple.²¹ The Granny Smith is a tart green apple that originates in Australia. It is named after Maria Ann Smith (nee Sherwood) (1799–1870) who, somewhat by accident, grew the first apple in 1868 in her orchards in what is now the Sydney suburb of Eastwood. Maria had arrived with her husband Thomas and five children from England in 1839. By 1856, the Smiths had ten hectares of good farming land, which they used to grow fresh produce for the Sydney market. Maria had worked as a midwife in the township earning her the nickname 'granny' before she took over the orchard upon the death of her husband.²²

The mass spectrum of the apple volatiles was published in a tabulated form in 1951 and revealed prominent ions indicative of the presence of esters ethyl and propyl acetate, propionate, *n*-butyrate and *n*-valerate.²¹ These findings were later confirmed in separate GC–MS studies.²³ Impressed by the many capabilities of mass spectrometers, Morrison contributed an article to the Royal Australian Chemical Institute (RACI) journal in the same year explaining the virtues of mass spectrometer for chemical applications including the determination of bond energies.²⁴

Oliphant from the Cavendish to Canberra

Aston also had a hand in the initiation of mass spectrometry studies in Western Australia through his interactions with Adelaide-born Marcus (Mark) Oliphant. Oliphant graduated from the University of Adelaide in 1929 and undertook his postgraduate studies toward a Ph.D. in Cambridge supported, like Wark, by an 1851 Exhibition Scholarship. He presented a research plan to study the effect on metal surfaces by the bombardment of positive ions, under the then Director of the Cavendish Laboratory, Ernest Rutherford. This topic was probably of more interest to Rutherford's predecessor Joseph John (J.J.) Thomson than Rutherford himself, but nonetheless he gave it his support. Oliphant has affectionately recalled Thomson's teachings during these years:²⁵ 'He gave every year a course of lectures on electricity in gases which were most interesting and well delivered, except that his top set of teeth came loose with a click now

and then and the grimace to push them back up again was often interpreted by newcomers as a grin'.

After the submission of his doctoral thesis entitled *The Neutralization of Positive Ions at Metal Surfaces and the Emission of Secondary Electrons*, Oliphant remained at the Cavendish Laboratory first as a Senior Scholar and then as Assistant Director of Research through 1936 during which time he began his work on isotopes. Oliphant has described his interaction with Aston during this period in which he and Rutherford discovered tritium from the 'transmutation' of deuterium.²⁶ Oliphant certainly received help from Aston and has recalled visits to his laboratory at the Cavendish in what was known as the garage. 'Aston's laboratory was a dingy, darkened room in a corner of the ground floor, its walls covered with discarded apparatus and with samples of rare gases in tubes over mercury which he had separated by fractionating residues from liquid air.'²⁵ He has also referred to Aston's generosity less affectionately. 'Aston was the laziest man I ever knew in physics... He was seldom in the Cavendish Laboratory, but when he was he made a great fuss if anyone but he used the storage batteries in the basement, and was still more angry if a spark discharge anywhere produced radiation which upset his mass spectrograph. He was upstairs to me in an instant if I used outgassing equipment during the late afternoon on the rare occasions when he was at work. However, on the whole I got on well with him, though I was unable to persuade him to allow me access to his collection of all the rare gasses stored over mercury.'²⁶

A photograph of the Cavendish staff of 1934 (Fig. 2) shows Oliphant seated on the bottom row, far right in the august company of Thomson, Rutherford, Aston and many others. At the annual Cavendish black-tie dinner, satirical songs written by research workers about their supervisors would be sung. In 1922, after receiving the Nobel Prize in

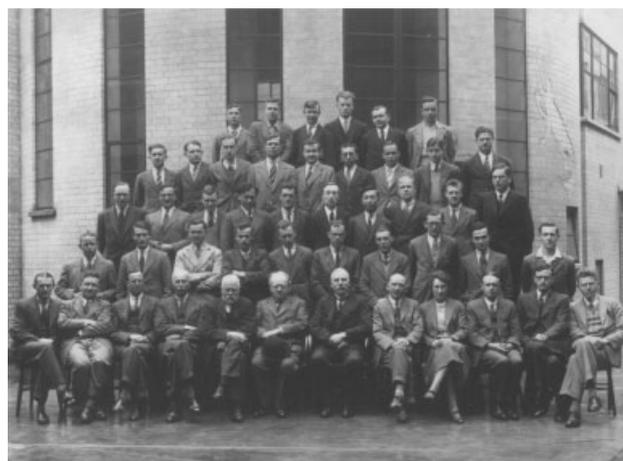


Figure 2. Photograph of scientists of the Cavendish Laboratory, Cambridge University 1934. Front row: N. Feather, J.D. Cockroft, Dr J. Chadwick, Dr F.W. Aston, Dr G.F.C. Searle, Prof. Sir J.J. Thomson, Prof. Lord Rutherford, Prof. C.J.R. Wilson, Miss A.C. Davies, G. Stead, P.I. Dee, M.L.E. Oliphant. Source: Kelvin Fagan, Photography Department, Cavendish Laboratory.

Chemistry, Aston was featured in a verse penned by Edmund Clifton Stoner.

*'So Aston made a cute machine for atom separations,
The atoms passed through fields serene, magnetic poles they
went between,
And made some marks upon a screen, apart from their
relations.
The numbers whole were soon made out, by methods neat
and clever;
Of this there was no manner of doubt, no probable, possible
shadow of doubt,
No possible doubt whatever.'*

After a period of over a decade as Poynting Professor of Physics at the University of Birmingham (Aston's birthplace and educator in physics), where we worked to develop microwave radar, Oliphant returned to Australia in 1950 to the Australian National University (ANU). ANU was established under a 1946 act of the Commonwealth of Australia's parliament. At least initially the university was to contain four research schools; one focusing on medical research, one in the physical sciences and two in the social sciences. To attract someone of Oliphant's calibre required adequate resources and excellent laboratory facilities. During the negotiations, it was arranged for Oliphant to visit and meet the then Prime Minister of Australia Joseph Benedict (Ben) Chifley. Their meeting reportedly began with a 'walk in the park' followed by dinner at the Savoy hotel. Oliphant told Chifley he needed £500 000 or more to set up his lab. Although more than four times that which had been suggested to the government of the day, Chifley gave the instruction that if Oliphant could be persuaded to return to Australia, he would do all that was necessary to raise the funds. Against the advice of Australian Howard Florey (who shared the Nobel prize in medicine in 1945 for the discovery of penicillin) that he would find Canberra a 'hole in the ground and a mountain full of promises', Oliphant accepted the offer.²⁷

Before commencing his position as Director of the Research School of Physical Sciences at the newly formed ANU, Oliphant visited the Physics Department at the University of Western Australia (UWA) in Perth. It was here that he recommended that a mass spectrometry laboratory be established to measure the age of rocks in Western Australia, using the same radioactive decay technique that Aston himself had used in 1929.¹⁴ Encouraged by Oliphant, Peter Jeffery embarked on a mission to build a mass spectrometer for such geochronological measurements.¹¹

The instrument builders: Morrison at CSIRO and beyond

Proceedings of the first Australian conference on mass spectrometry indicate that the first mass spectrometer built in Australia was a 60 degree Nier-type instrument constructed in the Physics Department at the University of Melbourne. This instrument became operational in 1947 but the low resolutions obtained and filament problems led to the subsequent construction of an all metal spectrometer in 1948 which was used as an isotope separator for the production of microgram quantities of isotopes of lithium, magnesium,

zinc and other as his counterpart, Jeffrey began to build his instrument; Morrison at CSIRO focused much of his early work on measuring ionization efficiencies and appearance potentials,^{1,2,28,29} and later, photoionization efficiencies³⁰ and bond strengths using the commercial CEC instrument. With Graham Hercus, Morrison built circuitry to obtain ionization efficiency curves in less than 10 min.³¹

At the same time, he set about trying to educate colleagues of the virtues of mass spectrometry. Perhaps, it was the esoteric designs of the in-house-built mass spectrometers, or the sweat and tears (and occasional profanity) that it sometimes took to operate them or the general disrespect with which mass spectrometrists (to this day) treat their analytes, many chemists of the day had little time for mass spectrometry. The devotees faced a significant challenge, since as Morrison recounts,¹⁶ even the manufacturer of the commercial CEC 21102 gave advice in the operating manual that recommended a dime be placed on the magnet of the instrument as an offering to the gods to ensure uninterrupted operation. While at CSIRO, Morrison reported on new programs to assist with the interpretation of mass spectra recorded on this instrument.³²⁻³⁴

An entertaining, and recommended, fuller account of Morrison's career and many contributions to mass spectrometry has been reported elsewhere by the man himself.¹⁶ In brief, Morrison moved to Latrobe University in Melbourne in 1967 as Foundation Professor of Physical Chemistry. With John Smith (who had previously worked with Jeffery at UWA), he built a fast-scanning GC-MS instrument using a laminated 1.5 ton magnet, computer-controlled by means of a Digital Equipment Corporation PDP-9. From 1974, with his student Don McGilvery, Morrison built a triple quadrupole mass spectrometer for studying the photodissociation of mass-selected ions.³⁵ During a meeting with friend and colleague Christie Enke at the annual ASMS Conference in Washington, D.C., Morrison offered Enke's then student Richard Yost the opportunity to visit Latrobe to use the instrument for analytical tandem MS/MS studies.⁷ These early experiments, combined with computer simulations of ion trajectories using SIMION (a suite of programs written and developed by Don McGilvery as part of postgraduate studies⁸ as described in a later section) were instrumental to the later construction of a similar instrument at Michigan State University. Regrettably, although Morrison's laboratory was used to demonstrate the practicality of tandem mass spectrometry on a triple quadrupole instrument,⁷ he was not honoured along with Enke and Yost when the ASMS award for a distinguished contribution to mass spectrometry was made in 1993.

When Peter Derrick joined the academic staff at Latrobe in 1975, he embarked upon the construction of several instruments for field ionization and desorption studies including a grand-scale magnetic-sector mass spectrometer that featured an 8-ton magnet.³⁶ This instrument was moved to the University of New South Wales (UNSW) in Sydney, where Derrick was appointed Professor and Head of Chemistry, before it was relocated with him to the University of Warwick. While at UNSW, Derrick also built an early TOF/TOF mass spectrometer.⁹ He also worked on energy transfer, loss

and mass discrimination effects observed during collision-induced dissociation experiments.^{37–39} In the 1980s, Michael Guilhaus joined the academic staff at the UNSW and has continued the legacy of building mass spectrometers in Australia including the conceptualization⁴⁰ and development of orthogonal acceleration¹⁰ now employed in many TOF-based mass spectrometers. Guilhaus received the Curt Brunnée award from the International Mass Spectrometry Society (IMSS) in 1997 in recognition of his achievements in this area.

The Jeffery years

Jeffery has given an account of the trials and tribulations of building a mass spectrometer in the early 1950s in a small, geographically isolated Physics Department.¹¹ Without funds to purchase a commercial mass spectrometer, home-made electromagnet, diffusion pumps and electronic units were constructed and water pipe and copper tubing sequestered in order to assemble his instrument. The spectrometer leaked like a sieve and was virtually held together by a fast-setting solution called *glyptal* that was used to seal vacuum leaks. Small Acorn-954 amplifiers worked intermittently but by 1955, when Jeffery's research team comprised Bill Compston, David Greenhalgh, John de Laeter, Colin Cole, Bruce Kendall and Glen Riley, the group published a paper on carbon isotopes on the original instrument, the flight tube of which is depicted in Fig. 3.⁴¹

A second mass spectrometer was constructed using a tube donated by the Carnegie Institute of Washington together with a small grant to assist the research. This mass spectrometer was used to date rocks by monitoring the radioactive decay of uranium to lead, and the first results on this instrument were published in 1959.⁴² Age determinations based on the decay of uranium to lead is the classic geochronological technique. Primordial lead consists of four isotopes, of which ^{206,207}Pb are the radiogenic end products of ^{238,235}U, respectively. Changes in the isotopic composition of lead caused by radiogenic decay can be monitored relative to the invariant ²⁰⁴Pb. The half-lives of ^{238,235}U of 7.1×10^8 and 4.5×10^9 years, respectively, are ideally suited to measuring the age of terrestrial rocks and minerals. The timing of events is



Figure 3. The original mass spectrometer flight tube used by Peter Jeffery at UWA in the mid-1950s. Shown in the photograph (left to right) are John Budge (technician), Bill Compston and John de Laeter (then research students).

of fundamental importance to geology, and a large number of geochronological techniques, embracing both short-lived and long-lived radioisotopes, have been developed over the past 50 years. The mass spectrometer can accurately measure both the isotopic composition and the elemental abundance of the parent and daughter isotopes involved in these decay schemes, and is therefore an indispensable component of geochronology. This Carnegie-sourced instrument was later converted to a thermal ionization mass spectrometer (TIMS) by Kendall for a project to measure anomalies in the levels of potassium in cancerous tissue. The results of this were published in *Nature*⁴³ and led to the adaptation of the ion-source assembly to enable samples to be rapidly exchanged without breaking vacuum conditions or adjusting the ion-source conditions.

Jeffery was awarded a Carnegie Fellowship in 1955 that enabled him to spend a year at that Institute in the United States where he worked on isotope ratio studies for K–Ar and Rb–Sr. On his return to UWA, he introduced these two techniques to complement the existing U–Pb method, thus establishing an extremely productive age-dating program with the support of Alan Wilson from the Geology Department.⁴⁴ Wilson later went to the University of Queensland where he established a stable-isotope laboratory. Compston rejoined the team after a postdoctoral fellowship at the California Institute of Technology and an important application of the Rb–Sr technique was made by Compston and Jeffery in 1959.⁴⁵

Despite the excellence of his geochronological research program, Jeffery decided to terminate the work in 1961 because he realized that the demand for geological dating would far outstrip the capabilities of a small, underfunded Physics Department.¹¹ He went to the University of California at Berkeley to work with John Reynolds, and on his return to UWA instituted a research program in nuclear astrophysics. Compston went to the Geophysics Department at the ANU, a department in Oliphant's Research School of Physical Sciences, to foster a program in geochronology. Kendall went to North America, later to work for a mass spectrometer company (Nuclide Analysis Associates), and Riley went to the Australian Atomic Energy Commission to establish a mass spectrometric facility for nuclear measurements.

The first research student in Jeffery's reconstituted research group in 1962 was one of the authors John de Laeter, whose Ph.D. research involved a study of the isotopic composition of tin in meteorite materials using the adapted Carnegie TIMS instrument.⁴⁶ A photograph of part of this instrument is shown in Fig. 4. The group then acquired a nuclide analysis gas-source mass spectrometer, and this instrument was used by another student (John Hagan) to carry out research on the rare gas Ne to search for muon-induced anomalies in terrestrial rocks.⁴⁷ An important innovation to improve the separation of gases in this project using liquid helium was made possible by virtue of the fact that Jeffery's group was located in a Physics Department.

Another instrumental 'breakthrough' was prompted by the laborious method of measuring the nine isotope ratios of



Figure 4. A photograph of the TIMS at UWA that was used in the nuclear astrophysics program in the 1960s.

tin using chart recorder paper, rulers and hand-cranked calculators. The arrival of one of the world's first time-sharing computers (Digital Equipment Corporation PDP-6) in the Physics Department in 1964 prompted the group to digitize the ion beam signals on the TIMS machine and feed the output on-line to the PDP-6, where the isotope ratios could be fed back to the TIMS laboratory in real time.⁴⁸ Another to join the nuclear astrophysics program was Kevin Rosman, whose research project was the isotopic composition of zinc in a variety of terrestrial and meteoritic materials. He and Jeffery used a liquid nitrogen-cooled 'cold finger' in the ion source of the TIMS machine. This had the effect of reducing hydrocarbon contamination, thus improving the quality of the isotope measurements.⁴⁹ A cold trap is now an accepted component of modern mass spectrometers. Thus, Jeffery and his students made a number of small, but nevertheless important, contributions to mass spectrometry instrumentation during the period from the mid-1950s to 1971.

On Jeffery's retirement, mass spectrometry research in the Physics Department at UWA was terminated, but his legacy was the continuation of this area of research by his former students at the ANU in Canberra and at Curtin University in Western Australia. Elsewhere at the University of Queensland, Wilson, a colleague of Jeffery, was appointed to the Geology Department in 1960 to set up a stable isotope and K–Ar facility in conjunction with the Chemistry Department. More recently, Ken Collerson has established the Advanced Centre for Queensland University Isotope Research Excellence (ACQUIRE), where a comprehensive range of problems are being pursued.



Figure 5. Photo of Stewart Walker with violin at the ANZSMS18 conference in Lorne, Victoria serenading Fred McLafferty (seated) with the 'McLafferty Rearrangement'.⁵³ Photo courtesy: Gary Willett, University of New South Wales.

Detectors and musical ions

The construction of mass spectrometers in Australia by Morrison, Jeffery and others has not been limited to ion sources, flight tubes and magnets, but has included the fabrication of ion detectors. In the mid-1950s, Jim Morrison together with Hans Hurzeler began to fabricate electron multipliers of a 2% magnesium–silver alloy.²⁹ In an extraordinary activation experiment, Morrison has described the coupling of the detector output to an audio amplifier and loudspeaker.¹⁶ By doing so, they were able to detect an audible difference in the sound made by a singly charged polyatomic bromine ion of m/z 79 impinging on the detector than its multi-atomic counterpart, the pyrdinium ion. There must be a musical vein running through members of the mass spectrometry community in this country, for Stewart Walker, convener of the 20th meeting of the Australian and New Zealand Society for Mass Spectrometry (ANZSMS20), has penned an original composition known as the *McLafferty rearrangement*.⁵⁰ Stewart performed his work on violin serenading Fred McLafferty at the previous Society conference (Fig. 5). True to its name, the six-bar tune is rearranged every time it is played and appears to be the first musical composition dedicated to a gas-phase ion process.⁵⁰

As a consequence of the research on ion detectors at the CSIRO, the company ETP was established in Sydney in 1976 to commercialize and develop detector technology. The company introduced its first-generation electron multipliers with replaceable dynodes in 1982, and a decade later developed an active-film technology that provides multipliers with greater stability at ambient conditions. The company is now a division of Scientific Glass Engineering (SGE), another local company established in the 1970s by Ernest Dawes in the garage of his Melbourne home, but it continues to supply both end-users and manufacturers of mass spectrometers throughout the world.

SIMION

Improvements in mass spectrometer design are greatly aided by a better understanding of ion behaviour and ion optics. During the 1970s, Don McGilvery, then a

postgraduate student with Morrison at Latrobe, wrote and compiled a set of programs for electrostatic potential and ion trajectory calculations known as SIMION. This work formed part of his Ph.D. research, which was completed in 1978,⁸ and was utilized as a design tool for much of the subsequent instrument construction within the department. This included the design and construction of the tandem quadrupole mass spectrometer for the study of ion photodissociation induced by a tunable dye laser⁵¹ and a second instrument built with John Traeger.¹⁶

After release of the source code, the program was advanced and refined to run on PCs by David Dahl in the United States.⁵² McGilvery and Dahl shared the American Society for Mass Spectrometry's Distinguished Contribution to Mass Spectrometry award in 1998 to recognize the widespread use of the algorithm today in instrument design. By this time, McGilvery was working at Monash University where, with Richard Morrison, a Macintosh version of the program (MacSIMION 3D) was developed.⁵³ A number of triple and pentaquadrupole⁵⁴ mass spectrometers for tandem mass spectrometry experiments have been constructed at Monash and many have made use of the SIMION software. Screen shots of the original program and its latest incarnation for Macintosh computers are shown in Fig. 6.

The ion chemists

One of the earliest chemists in Australia to exploit mass spectrometry was Ian Lauder. Lauder successfully built his own mass spectrometer from a Nier–Johnston design at the University of Queensland and employed it for oxygen tracer mechanistic and kinetic studies of chemical reactions.^{3,55} A commercial instrument in the form of an Atlas CH4 was acquired by the University around 1963.

During the 1960s, mass spectrometry was widely applied to the structural elucidation of natural products and other organic compounds. The rules of ion fragmentation were being learned, and libraries of electron impact MS data were beginning to be assembled to assist with chemical structure identification. This period saw the arrival of a number of commercial instruments to the shores of Australia. Among the first was a Metropolitan Vickers MS2 used by Jim Green and Jack Garnett at the UNSW for studies of radiation chemistry. Ian Gregor, a graduate of the University of New England who received his doctorate from UNSW is another early UNSW-based mass spectrometry researcher. Gregor applied mass spectrometry to study inorganic compounds, particularly fluorinated compounds, and metal complexes over four decades beginning in the 1960s^{56–60} both independently and through his collaborations locally with Jack Garnett, Derek Nelson, Michael Guilhaus and Gary Willett and abroad with Keith Jennings and Nico Nibbering. These studies were aided by the addition of a Vacuum Generators VG model MM16F instrument, and from the late 1980s, a Bruker CMS 4.7 T Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. Studies of metal complexes have continued at UNSW by Willett together with colleagues Ian Dance and Keith Fisher. Willett is a Latrobe graduate who completed postdoctoral studies with Tomas Baer in North Carolina. His major research interests

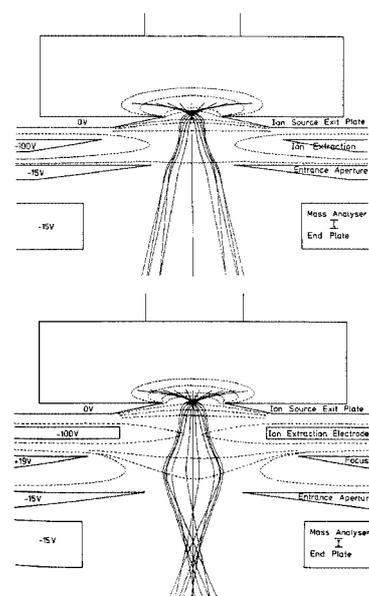


FIGURE 5.1

Trajectory plots for the ion source and lens region without (upper) and with (lower) the focus electrode. The equipotential contours (dotted lines) are at negative 0.05, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0 and 50.0 volts from top to bottom in each plot. The ion trajectories (solid lines) were started at points along the electron beam and traced to the entrance of the first mass analyser. Substantially improved focusing is observed for the lower plot. The scale used for both simulations was 0.2 mm/grid point. However the figure has been drawn with the horizontal scale expanded by a factor of four to make the trajectories more easily followed. The use of cylindrical symmetry allows the two dimensional plane to accurately represent the system.

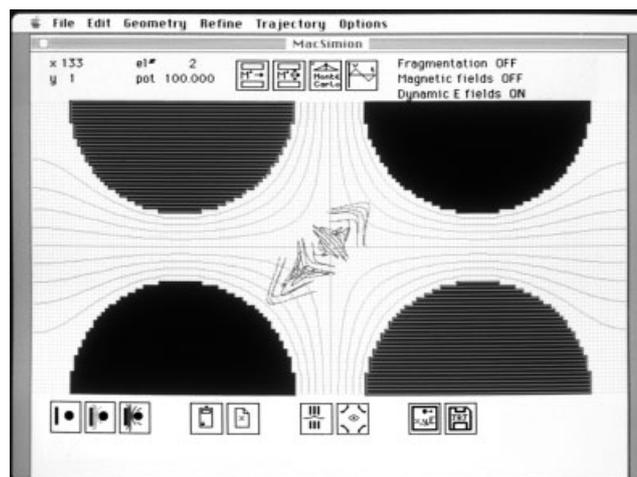


Figure 6. Screen shots of the original SIMION-simulated ion trajectory software (5.1, top) and that of the latest incarnation (SIMION 3D) for Macintosh computers (bottom). Courtesy: Don McGilvery, Monash University.

include the gas-phase chemistry of laser-ablated metals,⁶¹ the mass spectrometry of fullerenes and metallofullerenes^{62,63} and more recently the analysis of nanoclusters⁶⁴ and self-assembled monolayers.⁶⁵ Most of this research has exploited the benefits of FTICR instruments using the initial 4.7 T instrument and a subsequent high field 7 T Bruker Apex FTICR mass spectrometer fitted with a pulsed molecular-beam laser cluster source acquired in 1997.

Adelaide-born Jim Shannon was another early advocate and pioneer in the application of mass spectrometry in Australia. Shannon graduated from Adelaide University in 1949 and received his doctorate from Imperial College in 1954. He joined the Division of Coal Research at CSIRO in

Sydney the following year. Jim's arrival has been described as a 'breath of fresh air, if not a hurricane, blowing (in) from the frontier world of high-powered science into the active but quaint and isolated world of coal research in Australia'.⁶⁶ Realizing the power of mass spectrometry in combination with NMR spectroscopy for solving organic structures, the division subsequently placed an order for an Atlas CH4 mass spectrometer, an instrument choice Shannon vehemently defended. The instrument arrived in 1961 with another installed in the Defence Standards Laboratory in Melbourne a year later. Shannon published an early work on the structures and reactions of substituted benzyl alcohols.⁶⁷ He also undertook work on the characterization of metal-containing compounds and complexes and discovered metal-valency effects during ion fragmentation. Jim was also an advocate of proper 'electron-bookkeeping' to report ion fragmentation and rearrangement processes and proposed the odd and even electron ion notation (+• and +)⁶⁸ and an arrow system similar to the fish-hook and double-headed arrows in use today. He also argued against the use of the term quasi-molecular ion for protonated ions formed in chemical and field ionization sources.⁶⁹

With MacDonald, Lacey and others at CSIRO, and in collaboration with researchers in New Zealand, Shannon worked to apply mass spectrometry to characterize a wide range of chemical structures.⁷⁰ His interests in the applications of mass spectrometry also extended to biologically sourced compounds. These included the isolation and identification of non-protein amino acids in Australian seaweeds,⁷¹ the venom and gland secretions in an Australian ant species *Camponotus intrepidus*⁷² and cyclic depsipeptides from fungi.^{4,5}

In 1968, a reorganization of CSIRO led to Shannon's lab being moved to Canberra within the Division of Entomology. As he has conveyed, he never settled in the Australian capital and returned to Sydney to take up an appointment as Professor of Chemistry at the UNSW. He was appointed Australasian editor of the newly established journal *Organic Mass Spectrometry* (OMS), and continued his studies using chemical ionization mass spectrometry on a newly purchased Associated Electrical Industry (AEI) (later Kratos, now Shimadzu) MS902 instrument. Jim's contributions to mass spectrometry have been recognized in several published tributes^{66,73} and a special issue of OMS in October 1992.

Work on the application of mass spectrometry to the study of natural products, particularly from insect venoms^{74,75} and botanical oils,^{76,77} has been continued at UNSW by Joseph Brophy. Sample preparation is often critical to the success of analytical mass spectrometry in these studies, but as reported by Derek Nelson this need not be the case. In an interesting experiment, an ant was placed directly into the insertion probe and subjected to chemical ionization using isobutane as the reagent gas. An ion peak at m/z 169 was detected and its identity was established by linked-scan MS-MS techniques as iridodial.⁷⁸ This compound is marketed as a natural medicine for 'gene repair and tumour regression' in cancer patients. With Derek Nelson and others, Brophy also developed a number of instrument advances including the development of microprocessors for

controlling a double-focusing instrument for linked scans and voltage stepping^{79,80} and a timing galvanometer for obtaining elemental compositions for ions on low-resolution instruments.⁸¹

In Tasmania, Noel Davies has extensively applied and developed mass spectrometry to natural product analysis and pharmacological studies over two decades. This work has included the characterization of volatiles secreted from two Australian marsupials, the koala⁸² and brushtail possum.⁸³ At Flinders University in Adelaide, both Malcolm Thomson and more recently Stewart Walker have applied mass spectrometry to pharmacology and forensic science.

Another early devotee of mass spectrometry for structure elucidation was John Bowie. Bowie joined the chemistry department at the University of Adelaide from Cambridge in 1966. Bowie had accepted an ICI Postdoctoral Fellowship to work with (Lord) Alexander Todd who subsequently paired him with Australian Don Cameron, a Salters' Fellow in Todd's lab working on the natural product chemistry on aphid pigments. Dudley Williams had recently arrived at Cambridge from Carl Djerassi's laboratory in Stanford, and it was Williams' enthusiasm and energy that encouraged Bowie to moonlight in the field of mass spectrometry.

On his arrival at Adelaide, Bowie wasted no time in adopting mass spectrometry as his central research tool. Against convention, Bowie was an early advocate of negative ion mass spectrometry employing an early Hitachi RMU-7D mass spectrometer for EI-MS measurements. These studies were extended with chemical and fast-atom bombardment ionization sources in mass-analysed ion kinetics energy spectra (MIKES) experiments on a reverse-geometry (RG) VG-ZAB 2HF mass spectrometer that arrived in the mid-1980s. Using these and other more recently acquired commercial instruments, the Bowie group has conducted an astonishing array of work resulting in over 500 publications over a period of 40 years and is a world leader in negative ion mass spectrometry. Bowie's work began with structural elucidation of natural products such as quinines⁸⁴ and the constituents of aphids,⁸⁵ developed to studies of the fragmentation pathways and processes of a wide range of organic ions in the positive and negative ion modes,⁶ the formation and reaction of ions of the cosmos⁸⁶ and the identification and characterization of bioactive peptides secreted (with some electrical stimulation) from Australian frog skins in a particularly successful collaboration with Michael Tyler of the Zoology Department.⁸⁷ Bowie's group has been studying the glandular secretions for over a decade, the work begun by David Stone,⁸⁸ and among the chemical cocktail, has identified and characterized by mass spectrometry over 180 bioactive peptides, some of which possess anti-microbial and anti-cancer properties. Among these is the 25-residue peptide splendipherin from the tree frog *Litoria Splendida*, the first aquatic pheromone of a frog to be reported.⁸⁹ Bowie's immeasurable contributions to mass spectrometry have been well recognized, and he has been awarded numerous medals and prizes including a Doctor of Science from Adelaide University. A recent appreciation is featured in a special issue of the Australian Journal of Chemistry to commemorate his 65th birthday.⁹⁰

Austrian-born Berthold Halpern was another scientist who contributed significantly to the application of mass spectrometry in Australia including the analysis and sequencing of peptides. Educated at the University of Sydney, Halpern majored in organic chemistry and completed his honours research in natural product chemistry before moving to Monsanto Chemicals where he later became group leader. After completing his Ph.D. studies on a Salters Scholarship with Professor Derek Barton at Imperial College London from 1957 to 1959 on the syntheses of tetracycline, he returned to Australia to Monsanto briefly as a Research Manager before taking up an offer as a Senior Research Fellow in 1962 working with Professor Fred Dwyer at the ANU in the unit of Biological Inorganic Chemistry at the John Curtin School of Medical Research.⁹¹

Here Halpern's research on the chiral syntheses of amino acids using coordination complexes as resolving agents^{92,93} led to several papers on peptide syntheses including the use of a new protecting group dimesone.^{94,95} The use of dimesone as a protecting group for amino acid and peptide chemistry was adopted by the private company Syntex in Mexico City where Halpern spent two years in 1963–1964 on a research fellowship, after Dwyer's death. In 1964, Halpern was invited by Nobel Laureate Professor Joshua Lederberg to fill the position of Senior Scientist in the Department of Genetics at Stanford University where he remained before accepting the chaired founding Professor of Chemistry at the University of Wollongong in 1970.

It was back in Australia that Halpern designed experiments for the detection of amino acids and their chirality using gas chromatography and mass spectrometry.⁹⁶ His successful application of mass spectrometry to amino acid and peptide chemistry resulted in his appointment to the NASA Lunar Science Program at the time of the manned moon mission and took part in the chemical analysis of moon rocks.^{97,98} A new, automated GC–MS computer system was developed by Halpern together with Reynolds and others during this time in order to facilitate biomedical applications.⁹⁹ The computer was designed to operate the quadrupole and manage data collection and processing with the GC–MS system used for analysis of the Apollo 11 and 12 lunar samples in efforts to identify amino acids, peptides and organic compounds in general.

GC–MS was also used by Halpern's group for sequencing small peptides^{100–103} and for a range of biological applications. A method of sequencing proteins was also developed involving cleaving the protein into dipeptide fragments with a dipeptidase, with the hydrolysate derivatized and analysed by mass spectrometry. The dipeptides analysed were compared with the hydrolysate of the whole protein to enable the sequence to be constructed. Halpern was elected a Fellow of the Australian Academy of Sciences in 1978 shortly before his death in 1980. His contributions to biological mass spectrometry are to be commemorated in a special symposium at Wollongong this year. Research in this area has been impressively advanced at Wollongong in more recent years under the leadership of Margaret Sheil. Her primary interests have concerned the study of lens crystallins¹⁰⁴ and non-covalent oligonucleotides/DNA in complex with small drugs, metals

ions and proteins.¹⁰⁵ Sheil joined the Chemistry Department in 1990 after graduating with Peter Derrick (then at UNSW) and working at ANU with John MacLeod.

Like other Australian scientists of the period, John MacLeod adopted mass spectrometry in concert with NMR spectroscopy for structure elucidation. MacLeod graduated from the University of Queensland and undertook postdoctoral studies with Carl Djerassi at Stanford on the mass spectral characterization of substituted hydrazones and cyclic ketones. He returned to Australia and joined the academic staff of the Research School of Chemistry of the Australian National University in 1967 occupying the same office for over 35 years. Here he applied mass spectrometry to the characterization of a wide range of natural products,^{106,107} plant metabolites^{108–110} and gas-phase ion studies, the latter often in conjunction with Leo Radom who conducted companion theoretical *ab initio* molecular orbital calculations.¹¹¹ John was also an ambassador of mass spectrometry in Australia and served as Chairman and President of the Australian and New Zealand Society for Mass Spectrometry (ANZSMS) on several occasions before his retirement.

Radom's internationally renowned research in computational quantum chemistry and the application of *ab initio* molecular orbital theory has greatly aided our understanding of gas-phase ions.^{112,113} Radom graduated from the University of Sydney with honours in 1966 and was awarded a Ph.D. from the same university. After postdoctoral studies at Carnegie-Mellon University, he returned to Australia and rose through the research–academic ranks at ANU becoming a Professorial Fellow in 1990 and full Professor a year later. Among his many awards, Radom was awarded the Maccoll Prize from the British Mass Spectrometry Society in 1991. Still active, Radom returned to Sydney as a Professor of Chemistry in 2003.

In Melbourne, Quentin Porter focused his investigations largely on heterocyclic compounds initially using an AEI MS9 mass spectrometer beginning in the early 1970s. His research included studies of the fragmentations and rearrangements of aziridines,¹¹⁴ substituted hydrazines¹¹⁵ and investigations of a heteroanalogue of the Diels–Alder reaction.¹¹⁶ With John Baldas, Porter wrote a book on the mass spectrometry of heterocyclic compounds that was greatly revised and expanded in a second single-author edition,¹¹⁷ which remains an authoritative review of the subject.

Studies of ion chemistry in the gas phase and the application and development of mass spectrometry in the chemical and biological sciences continues to this day throughout Australia. Many of the laboratories described above have served as training grounds for today's researchers with primary interests in mass spectrometry. These include John Traeger at Latrobe who works on photoionization mass spectrometry,¹¹⁸ Richard Morrison at Monash,¹¹⁹ Ellak von Nagy-Felsobuki at Newcastle,¹²⁰ Philip Marriott at RMIT who applies GC–MS,¹²¹ Richard O'Hair at Melbourne¹²² and Stephen Blanksby¹²³ at Wollongong who work in fundamental ion chemistry, and Simin Maleknia¹²⁴ at Griffith and author Kevin Downard^{125,126} at Sydney who work to

develop mass spectrometry for studies of protein structure and interactions.

Early geoscience MS at the Australian National University

Bill Compston's appointment to the Department of Geophysics at the ANU in Canberra in 1961 coincided with the appointment of Ian McDougall who joined John Richards in the K–Ar laboratory that was equipped with an AEI MS2 mass spectrometer, and shortly thereafter, a glass gas-source mass spectrometer supplied by Reynolds from the University of California. These appointments had far-reaching effects on the development of isotope science in Australia, and both Compston and McDougall spent the rest of their professional careers at ANU on these endeavours. The MS2 was converted into a thermal ionization machine for the Rb–Sr research program, and this instrument was supplemented by the acquisition of a Nuclide Analysis Associates 30-cm radius of curvature TIMS purchased by the Bureau of Mineral Resources, Geology and Geophysics (now Geoscience Australia). The Bureau recognized the essential role that geochronology would play in understanding the geology of Australia, and has continued to provide funds for instruments and research staff up to the present day. The influence of the Bureau on the development of mass spectrometry in this country cannot be underestimated, as has been the interest and support of the State Geological Surveys.

The limitations of these two commercial instruments led Compston to the concept of building a high-sensitivity TIMS in-house. In 1967, a physics graduate from Canada (Stephen Clement) was recruited as a Ph.D. student at ANU to design a new instrument using beam-transport theory in its ion optical design. Ion beam-transport methodology had been developed to improve the ion optical design of nuclear accelerators, and is a good example of the cross-fertilization of ideas from different disciplines. The new TIMS, named MSZ, was built in the Department's workshops and proved to be an instant success. At about the same time, another mass spectrometry group member in Pieter Arriens, introduced a computer-based data handling system that linked all the mass spectrometers to a single large computer.

The completion of the MSZ coincided with the start of the National Aeronautics and Space Administration (NASA) Apollo lunar program, and the return of lunar samples to Earth. Compston was selected by NASA as a Principal Investigator of the Apollo program with the objective of dating the age of lunar samples using the Rb–Sr technique. A new clean room was constructed in the department for this project. The ANU team successfully measured whole rock ages of the lunar samples and then analysed mineral separates to obtain internal isochrons to examine the age of eruption of lunar basalts.¹²⁷ This involved the isotope analysis of extremely small amounts of samples that were ably measured on the sensitive MSZ.

In 1969, an AEI MS12 gas-source mass spectrometer was purchased to enable the U–Pb geochronological technique to be extended at ANU, and Virginia Oversby was recruited from the Lamont Geophysical Laboratory in the United States with this aim in mind. As future events unfolded, the decision to incorporate the U–Pb system at the Research School

of Earth Sciences (RSES) had far-reaching implications. Initially, Pb samples were analysed as the gaseous iodide, but when the silica gel ion enhancing technique was discovered, Compston's group utilized the more sensitive solid source MSZ mass spectrometer to analyse Pb. The ability to analyse zircons using the U–Pb technique enabled age constraints on granitic magmas to be elucidated, and highlighted the importance of inherited zircons in understanding the genesis of these granites.¹²⁸ This led to the idea of analysing the zircons *in situ* without the need for laborious chemical processing. However, no commercial ion probe mass spectrometer existed at that time that possessed both the sensitivity and resolution to successfully measure the isotope ratios of U, Th and Pb with high accuracy. It was realized that an ion sputter source would be required to ionize the target atoms with high sensitivity, and therefore the resultant energy spread in the ions would require a double-focusing mass spectrometer to be constructed.

While these developments in solid source and secondary ionization mass spectrometry (SIMS) were proceeding, considerable progress was being made by McDougall and his K–Ar group. The original research on K–Ar geochronology was expanded to include Ar–Ar dating using the nuclear reactor at the Australian Atomic Energy Research Establishment to irradiate samples with neutrons. Later, a gas mass spectrometer was acquired and Masahiko Honda was appointed to develop a research program in noble gas analysis.¹²⁹

Malcolm McCulloch was recruited in 1979 to establish the Sm–Nd geochronological technique, and a then state-of-the-art automated multi-collector Finnigan MAT 261 was acquired to enable a range of isotope studies including geochemical tracing and modelling using the Sm–Nd system, the K–Ca system for petrogenic work and a search for fission products in U deposits to be pursued. The RSES then acquired an inductively coupled plasma mass spectrometer (ICP-MS) in 1992 and the group became involved in trace element studies.¹³⁰ The capability of ICP-MS was enhanced with the purchase of a UV Excimer laser for *in situ* trace element analysis, and this technique has been exploited in ore genesis research.

Another instrumental development at ANU occurred in 1984 when a 61-cm radius, 180° sector double-focusing magnet, using a non-radial field, with a five cup Faraday Cup assembly, was constructed by Tezer Esat.¹³¹ The charge collection system enables extremely small ion currents to be measured successfully, while preserving the advantage of Faraday Cup multi-collection. High-value resistors were replaced with capacitors in the feedback loop of the electrometer amplifiers, which had the effect of eliminating current noise and reducing the background signals. The performance characteristics of this charge-coupled TIMS in the precise isotope analyses of Th with ion beam currents as low as 10⁻¹⁶ A has been described.¹³² Technological advances now enable channeltrons to be used in place of electron multipliers in multi-collector mode, but charge collection is still a viable alternative in certain applications.

The University of Adelaide established a geochronological research program in the late 1960s under the leadership

of John Cooper, an ANU graduate. A commercial company (AMDEL) provided an age-dating service shortly thereafter when Alan Webb was transferred from the University of Queensland in 1969. Three Victorian Universities – Melbourne, Latrobe and Monash – established a consortium named the *Victorian Institute of Earth and Planetary Sciences* (VIEPS) in the mid-1990s in order to share mass spectrometric equipment and encourage collaborative research in the geological sciences. A similar collaborative scheme was also developed between CSIRO and three universities in the Sydney area. Much of the mass spectrometric equipment was located at the CSIRO Laboratories in North Ryde. In recent years, Macquarie University also has developed a vigorous isotope research program in geology.

Another SHRIMP on the drawing board

In 1973, the new RSES was formed at ANU with Professor Anton Hales as the Foundation Director. The additional autonomy of the new school and the personal support of Hales led to the decision to design and construct a sensitive high-resolution ion micro probe mass spectrometer that was given the (imaginative) acronym SHRIMP. This was a challenging project that would not have been possible in any other university in Australia at that time, because of funding constraints and workshop limitations. However, the undertaking had the advantage of having Compston as the leader of the project, and his physics background and previous experience of building MSX gave confidence to those making the decision to go ahead. Clement was appointed to the staff with the challenge of designing the ion probe using, as a basis, the ion optical theory of the Japanese physicist Matsuda.¹³³ The ultimate success of the venture was heavily dependent on Compston's vision and persistence, Clement's ability to design ion optical systems as well as the support of RSES, including the exceptionally talented workshop staff. Compston has given an account of the difficulties encountered in building SHRIMP and the range of projects that can be undertaken using this sophisticated instrument.¹² The first isotope ratios for Pb from galena samples were measured in 1980, and the first analytical results were published in the international literature in 1983.¹³⁴

The success of SHRIMP in dating zircons and other accessory minerals containing U and/or Th led to an enormous demand for instrument time from a variety of researchers both in Australia and overseas. It was therefore decided to design and build a second generation SHRIMP II, backed by substantial financial assistance from the Bureau of Mineral Resources. However, it was realized that even the excellent workshop facilities in RSES would be unable to cope with the demands of building a new instrument, particularly as other research consortia had expressed interest in purchasing the Mark II instrument. The University's commercial arm (ANUtech Pty. Ltd.), agreed to build the new instrument, with Clement undertaking the design in collaboration with Compston. The resultant instrument was installed at the RSES in 1992 and proved to be a more flexible machine than SHRIMP I in that a variety of ion sources could be fitted, the primary ion



Figure 7. A photograph of a SHRIMP II instrument located at Curtin University.

column was designed for Köhler illumination and many of the spectrometer functions were performed under computer control.¹²

The first commercial version of SHRIMP II was installed at Curtin University in 1993 (Fig. 7), and later a number of these mass spectrometers were installed around the world. Subsequently, a multi-collector system for SHRIMP II has been designed and installed successfully on some of these instruments. Another innovation has been the use of a Cs ion source for stable-isotope analysis. An interesting development in the evolution of SHRIMP has been the design, construction and installation at RSES of SHRIMP RG, a modified version of SHRIMP II, in which the position of the electrostatic analyser and the magnet are transposed to afford higher mass resolutions without any deterioration in sensitivity.¹³⁵ The new instrument was also installed at Stanford University in a United States Geological Survey/Stanford University joint venture, under the initial direction of Trevor Ireland, an ANU graduate.

A renewal of geological mass spectrometry in western Australia

After completing a postdoctoral fellowship at McMaster University in Canada, Jeffery graduate John de Laeter returned to Western Australia to introduce a TIMS-based research program in the Physics Department of the newly formed Western Australian Institute of Technology (WAIT) in Perth in 1968, and was later joined by Rosman in 1970. An AEI MS12 was purchased and a Rb–Sr geochronological program was instituted, together with fission product studies and an investigation of the cosmochronological implications of the $^{176}\text{Lu}/^{176}\text{Hf}$ decay scheme.¹³⁶ This mass spectrometer was badly damaged in 1971 by a fire in an adjoining chemical laboratory and had to be laboriously rebuilt. Fortunately the machine was insured, and so a second MS12 was installed, probably the last one sold by AEI.

The mass spectrometry group at WAIT (now Curtin University of Technology) diversified the geochronology program to include the Sm–Nd, K–Ca and U, Th–Pb techniques during the period from 1975 to 1985. In 1993, a consortium comprising Curtin University, the Geological Survey of Western Australia (GSWA) and UWA acquired

the first commercial SHRIMP, built by ANUtech Pty. Ltd. The performance characteristics of this SHRIMP II have been described, and the success of this instrument did much to influence the opinion of the international geochronological community as to its value.¹³⁷ Although zircons have been used extensively for geochronological analysis, a number of accessory minerals have also been utilized for age-dating purposes including xenotime, which has proved to be of value in the petroleum industry.¹³⁸ SHRIMP II was recently used to measure the age of zircons from the Jack Hills area to be approximately 4400 Ma – the oldest terrestrial material ever measured.¹³⁹ A VG 354 TIMS was installed in the Mass Spectrometry Laboratory in 1985, and continues to perform at a high level. More recently, a Triton mass spectrometer has been installed.

Another major aspect of the WAIT/Curtin isotope research program has been chemical metrology – the determination of the isotopic composition and atomic weight of an element to the highest possible accuracy. The isotopic compositions and atomic weights of the following elements have been determined by the group – Ba, Te, Sn, Pd, Ga, Ge, Sb, Lu, Yb, Mo, Zn, Cd, Ta and La – and these results are discussed in a recent review of the *Atomic Weights of the Elements*.¹⁴⁰ Ion enhancing media were used extensively to improve the ionization efficiency of many of these elements.¹⁴¹ The Curtin mass spectrometry group has had a long-term involvement with nuclear astrophysics and in planetary science in which studies of the isotopic behaviour of Cd, Sn and Te in meteoritic and lunar materials have been investigated.¹⁴²

In 1998, the State Government of Western Australia funded a Centre of Excellence in Mass Spectrometry (dedicated in the name of one of the authors) to a consortium comprising Curtin University, UWA, the CSIRO and GSWA. This enabled a second SHRIMP to be installed together with an ICP-MS, a U-He/K-Ar/Ar-Ar facility and a stable-isotope mass spectrometer. A number of GC-MS instruments have also been installed for organic geochemistry research, building on a long-standing research program. Approximately 50 graduate students and staff are associated with this Centre that hosts a number of international visitors each year. The instrumental capability of the Centre, together with the associated facilities, has placed mass spectrometry-based research in a strong position to contribute to a range of geochemical, geological and nuclear projects and environmental research into the twenty-first century.

Mass spectrometry has also been increasingly utilized in environmental science in recent years. A major contribution to climate change studies has been achieved by measuring the age of corals using the U Series Disequilibrium technique. Traditionally, coral ages have been determined by radiochemistry by counting alpha particles. The alternative method is to measure the accumulated daughter product ²³⁰Th by isotope dilution mass spectrometry (IDMS). This mass spectrometric technique not only produces more accurate coral ages than direct counting, but also enables older corals to be dated. Corals can not only provide information on the variation of sea level as a function of time, but can also give seawater temperature data by precise measurements of

their Sr/Ca ratios. Highly precise values for Sr/Ca ratios can be best obtained by IDMS. Such Sr/Ca and ²³⁰Th measurements can be combined with O isotope ratios to give an integrated isotope analysis of these climatic parameters as a function of time.¹⁴³

The unique nuclear characteristics of Pb provide the opportunity to apply isotope techniques to the problem of Pb pollution in the environment. Clair Patterson, at the California Institute of Technology, pioneered the use of IDMS for environmental lead measurements. He developed clean-room methodologies for processing samples which enabled him to measure the elemental abundance of picogram quantities of Pb in ice core samples, and created an awareness of the importance of contamination problems in the measurement of environmental Pb. Subsequently, Rosman and his colleagues at Curtin University extended these studies by measuring the isotopic composition of Pb in polar ice cores as a function of time, and showed that sources of Pb pollution can be traced to their origin in both modern and ancient environments.¹⁴⁴ A new advanced ultraclean environment (ACE) laboratory has recently been constructed at Curtin University, in which ice cores can be decontaminated and prepared for sensitive mass spectrometric analysis. This will enable higher sensitivities to be attained than in the past. Brian Gulson¹⁴⁵ has described similar isotope studies in which the decay of ^{235,238}U to ^{207,206}Pb respectively, and ²³²Th to ²⁰⁸Pb, can be utilized in medical studies such as the biokinetics of Pb in human pregnancy. In a large-scale isotope study of Pb in human health, Gulson has detected changes in the isotopic composition of blood Pb from dietary sources and the contribution of skeletal Pb to blood Pb.

A further application of mass spectrometry to environmental science has been the examination of the mobility of radioisotopes in the Earth's crust. The determination of the nuclear parameters of reactor zones at the unique Oklo Natural Reactor in Gabon, West Africa has enabled the geochemical behaviour of numerous elements in geological repositories to be investigated. Many fission products have been retained in the uraninite ore bodies themselves and in the geological material in which the ore bodies are contained.¹⁴⁶ These studies provide important information regarding the problem of the storage of radioactive waste in natural geological repositories over extended periods of time.

Accelerator mass spectrometry in Australia

Accelerator mass spectrometry (AMS) is a beautiful example of transferring a technique developed in one discipline (namely, nuclear physics) to another (earth sciences) with great advantage to applications based on short-lived radionuclides such as ¹⁴C. The foremost advantage of AMS is that it provides a quantum jump in sensitivity to the measurement of isotope ratios with values below 10⁻¹² in magnitude. The basis of AMS is to discriminate between atomic species in the ion source by using negative ions to destroy interfering molecular species, and then count the individual accelerated ions of interest. Tandem accelerators, previously used in nuclear research, have been fitted

with mass and charge spectrometry to eliminate unwanted charge states, using ion energies ≥ 6 MeV, with the ability to use ground potentials at the source and collector. The fundamental difference between conventional mass spectrometry and AMS is one of energy – MeV rather than keV – and the technique is such that it can be used for all elements (except the noble gases). The exceptional sensitivity and mass resolution of AMS permits short-lived radionuclides such as ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl and ^{129}I to be measured.¹⁴⁷

The Australian National Science and Technology Organisation (ANSTO) installed the Australian National Tandem Research Accelerator (ANTARES), a 10 MeV tandem accelerator (previously operated for nuclear research at Rutgers University in New Jersey, USA), at the Lucas Heights Research Establishment in New South Wales in 1991.¹⁴⁸ ANTARES has been used in many radioactive dating applications in quaternary science and global climate change.¹⁴⁹ It can be used in nuclear safeguard projects by detecting short-lived fission products such as ^{129}I in samples taken from the suspected region. Two authoritative works on the subject of AMS have been published from this highly productive facility.^{150,151} An AMS laboratory headed by Keith Fifield is also operated by the Research School of Physical Sciences and Engineering at ANU in association with staff from the RSES.

A community down under

In 1970, a community of Australian scientists who were working and were interested in mass spectrometry established a formal society originally known as the *Australian Society for Mass Spectrometry*. Jim Shannon is credited with advocating a change to the society's name at its first meeting in August the following year which resulted in the formation of ANZSMS. Among the oldest societies for mass spectrometry in the world (the British and American societies were incorporated in 1964 and 1969 respectively), ANZSMS has maintained a solid membership and has held a major biannual conference throughout Australia and New Zealand ever since.⁵⁰

Membership was initially free though subject to an initial admission fee (\$A 2) to help establish the society. The first chairman of the society was Barry Batts of the School of Chemistry of Macquarie University, who remains an adjunct professor there. Batts' interests in mass spectrometry involved analytical and isotope studies to investigate the chemistry and properties of petroleum, coal, shale oil and other environmental materials.

Minutes from the first annual general meeting report that there were 171 original members, of whom 145 were registered for the first conference. The first conference was held at Macquarie University in Sydney in August 1971, five years ahead of the annual ASMS-badged conferences. The statement of receipts and expenditure show that there were 163 registrants and 7 exhibitors present. A similar number attended the second conference in February 1973 in Melbourne. By 1975, John MacLeod of the ANU had become chairman of the Society. He returned to this role in 1984 and convened the ninth biannual meeting of the Society at ANU that year. A photo of some of the attendees at ANZSMS9



Figure 8. Photo of some of the delegates of ANZSMS9 held at the Australian National University, Canberra 1984. Photo features the convener John MacLeod (second row, second left), Jim Morrison (second row, second right), Bob Murphy (back) and Mike Lacey, Leo Radom, Alan Maccoll and Fred McLafferty (in front row).

shows John together with Jim Morrison, Leo Radom, Fred McLafferty, Alan Macoll and Bob Murphy (Fig. 8).

John MacLeod made significant contributions to the mass spectrometry community in Australia both in terms of his science and the society. He was chairman of ANZSMS from 1975 to 1976 and again in 1984, and president following the establishment of separate central and conference organizing committee from 1994 to 1998. John was also part of a steering committee that led to the formation of the International Mass Spectrometry Society (IMSS) for which he served as secretary from 1997 to 2000. John Traeger from Latrobe University succeeded MacLeod as President of ANZSMS from 1999 to 2002 and has taken on the role again in 2004 while also serving as vice president (Society) for the IMSS.

Commencing in 1990, the Society established the Morrison lecture in honour of Jim Morrison, which recognizes his significant contributions to mass spectrometry in Australia. The first recipient was Michael Guilhaus, with John MacLeod, Tom Baer, Bill Compston, John Bowie, John Traeger, Roger Summons, Margaret Sheil⁵⁰ and Murray McEwan taking subsequent awards. In 1996, ANZSMS also began to support visiting speakers to tour Australia and New Zealand on a semi-regular basis, usually between conferences. The first of these was Graham Cooks from Purdue University. Plans for an ANZSMS medal and an award for early career researchers are underway.

Mass spectrometry may be an instrument-based science, but it is people who advance the field. Australia has an active research community who meet regularly at the biannual ANZSMS conference and elsewhere to discuss and present their latest research results. Overseas visitors attending local conferences are continually impressed by the innovative and original research conducted here. Despite its geographical isolation from many other researchers in mass spectrometry, Australia's community of scientists continue to make significant contributions to the advancement of the

field that will keep mass spectrometry at the forefront of scientific research in the years ahead. The prognosis for the future of mass spectrometry in Australia is bright in that the country now possesses a wide range of instruments and expertise to tackle any problem in the ever-widening array of applications of mass spectrometry. But like mass spectrometrists elsewhere, we are in debt to the field's pioneers who lay the foundations before us.

Closing remarks

Aston was a seasoned and eager traveller who first visited Australia in 1908 during a round-the-world trip with monies left to him upon the death of his father. He travelled to Ceylon, Burma, Java, Australia, New Zealand, across the Pacific to Hawaii, the United States and Canada.¹⁵² He returned to Australia again in 1938 on the ocean liner SS Otranto (shown in Fig. 9 in Sydney Harbour), after taking part in the Indian Science Congress in 1937, on what was his last trip abroad. A keen amateur astronomer, Aston visited Japan on route to view a solar eclipse and gave a special lecture at the Imperial University of Tokyo on mass spectra and isotopes.

Although he did not live long enough to see the field that he founded flourish in Australia, with his love of both science and outdoor sports, he would have surely approved of the Australian lifestyle. Aston was a keen skier and rock climber, played tennis and swam.¹⁵³ He even made attempts to learn to fly, crashing an experimental aircraft in 1914 while stationed in Farnborough at the Royal Aircraft Factory during World War I, along with J.J.'s son George Thomson. But Aston reserved his greatest compliment for what he called *surf-riding*, which he reportedly learnt during his travels to Honolulu.¹⁵⁴ This to Aston was the finest sport in the world and one he may have become acquainted with first in Australia. Perhaps he likened riding the peaks and troughs of the surf to scaling a human-sized mass spectrum. Certainly, Australia's ocean beaches would have been a fertile training ground for Aston if he had ventured into the



Figure 9. Image of the 20 000 ton ocean liner SS Otranto in Sydney Harbour (#2 – built 1926, scrapped 1957) on which Aston sailed to Australia. Source: Björn Larsson, Maritime Timetable Images.

surf here. Indeed, these very beaches proved such a powerful drawcard as to convince Scottish-born Jim Morrison to take up Ian Wark's offer to live and work here. And the rest, they say, is history.

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