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PETER H. DAWSON, Ph.D. 1937 – 2015

AN APPRECIATION OF THE SCIENTIFIC RESEARCHES OF Dr PETER H. DAWSON

by

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ABSTRACT

Upon the death of Peter H. Dawson in 2015, mass spectrometry lost a major figure. Within the area of radiofrequency quadrupole electric fields applied to mass spectrometry, Dawson stands alongside its pioneers Wolfgang Paul, Nobelist and inventor of the technology, and Wilson Brubaker, who identified and overcame the deleterious effects of fringing electric fields on quadrupole mass filter performance. Seventy-one of Dawson's 97 scientific publications are concerned with quadrupole mass analyzers, ion traps and monopole mass spectrometers. Of especial note are his book and review articles in which he disseminated information on the theoretical fundamentals and practicalities of these systems to a wider audience, thereby having a major impact on the development of this important field of endeavour.

The scientific researches of Dr Dawson and his advice and counsel, influenced to a major degree, and to the better, the research careers, teachings and the lives of the authors of this

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piece. Their combined researches quadrupole devices led to the commercialization of the ion trap as a mass spectrometer by which mass spectral information became available at greatly reduced cost. Thus, the advent of commercial ion trapping instruments permitted a greater use of mass spectrometry in both technically advanced countries and those less well advanced. The greatest impact in health services was mass spectrometric analysis of environmental problems, well and stream water, food free of pesticides, etc., and forensic sciences. Our combined indebtedness to Dr Dawson is manifested by this appreciation of his scientific work, the highlighting of his main contributions, and creation of a substantive reference source to his work that can be used by other scientists. A comprehensive list of Dr Dawson's publications, including abstracts or summaries, has been arranged in chronological order of date of submission.

Introduction

Upon the death of Peter H. Dawson on 12 June 2015 at the age of 78, mass spectrometry lost one of its major figures of the late 20th century. Within the particular area of instrumentation based on the use of radiofrequency quadrupole electric fields, Dawson stands alongside its pioneers Wolfgang Paul, the inventor of the technology[1], and Wilson Brubaker, who first identified and showed[2] how to overcome the deleterious effects of fringing electric fields on quadrupole mass filter performance. Indeed, some 71 of Peter's 97 scientific publications (see Appendix I) are concerned with some aspect of quadrupole, ion trap and/or monopole

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[1] W. Paul, Electromagnetic Traps for Charged and Neutral Particles (Nobel Lecture). *Angew. Chem*. **29**(7) (1990) 739-748. .

[2] W.M. Brubaker, Proc. 5th Int. Conf. Stockholm, 1960; W.M. Brubacher, An improved quadrupole mass analyzer. In E. Kendrick (ed.). *Advances in Mass Spectrometry,* Vol. 4, pp. 293-299. London: Institute of Petroleum, 1968.

mass spectrometers; of especial note are his book and several review articles [11,24,29,52,60,64][3], in which he disseminated information on the theoretical fundamentals and practicalities of these systems to a wider audience, thereby having a major impact on the development of this important field of endeavour.

At the personal level, the research careers, the teachings and, indeed, the lives of the authors of this piece have been influenced to a major degree, and to the better, by the scientific researches of Dr Peter Dawson, as well as by his advice and his counsel.

As an illustration of this statement, in the mid-1960s, through reading the literature on residual gas analysis (RGA), JFJT first became familiar with the unique properties of the quadrupole mass filter (QMF), in particular the absence of a magnetic field and the fact that the principle of mass analysis does not depend on the kinetic energy of the ions as they pass through the filter when it is placed between the ion source and the detector. Thus, he secured funding to develop an instrument with which to measure the decay rates of metastable ions, using the QMF as a mass-selective time-of-flight device. The method required a means of storing ions for defined time intervals between their creation and passage into the QMF and, in 1968, he became aware of the two pioneering publications by Dawson and Whetten, in which they described their new three-dimensional quadrupole ion trap mass spectrometer, published that same year in the *Journal of Vacuum Science and Technology* [13,14].

Thus, working as one of the original academic staff at the then fledgling Kent University, JFJT, together with his first graduate student, Graham Lawson, and inspired directly by the

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[3] The reference numbers are taken from the chronological listing, generally in order of submission dates, of Dr. Dawson’s publications, 1962-1996, shown in Appendix I.

content of the two cited papers [13,14], which disclosed the method of pulse-ejecting ions from the trap for external detection, Todd and Lawson created a novel tandem instrument. This system incorporated an ion trap (termed by them the QUISTOR for ***QU***adrupole ***I***on ***STOR***e) acting as a mass-selective ion source situated at the front end of a quadrupole mass filter. As part of their characterisation of the system, Todd and Lawson, later to be joined by a second graduate student Ron Bonner, began a comprehensive study of low pressure ion/molecule reaction kinetics, in which the reacting ions and their products were stored for varying times in the QUISTOR prior to ejection and mass analysis by the QMF.

As a result of the appearance of their first publication by Lawson and Todd in this area[4], REM, who was at the time on sabbatical leave in Orsay, France, realised that the QUISTOR could be used as a 'test-tube' for the study of ion processes; consequently, since it was a relatively simple matter to cross the English Channel, he visited JFJT in Canterbury in 1973. Thus, was the JFJT-REM partnership in research collaboration, writing and editing launched; some 45 years later, this collaboration still remains active and productive. An article containing summaries of our respective researches during the first 25 years of this period was published in 1999[5].

It is as a result of our combined indebtedness to Peter Dawson, shown in Figure 1, that we have sought to present this 'appreciation' of his scientific work, not only to highlight the

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[4] G. Lawson, J.F.J. Todd, Radiofrequency quadrupole mass spectrometers. *Chemistry in Britain* **8** (1972) 373-380.

[5] J.F.J. Todd; R.E. March, A retrospective review of the development and application of the quadrupole ion trap prior to the appearance of commercial instruments. *Int. J. Mass Spectrom.* **190/191** (1999) 9-35.

main contributions that he made in a number of different fields, but also to act as a substantive source of reference to his work that other scientists may find to be of use.

To aid us in this task, we have prepared a comprehensive list of Peter's publications, including abstracts or summaries (see Appendix I) which we have placed in chronological order of date of submission, where known. Detailed perusal of this list led us to realise that his different fields of investigation can be categorised into a number of 'research themes' ('RT'), as presented in Table 1; these are indicated also in square brackets against the reference numbers in the list of Peter's publications. It should be noted that to some extent the classification has been subjective, and also that the subject matter of some publications may overlap into several themes. We have also condensed the listing to a sortable spreadsheet, which, together with a downloadable Excel file, is presented as *Supporting Information*.

A Brief Scientific Biography of Peter Dawson

Dr Peter Dawson was but 24 years of age when he arrived in Ottawa, in 1961, to take up a position as Post-doctoral Fellow with the Division of Chemistry of the National Research Council of Canada (NRCC). The previous six years had been spent at the University of London; three years of study as an undergraduate for a B.Sc. (Hons) degree in Chemistry followed by a further period of three years of research under the supervision of Dr A.J.B. Robertson that culminated in the award of a Ph.D. degree in Physical Chemistry. Equipped thus, Peter joined a distinguished group of scientists who have carried out research at NRCC; among those who have pursued physical chemistry were Dr E.W.R. Steacie and Drs P.B. Ayscough, R.J. Cvetanovic, H.E. Gunning, P. F. Knewstubb, K.O. Kutschke, F.P. Lossing, J.C. Polanyi, G.O. Pritchard, and A.W. Tickner. Some were permanent employees while others, like Peter, were holders of Post-doctoral Fellowships for a period of two years.

Dr Dawson's appointment at Ottawa overlapped that of Dr Peter F. Knewstubb's sojourn from Cambridge University, UK. Knewstubb, working with A.W. Tickner, had constructed a double-focussing mass spectrometer for the investigation of ionic species formed in gaseous discharges[6]. The field of discharge studies had been a fruitful one for research on excited atomic and molecular ions since the time of Robert John Strutt, the 4th Baron Rayleigh who, in his varied researches, discovered 'active nitrogen' in 1911 and was the first to distinguish the glow of the night sky. The design of 'static' mass spectrometers (where mass/charge resolution is achieved without the application of time-varying parameters, e.g. a magnetic field), such as that described by Knewstubb and Tickner, evolved from the study of discharge tubes with gaseous ions flowing from the ionization chamber to the detector[7].

Peter's first of five publications with A.W. Tickner [1,3,5,7,8] (which all concerned ion chemistry in glow discharges) discussed the detection of H_5^+ and, 'beginning at the beginning', not surprisingly cites as its first reference the classic 1912 publication by J.J. Thomson[8] concerning the formation of H_3^+, also in a hydrogen discharge. Peter reported that in a negative glow, H_3^+ was found to predominate and its reaction to form H_4^+ occurred readily. In addition to ions of *m/z* = 1, 2 and 3, those having *m/z* = 4 and 5 were detected. While the former may be accounted for as H_2D^+, the latter cannot be ascribed in this way since its counterpart appeared at *m/z* = 10 when a deuterium discharge is used; thus, the

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[6] P.F. Knewstubb, A.W. Tickner, Mass spectrometry of ions in glow discharges. I. Apparatus and its application to the positive column in rare gases. *J. Chem. Phys.* **36**(3) (1962) 674-683.

[7] For a discussion of the differences between 'static' and 'dynamic' mass spectrometers, together with and historical account of the development of mass spectrometry, see R.E. MARCH, J.F.J. TODD. 'An Appreciation and Historical Survey of Mass Spectrometry'. Ch. 1 in Practical Aspects of Trapped Ion Mass Spectrometry: Theory and Instrumentation, R.E. March & J.F.J. Todd (Eds.) Vol. 4. CRC Press, Boca Raton, FL, 2010.

[8] J.J. Thomson, Further experiments on positive rays, *Phil. Mag*. **24 (**1912) 209-253.

observation of H_5^+ was claimed. Although it was reported that a complete investigation of the hydrogen discharge was being undertaken, no results were reported subsequently.

Simultaneously with the publication of the Dawson and Tickner papers (which included one paper [3] also with Knewstubb as a co-author) were three publications [2,4,6] from Dawson and Robertson that resulted from Peter's doctoral research in London. The reaction of propylene on heated niobium filaments was investigated [2] at pressures of about 10^{-6} mm Hg using mass spectrometry so as to provide a comparison with simple unsaturated hydrocarbons. As a metal with a high melting point and low vapour pressure, niobium is particularly well suited for high temperature catalytic studies. However, pure niobium filaments could be obtained only by extensive outgassing with residual water present due to a relatively high carbon content of ~one atomic %; continuous pumping of the heated niobium filament resulted in decarburization to a state in which further loss of carbon was not possible. Basically, propylene self-hydrogenated to propane while acetylene [4] decomposed completely to carbon and hydrogen, provided that the niobium filament has been extensively outgassed. Of the saturated hydrocarbons investigated [6], the sole reaction path observed for ethane, propane and *n*-butane was that of radical formation, that is, of ethyl, propyl, and butyl radicals, respectively. Hydrogen-atom loss to form radicals is a process of some importance for propane and *n*-butane but less so for ethane. Methane reacted only in the presence of water vapour whereupon only CO was detected. In ammonia glow discharges, both ion clusters [7] and electron-ion recombination coefficients [8] were studied. For the final glow discharge experiments on H_2 – D_2 exchange reactions, the ions present were observed directly by mass spectrometry [10].

In 1963, Dr Dawson left NRCC to take employment as a Research Scientist in the area of Electron Physics with the General Electric Company, working with N. Rey Whetten at *GE*'s [**PRINTER: this symbol has been created using Brush Script M font; please use the official 'GE' logo if possible. Thank you.]** prestigious research facility in Schenectady, New York, USA. At the time, Whetten[9] was involved with developing tubes for colour television, where one of the problems encountered was interference from back-scattered electrons and secondary electron emission. Peter's first communication published while he was at *GE* concerns 'secondary electron emission yields from certain ceramics' [9].

From a personal discussion between Peter Dawson and one of us (JFJT) held in *ca* 1970, it is recalled how Peter explained that every Friday afternoon he and Whetten 'broke out' from their researches in the lab and had tea-time sessions in which one of them talked about something of interest that they had read about in the literature during the previous week. Working in the high vacuum field they were obviously aware of the use of quadrupole mass filters ('QMFs'), and of monopoles, for residual gas analysis[10], and it was in one such discussion that Peter described a publication[11] he had seen on Wolfgang Paul's three-dimensional quadrupole ion trap ('QIT') mass spectrometer.

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[9] N. Rey Whetten, Oral History Interview with Roger Young (1998), available at https://www.avs.org/About/History/Historical-Interviews/AVS-Historical-Interviews (accessed 7 October 2018)

[10] K.G. Günther, Gas-analyzing method and apparatus. *US Patent* 3,075,076 (1963) (Filed 11 December, 1959; German priority date 12 December, 1958); Günther, K.-G. A partial pressure vacuum gauge working according to the principle of the electrical mass filter. *Vacuum* **10** (1960) 293-309.

[11] Wolfgang Paul and Helmut Steinwedel, Apparatus for separating charged particles of different specific charges, *U.S. Patent* 2,939,952 (1960) (Filed 21 December, 1954; German priority date 23 December, 1953).

Although somewhat removed from the thrust of the company's main lines of research, Dawson and Whetten sought to see how the mass spectral performance could be improved by (a) utilising the RF/DC scanning method employed in the QMF and (b) pulse-ejecting the ions for detection, rather than using Paul's complex 'resonance detection method' as described by Fischer[12]. Thus, they hoped to develop a commercial miniature mass spectrometer that had high sensitivity and good dynamic range for partial pressure measurement applications. In the event it was found that the anticipated improvements in mass spectral performance were compromised by neutral background gas scattering of the ions. Also, compared with the QMFs instrumentally, the QIT was rather more complex; in addition, the former devices were becoming progressively smaller through the advent of space applications (in which *GE* also had an interest). As a result, the ion trap mass spectrometer was not the commercial success that they were expecting. Whilst this must clearly have been a set-back at the time, with hindsight, of course, one can see that the field of mass spectrometry as a whole has benefitted hugely from the pioneering studies that Dawson and Whetten undertook in the short period of six years while Peter was at *GE*, and later by Peter Dawson on his own at Laval Université, Québec City and at NRCC in Ottawa; these covered a wide-range of issues relating to the theory, design and performance of quadrupole, monopole and ion trap mass spectrometers[13].

Considering now this endeavour in more detail, we find that beginning in 1968, Dr. Dawson published 19 consecutive papers and patents [11-29] dealing with quadrupoles, monopoles

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[12] E. Fischer, Three-dimensional stabilization of charge carriers in a quadrupole field, *Z. Phys.*, **156**(1) (1959) 1-26.

[13] R.E. March, J.F.J. Todd. Radio frequency quadrupole technology: Evolution and contributions to mass spectrometry. *Int. J. Mass Spectrom.* **377** (2015) 316-328.

and ion traps; N. Rey Whetten was a co-author for 16 of these publications. Following the discussion of flow systems for the monopole and quadrupole mass filter [11], Dawson and Whetten published three papers [13,14,25] together with a patent [12] that were significant for the development of mass analyzers. They revealed that ions could be ejected efficiently from a quadrupole ion trap through holes in one of the end-cap electrodes and be detected externally, thereby avoiding the difficulty of mass-selective detection. As a direct consequence of prolonged ion storage, ions become susceptible to non-linear resonance effects caused by small distortions in the field, including those due to centrally-positioned apertures in the end-cap electrodes. Non-linear resonances cause ions to follow unstable trajectories under conditions when, normally, they would be contained. Non-linear resonances occur as lines of instability where these lines, when plotted on a stability diagram, pass through the $\beta_z = 0$, $\beta_r = 1$ point and interfere with normal operation. Imposition of a variable DC bias voltage between the end-cap electrodes has the effect of moving the operating point to a lower a/q scan line and to higher q values; however, the bias voltage does not shift the non-linear resonances.

These publications included an explanatory/tutorial chapter that dealt in detail (to the extent of 126 pages) with mass spectroscopy using radiofrequency quadrupole fields [24]. The remainder of the 19 consecutive papers and patents dealt successively with ion storage in three-dimensional, rotationally symmetric, quadrupole fields; partial pressure measurement; the monopole and quadrupole ion trap as mass spectrometers; non-linear resonances and peak shapes; circular rods and peak shapes; a miniature quadrupole mass spectrometer; fringing fields; and, in 1971, a chapter of 60 pages entitled ‘Quadrupole mass spectrometry’ [29].

In 1969, Dr. Dawson entered into academia with an appointment as Research Professor at Laval Université, Québec City, as noted earlier, where he continued research in the field of quadrupole devices both alone and assisted by a succession of graduate students, *viz.* R.D. Suart [30], W.G. Tam [33], and C. Lambert [38,40,43]. Dawson published four papers on chemical lasers, one with Suart and G.H. Kimbell [30], one with Kimbell alone [32], one with Tam [33] and a single author paper [35]. In the period January 1972 to December 1975, Dawson published nine papers on quadrupole devices [31,34,37-43] and was awarded U.S. Patent 3,925,662 [36] for the invention of a focussing "dipole" mass spectrometer.

In 1974, Dr. Dawson returned to the government scene at the National Research Council of Canada in Ottawa, initially as Research Officer in the Division of Physics ultimately rising to become Director-General of the NRC Institute for Microstructural Sciences. By 1978, he had published five papers on secondary ion mass spectrometry [42,45,48,49,51] and three papers dealing with quadrupole mass analyser performance [46], the use of phase-space analysis in quadrupole devices [47], and the design and performance of the quadrupole mass filter [50]. His major release in 1976 was *Quadrupole Mass Spectrometry and Its Applications* [52] published by Elsevier; this tome was a tour de force on the part of Dawson and represents a major landmark contribution to the field. Although his intention was to produce a systematic text, he adopted a multi-author format that provided a broader-than-usual viewpoint. Recapitulation in various chapters was kept to a minimum by the circulation of drafts among authors. The first five chapters covering 'Introduction', 'Principles of operation', 'Analytical theory', 'Numerical calculations', and 'Fringing fields and other imperfections' were authored by Dr Dawson himself, and subsequent chapters by W.E. Austin, A.E. Holme, J.H. Leck of the University of Liverpool ('The mass filter: design and performance'); R.F. Herzog of the University of Southern Mississippi ('The monopole: design and performance'); J.F.J.

Todd, G. Lawson, R.F. Bonner of the University of Kent (‘Quadrupole ion traps’); J.P. Carrico of Bendix Research Laboratories (‘Time-of-flight spectrometers’); J.F.J. Todd of the University of Kent (‘Applications in atomic and molecular physics’); G.R. Carignan, University of Michigan (‘Applications in upper atmosphere research’); M.S. Story of Finnigan Corporation (‘Applications to gas chromatography’); and G. Lawson of the University of Kent (‘Medical and environmental applications’). Impetus for this volume came from the rapid proliferation of quadrupole mass filters in the preceding decade. Dawson’s book, in turn, provided further stimulus for widespread research of the action of radiofrequency quadrupole fields and their utilization in mass analyzers such as the quadrupole mass filter, the monopole, the three-dimensional quadrupole ion trap and combinations of quadrupole devices with time-of-flight spectrometers. *Quadrupole Mass Spectrometry and Its Applications* was reprinted on July 21, 2005, as an “American Vacuum Society Classic” by the American Institute of Physics under ISBN 1563964554.

Despite possibly being enticed to bathe in the glory reflected from his well-received book, Dr. Dawson published, in rapid succession, papers on collision processes [53,71], fringing fields, ion transmission, resolution and ion acceptance [54,92,95,96], non-linear resonances [56], application of SIMS [55,57,58,61,72,82,85], application of matrix and phase-space methods to the study of ion optics [59,64,65,75] and a review [60]. Parenthetically, Dawson’s paper on collisions within the 3D QIT [53] highlighted the dramatic difference in ion behaviour in dynamic fields in comparison with that in static fields. Ion/neutral collisions are anathema in static field instruments, whereas in dynamic fields, ion/neutral collisions “will lead to the stabilization of some ion trajectories and the destabilization of others”. Furthermore, “after many collisions all the stabilized ions would tend to move towards the centre of the device and have very low energies”. A reference in this paper [53] is the first publication[14] in this field by the March group that had made their calculations available to Dr Dawson prior to their publication.

In 1981, there was an abrupt change in the pursuits of Dr Dawson due to the granting of a patent to Enke, Yost and Morrison for a triple-stage quadrupole (TSQ) mass spectrometer[15]. Dawson commenced a collaboration with the group at SCIEX and there was a flurry of patents [62] in the field of tandem mass spectrometry using three quadrupole rod sets in-line. In rapid sucession throughout the period 1982-1986, sixteen research papers in the field of triple-stage quadrupole instruments and performance were published: that is, five publications in theory and instrumentation and eleven in applications. With respect to theory and instrumentation, two papers [66,67] were co-authored with researchers Barry French, Adele Buckley, Don Douglas and Doug Simmons from SCIEX; and one paper was co-authored with each of John Fulford, Don Douglas and W.-F. Sun [68,73,77], respectively. Of the publications on applications, collaboration with SCIEX continued with the determination of sulfa drugs in biological fluids, co-authored with Jack Henion and Bruce Thomson (SCIEX) [69], followed by ten publications focused on activity within the collision cell of the TSQ mass spectrometer. Dawson was the sole author in some cases [70,74,86,87], was co-author for four papers with W.-F. Sun [71,81,84,91] including the results of a round robin on the reproducibility of standard operating conditions for the acquisition of library MS/MS

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[14] R.F. Bonner, R.E. March, J. Durup, The effect of charge exchange reactions on the motion of ions in three-dimensional quadrupole electric fields. *Int. J. Mass Spectrom. Ion Phys.* **22** (1976) 17-34.

[15] C.G. Enke, R.A. Yost, J.D. Morrison, Tandem quadrupole mass spectrometer for selected ion fragmentation studies and low energy collision induced dissociator therefor. *U.S. Patent* 4,234,791 (November 1980).

spectra using TSQ-MS [77], for one with Don Douglas [76], and one concerning synthesis in a collision cell with J.P. Schmit and N. Beaulieu [78]. In the same period, Peter continued surface studies with M.L Denboer on electron-induced desorption of O^+ from W, Mo and Co [72] and with V.S. Sundaram for both CO chemisorption on a platinum surface [82] and electron-stimulated desorption of O_2 from platinum [85]. With Y. Bingqi, Dawson both studied the emittance of ion sources in quadrupole MS [75] and began an exploration of the second stability region [39,79,80,83].

Looking back, the period from about 1985 to 1990 could be characterized as a somewhat drawn-out finale for Peter's husbanding of the ensemble of quadrupole devices. The excitement of tandem mass spectrometry with the TSQ mass spectrometer had brought forth myriad papers that had contributed to the marked advancement of the field of mass spectrometry. What now? The next seven quadrupole papers were written by Peter alone and it seems as though he had been thinking of a variety of aspects of the performance of quadruple devices but had been too involved to clarify those aspects in his mind. The finale of his publishing career would consist of performance characteristics of an **r.f.-only** quadrupole [88,92,93]; **mass filter** performance [89]; **performance, design and applications** of quadrupole mass analyzers [90]; the quadruple mass filter and **modulated voltages** [92,93]; quadrupole mass filter with **varying Mathieu parameter** [94]; quadrupole mass filter with **bent and bowed rod sets** [95]; and **source-analyzer coupling** in the quadrupole mass filter [96]. This was the end of Peter's immense contributions to our knowledge and understanding of quadrupole devices and fields. Thank you, Dr Dawson.

Five years later, Dr Dawson published, along with R. Dalpé, B. Longpré and C. Caron, a bibliometric view of the state of Canadian research in semiconductors and photonics [97]. An interval of six years between publication of this work and his analysis of source-analyzer coupling [96] together with a marked change of field caused JFJT and REM to doubt the connection between Dr Dawson and this bibliometric view! However, with the assistance of Steven Leclair, NRC Archives Officer, we were able to contact Carl Caron who confirmed that Dr Peter H. Dawson was the author of the piece and that Carl had been a student at the time of preparation of the manuscript.

Upon concluding his work as Director-General of the NRC Institute for Microstructural Sciences, Dr Dawson returned to private industry forming the spin-off company Iridian Corporation, also in Ottawa.

A table summarising Peter Dawson's education and employment history is presented in Appendix II.

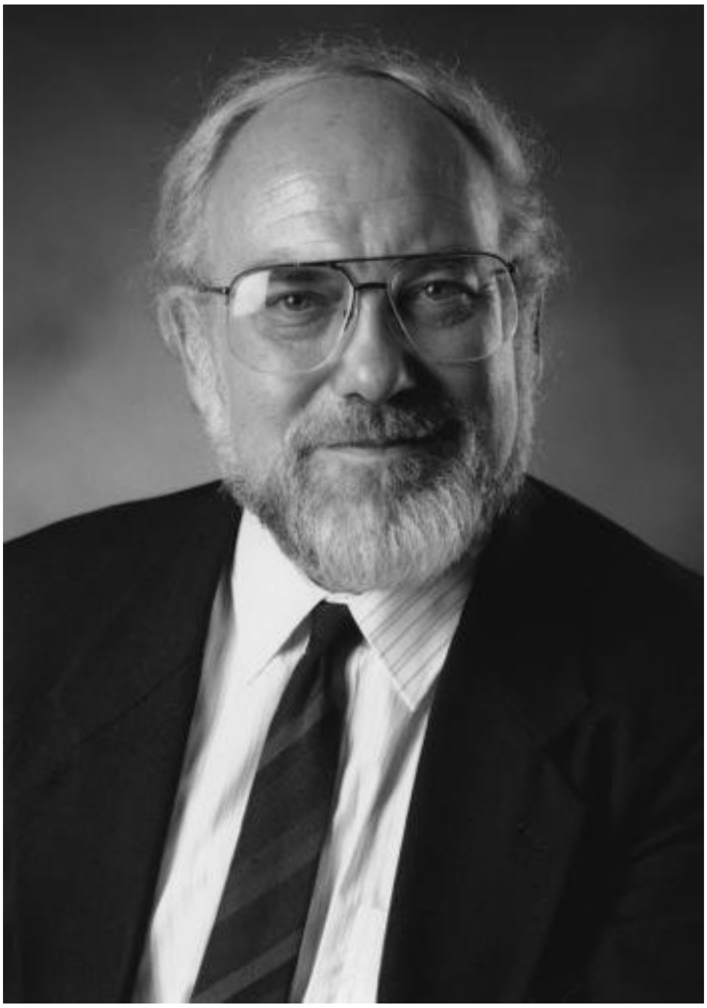

Fig. 1. Dr Peter H. DAWSON, Ph.D. 1937 – 2015

Table 1. Research 'Themes' Encompassed by the Publications of Peter H. Dawson

1.0 Gas-phase Chemistry

- 1.10 Electrical Glow Discharges
- 1.20 High-temperature Catalytic Reactions

2.00 RF Quadrupole Theory and Technology

- 2.10 General reviews, books, etc.
- 2.20 Quadrupole Mass Filter (QMF)
  - 2.21 Field imperfections; non-linear resonances; peak shapes
  - 2.22 Fringing fields; ion transmission; resolution; ion acceptance
  - 2.23 Application of matrix and phase-space methods; ion optics
  - 2.24 Higher stability zones
  - 2.25 RF-only quadrupole mass spectrometer
- 2.30 3D Quadrupole Ion Trap (3D-QIT)
  - 2.31 Field imperfections; non-linear resonances; peak shapes
  - 2.32 Collision processes
  - 2.33 Application of matrix and phase-space methods; ion optics
- 2.40 Monopole
  - 2.41 Field imperfections; non-linear resonances; peak shapes
  - 2.42 Fringing fields
  - 2.43 Application of matrix and phase-space methods; ion optics
- 2.50 Focussing 'Dipole'
- 2.60 Tandem MS: Triple Quadrupole MS
  - 2.61 Theory and Instrumentation
  - 2.62 Applications

3.00 Gas-phase Spectroscopy

3.10 Chemical Lasers

3.20 Vibrational Energy Transfer

4.00 Secondary Ion Mass Spectrometry (SIMS)

4.10 Instrumentation

4.20 Applications

5.00 Semiconductors and Photonics

(TABLE 2)

APPENDIX I

List of publications of Dr. Peter H. Dawson 1962 – 1996*

*Following the format given for the publications of John H. Beynon in *Rapid Commun. Mass Spectrom.* **18** (2004) 24-36.

The date of submission of the original manuscript is given, wherever possible, in parentheses after the names of the authors; the 'research themes' to which the publications have been assigned (see Table 1) are shown in square brackets before each reference. Abstracts or summaries have been included where these are available.

[1.10] 1. Detection of H_5^+ in the hydrogen glow discharge. *J. Chem. Phys.* **37** (1962) 672–673. (P.H. Dawson, A.W. Tickner). [21 May 1962].
[Letter, no abstract]

[1.20] 2. Catalytic reaction of propylene on incandescent niobium. *J. Chem. Phys.* **38** (1963) 280–281. (P.H. Dawson, A.J.B. Robertson). [6 Aug 1962].
[Letter, no abstract]

[1.10] 3. Mass spectrometry of ions in glow discharges. V. Oxygen. *J. Chem. Phys.* **38** (1963) 1031–1032. (P.F. Knewstubb, P.H. Dawson, A.W. Tickner). [12 Nov 1962].
[Letter, no abstract]

[1.20] 4. Decomposition of acetylene on incandescent niobium. *Trans. Faraday Soc.* **60** (1964) 1122–1130. (P.H. Dawson, A.J.B. Robertson). [7 Jan 1963].
The decomposition was investigated on niobium filaments at pressures between 5x 10^{-5} and 1 x 10^{-6} mm Hg. The probability P of reaction at a collision of C_2H_2 with the surface was given by $P = B \exp(-E/RT)$. Complete breakdown of C_2H_2 occurred causing deposition of C on the catalyst. The state of the catalyst surface was dependent on the past use of the catalyst, particularly its immediate pre-treatment, and states of widely different degrees of carburization, and the transitions from one state to another, were studied. Well-outgassed filaments showed great catalytic activity with P nearly unity at 850°C. A decline in activity occurred with use at the lower temperatures and seemed to be related to carburization. On slightly carburized filaments the activation energy for P was 36 kcal/mole and B varied with carburization from 102.8 to 104.1. With carburization sufficient to form Nb_2C, the characteristics of the reaction changed: B became constant at

109.3 with *E* of 77 kcal/mole. These filaments could also be made more active by a short high-temperature flashing, but the extra activity decayed as reaction occurred. At high temperatures *P* became unity on the slightly carburized filaments. Between *P* = 1 and *P* = 0.1 the Arrhenius relation failed, but the results could be interpreted quantitatively by a simple equation based on the idea of a molecular adsorption prior to reaction. [© Royal Society of Chemistry, 1964.]

[1.10] 5. Positive ions in the carbon Dioxide Glow Discharge. Proc. VIth Int. Conf. Phenomena in Ionized Gases, Paris, France 8-13 July 1963, Vol. II, Ed. P Hubert, E. Crémieu-Alcan, State Minister for Scientific Research, Atomic and Space Matters, Paris (1963), p. 79. (P.H. Dawson, A.W. Tickner). [8 July 1963].

[No abstract; no text available]

[1.20] 6. Reactions of methane, ethane, propane and *n*-butane on incandescent niobium filaments. *Trans. Faraday Soc.* **60** (1964) 157–170. (P.H. Dawson, A.J.B. Robertson). [12 Aug 1963].

The reactions were investigated by mass spectrometry using reactant pressures of ~10^{-5} mm Hg. With ethane, propane and *n*-butane the activity of the niobium as a catalyst was dependent on its pre-treatment. Both decarburization and carburization of the niobium by reaction of background gases occurred under various vacuum conditions, and there was a correlation between the catalyst activity and the state of carburization of the surface, or the metal underlying the surface. Extensively outgassed niobium filaments, which probably had low surface carbon concentrations, showed high catalytic activity. The probability *P* of reaction per collision of a molecule with the niobium was represented by $P = B \exp(-- E/RT)$ with low values of *E*, decreasing from ethane to propane to butane, and values of *B* near unity. On carburized surfaces *P* was less and *E* and *B* were greater. *E*, however, was not dependent on the extent of carburization when this became greater, but *B* decreased with increasing carburization. Whatever the state of the catalyst surface, free radicals were produced from ethane, propane and butane by loss of one atom of hydrogen. Reactions involving complete catalytic breakdown of the hydrocarbon or of the radical formed could also have occurred. Butyl radicals were found to be particularly reactive on the niobium. Reaction of methane was only observed in the presence of water vapour. Results were consistent with the idea of a direct interaction on the surface between methane and water. [© Royal Society of Chemistry, 1964.]

[1.10] 7. Ion clusters in the ammonia glow discharge. *J. Chem. Phys.* **40** (1964) 3745–3746. (P.H. Dawson, A.W. Tickner). [26 Feb 1964].

[Letter, no abstract]

[1.10] 8. Electron-ion recombination coefficients in ammonia. *Br. J. Appl. Phys.* **15** (1964) 1597–1597. (P.H. Dawson, A.W. Tickner). [27 Oct 1964].

It is suggested that the electron-ion recombination coefficient reported by Court and Sayers may be for the ion NH_4^+ rather than NH_3^+ since the reaction $NH_3^+ + NH_3 = NH_4^+ + NH_2$ occurs so readily. [© Institute of Physics and IOPScience, 1964.]

[1.10] 9. Secondary electron emission yields of some ceramics. *J. Appl. Phys.* **37** (1966) 3644–3645. (P.H. Dawson). [11 April 1966].

[Communication, no abstract]

The charging of ceramic insulators in electron devices may cause spurious effects. This has led to interest in their secondary electron properties. Secondary emission measurements for bulk insulators at room temperature have not been extensive. One problem is the avoidance of surface charging during yield measurements. Charging can be limited by using single-pulse methods and, if the surface has become positively charged, its potential can be re-established between pulses by flooding with very low-energy electrons. [© American Institute of Physics, 1966.]

[1.10] 10. Mass spectrometry of ions in glow discharges: application to H_2-D_2 exchange reactions. *J. Chem. Phys.* **45** (1966) 4330–4336. (P.H. Dawson, A.W. Tickner). [13 July 1966].

The negative glow of the dc glow discharge was used to study H_2—D_2 exchange by an ionic chain reaction. The ions present were observed directly by mass spectrometry. The chain carrier was H_3^+ and the chain length about 15 at 0.3 torr. The inhibition by added rare gases was examined and detailed comparisons are made with radiolysis experiments. Qualitatively the agreement is excellent. Several possible inhibition mechanisms are considered. [© American Institute of Physics, 1966.]

[2.10] 11. Quadrupoles, monopoles and ion traps. *Research/Development* **19** (1968) 46–50. (P.H. Dawson, N.R. Whetten). [No submission date given; published February 1968]

[No abstract]

This article describes the operation of the quadrupole mass filter, the monopole, and the newest entry to the field, which is not yet available commercially, the three-dimensional quadrupole spectrometer or ion trap. This device can store ions for long periods of time and has numerous exciting applications.

[2.30] 12. Three-dimensional quadrupole mass spectrometer and gauge, US Patent 3,527,939, Issue date 8 September 1970. (P.H. Dawson, N.R. Whetten). [Filed 29 August 1968 (continuation part of previous application filed 27 March 1967)].

A mass spectrometer and ion gauge employs opposed electrodes to form a containment region in which superimposed variable high frequency and direct current potentials on the electrodes establish a rotationally symmetric hyperbolic electric field so that ions of a given or selected *e/m*, depending on the values and frequency of the potentials, are trapped and stored for a controllable time period. Periodic voltage pulses applied to the electrodes sweep trapped ions through an aperture in one electrode to an electron multiplier and measuring circuits. By varying the intensities and frequencies of the potentials ions of differing mass can be separated and measured. [© US Patent and Trademark Office, 1970.]

[2.30] 13. Ion storage in three-dimensional, rotationally symmetric, quadrupole fields. I. Theoretical treatment. *J. Vac. Sci. Technol.* **5** (1968) 1–10. (P.H. Dawson, N.R. Whetten). [5 July 1967].

The theoretical basis for the trapping of charged particles in a three-dimensional, rotationally symmetric, quadrupole field is discussed. The authors have constructed both a sensitive mass spectrometer and an ion gauge based on ion storage. This paper presents background material for this work, based on numerically computed solutions to the differential equations of motion. Predictions are obtained concerning ion trajectories, resolution, sensitivity, storage, and peak shape. [© American Vacuum Society, 1968.]

[2.30] 14. Ion storage in three-dimensional, rotationally symmetric, quadrupole fields. II. A sensitive mass spectrometer. *J. Vac. Sci. Technol.* **5** (1968) 11–18. (P.H. Dawson, N.R. Whetten). [5 July 1967].

A mass spectrometer has been constructed in which ions are trapped in a three-dimensional, rotationally symmetric, quadrupole field. Ions of a specific charge to mass ratio are stored and then periodically drawn out of the trapping field into an electron multiplier. The ion trapping feature permits integration of the ion current over long periods of time. Electrodynamic ion trapping also enables a long effective path length to be attained in a small size device. Ions have been stored for several days using a low-resolution mode. Experimental data are presented concerning storage time, resolution, and sensitivity. Factors affecting the peak shape include storage time, resolution, and bias voltage between the end-caps. The theoretical basis for the trapping of charged particles in a three-dimensional, quadrupole field is discussed in a companion paper. [© American Vacuum Society, 1968.]

[2.30] 15. Partial-pressure analysis with three-dimensional quadrupole fields, Proc. 4th International Vacuum Congress, Manchester, 17-20 April 1968, IOP, London(1968) pp. 713-716 (General Electric Co., Schenectady, NY, Reprint 6159). N.R. Whetten, P.H. Dawson.

The three-dimensional quadrupole mass spectrometer permits ion storage and mass selection in a small volume. Ions of a single mass species may be trapped at one time, and pulsed out of the trap into an electron multiplier at selected intervals. The intervals may be lengthened if the pressure is low, since ion storage provides integration of the ion-formation rate. Distortions in the quadrupole field caused, for example, by errors in spacing of the electrodes, were found to produce poor peak shapes. Numerical computations of ion trajectories in the presence of higher than second-order potential terms agree with the experimentally observed peak splitting. The resonance dips occur at specific locations on the stability diagram. By applying a small d.c. bias voltage to one of the endcaps, the tip of the stable region can be shifted away from the region of the resonance lines, thereby improving the peak shape in spite of the presence of field errors. [© Institute of Physics, 1968.]

[2.40] 16. The monopole mass spectrometer. *Rev. Sci. Instrum.* **39** (1968) 1417–1422. (P.H. Dawson, N.R. Whetten). [20 May 1968; 13 June 1968].

Monopole mass spectrometer characteristics were determined by analyzing ion trajectories under various operating conditions. The trajectories were computed by numerical integration of the Mathieu equations of motion. The mode of operation was chosen to correspond with that in general use, with ion injection being parallel to the axis of the instrument. The simulation was made specific by considering a monopole under operating conditions such that an ion with *m/e*=72 spends 12 rf cycles within the field. Information was obtained concerning peak shape, sensitivity, and resolution. The influence of entrance and exit slit dimensions and of rod- Vee block spacing was determined. [© American

Institute of Physics, 1968.]

[2.31] 17. Non-linear resonances in quadrupole mass spectrometers due to imperfect fields I. The quadrupole ion trap. *Int. J. Mass Spectrom. Ion Phys.* **2** (1969) 45-59. (P.H. Dawson, N.R. Whetten). [9 August 1968].

Peak-shape distortions and peak-splitting are commonly observed phenomena with all members of the quadrupole family of mass spectrometers. Errors in electrode shape, or spacing, or harmonics in the r-f_ field may produce non-linear resonances. The resonances result in peak splitting by causing some ion trajectories to become unstable that otherwise, in a perfect field, would be stable and limited in amplitude. A theory of non-linear resonances in quadrupole fields was applied to the three-dimensional rotationally symmetric quadrupole ion trap to predict resonance locations in the Mathieu stability diagram. Numerical computation of trajectories was used to derive peak shapes for various amounts of distortion and to determine the extent of peak-splitting. The calculations were used to relate the performance to the spacing errors in assembling the electrode structure. The occurrence of resonances, in agreement with this theory, was experimentally demonstrated. A method is presented for obtaining good peak shapes in spite of the presence of field distortions, but with some loss in sensitivity. This method was investigated both experimentally and theoretically. [© Elsevier BV, 1969.]

[2.40] 18. Some properties of the monopole mass spectrometer. *J. Vac. Sci. Technol.* **6** (1969) 97–99. (P.H. Dawson). [14 August 1967].

Monopole mass spectrometer characteristics have been analyzed by determining ion trajectories under various operating conditions. The trajectories were obtained by numerical integration of the equations of motion. Peak shapes were derived for ions spending 20 rf cycles in the field, for various entrance/exit slit ratios, with ion injection parallel to the instrument axis. Comparison with earlier results shows that resolutions at half-height can be expressed as $(n/p)^2$, where n is the number of cycles an ion spends within the field and p is constant for a given exit slit-width. Ion injection at an angle to the instrument axis was also considered. Peaks then showed much less spread on the low mass side. For ions entering the field at a fixed angle, the peaks may exhibit a central dip if the exit slit width is too small. [© American Vacuum Society, 1969.]

[2.31] 19. Some causes of poor peak shapes in quadrupole field mass analyzers. *J. Vac. Sci. Technol.* **6** (1969) 100–103. (N.R. Whetten, P.H. Dawson). [14 August 1968].

The performance of quadrupole field mass analyzers can be degraded by imperfections in the field. The imperfections may be the result of geometrical errors in the electrode structure or time errors in the applied waveforms. von Busch and Paul considered the nonlinear resonances resulting from these errors for the quadrupole mass filter using an analytical treatment of the ion motion. The authors extended this work to the three-dimensional quadrupole mass spectrometer, and using numerical computation of ion trajectories calculated the extent as well as the position of the resonances. In this paper, new experimental data are presented showing the occurrence of nonlinear resonances and the agreement between theory and experiment. The effect of adjustments in electrodes spacing on peak shapes was investigated. The results demonstrate that an analysis of the nonlinear resonances can provide an indication of the errors that are present. A new type of instability was found in the three-dimensional quadrupole, and a tentative explanation is presented. [© American Vacuum Society, 1969.]

[2.30] 20. The three-dimensional quadrupole ion trap. *Naturwissenschaften*. **56** (1969) 109-112. (P.H. Dawson, N.R. Whetten). [16 December 1968].

[No abstract provided; the first paragraph of the paper is reproduced here.]

Charged particles may be “stored” or confined in a small volume by using a dynamic three-dimensional quadrupole electric field. For example, in a field of less than 1 cm^3, ions have been trapped for several days. The storage property has resulted in some novel applications of three-dimensional quadrupole electric fields. In this article, the geometry of the field is described and then some of its applicationsfor charged-particle storage are briefly reviewed . The Mathieu equation of ion motion and its solutions are discussed to illustrate how the ion trapping can be made mass-selective, and how the trap may be used in mass spectrometry. [© Springer-Verlag, GmbH, 1969.]

[2.21] 21. Quadrupole mass filter: circular rods and peak shapes. *J. Vac. Sci. Technol.* **7** (1970) 440-441. (P.H. Dawson, N.R. Whetten). [9 February 1969].

A frequently observed characteristic of quadrupole mass filters is the appearance, at high resolution, of a separate “precursor” peak on the low mass side of each mass peak. The present report shows that such false precursor peaks can result from the use of round rods (rather than hyperbolic rods) that are common in all commercial instruments. Round rods introduce sixth- and tenth-order terms to the ideal quadrupole field. We have computed the amount of sixth-order distortion introduced by the use of circular rods. The equipotential line produced at the surface of a round rod can be represented quite well by a quadrupole field with a large amount of sixth-order distortion. This distortion introduces a resonance line in the Mathieu stability diagram that at high resolution is near the edge of the peak on the low mass side. The resonance line can distort the peak to produce an apparent precursor peak. [© American Vacuum Society, 1970.]

[2.21] 22. Non-linear resonances in quadrupole mass spectrometers due to imperfect fields II. The quadrupole mass filter spectrometer and the monopole mass spectrometer. *Int. J. Mass Spectrom. Ion Phys.* **3** (1969) 1-11. (P.H. Dawson, N.R. Whetten). [10 February 1969; 9 May 1969].

Peak-shape distortions and peak-splitting are commonly observed phenomena with all members of the quadrupole family of mass spectrometers. Errors in electrode shape, or spacing, or harmonics in the r.f. field may produce non-linear resonances. The resonances result in peak splitting by causing some ion trajectories to become unstable that otherwise, in a perfect field, would be stable and limited in amplitude. In Part I a theory of non-linear resonances in quadrupole rotationally symmetric quadrupole fields was applied to the three-dimensional ion trap. In the present paper, the theory of non-linear resonances is applied to the quadrupole mass filter and to the monopole mass spectrometer. Numerical computation of ion trajectories was used to determine the extent of peak-splitting for various amounts of third and fourth order spatial distortion and to determine the positions of resonance lines in the stability diagram. The calculations were used in the case of the mass filter to relate the performance to possible spacing errors in assembling the electrode structure. The monopole operating point can be chosen to avoid the resonance lines. The focusing quality is; however, affected by the presence of distortions. For the monopole, peak shapes were determined from the computed ion trajectories. A small amount of one type of third-order distortion is shown to be beneficial. [© Elsevier BV, 1969.]

[2.30] 23. A miniature mass spectrometer. *Anal. Chem.* **42** (1970) 103A–108A. (P.H. Dawson, J.W. Hedman, N.R. Whetten). [No date].

Achievements to date hold promise for the development of a relatively inexpensive, lightweight, rugged instrument with good sensitivity, moderate resolution, and capability of easy operation from a central multi-station control. [© American Chemical Society, 1970.]

[2.10] 24. Mass spectroscopy using RF quadrupole fields, in: Adv. Electron. Electron Phys., Vol. 27, Academic Press, New York, 1970, 59–185. (P.H. Dawson, N.R. Whetten). [No date].

This chapter describes mass spectroscopy and the general theoretical background for charged particle motion in RF quadrupole fields and includes graphical illustrations of solutions to the Mathieu equations of motion of the particles. The evolution of mass spectrometers has been extremely rapid, reflecting inherent advantages such as their small size and weight and the absence of a magnetic field. The role of quadrupole mass spectroscopy has been greatest in the field of partial pressure analysis and in special applications. One limitation is that the RF power increases with the square of the ionic mass, and higher mass ranges can be obtained only by use of high power or low RF frequencies or very small radius instruments. Further evolution of the quadrupole and monopole may occur in different methods of utilizing the fields. The effective length of the instrument could be increased by multiple traverses of one or more devices. Alternatively the rods might be bent into a closed circle configuration. One might use to better advantage the focusing properties of quadrupole fields, as suggested by Lever in his exact focusing monopole. [© Elsevier BV, 1970.]

[2.30] 25. 3-D Quadrupole ion trap mass spectrometer. AFCRL-69-0185, General Electric Company, Schenectady, NY, 1969. (P.H. Dawson, N.R. Whetten). [18 April 1969].

Two mass spectrometers of the three-dimensional quadrupole type were constructed, along with the associated electronics. The electrodes of the mass spectrometers were accurately machined from stainless steel to the shape of hyperboloids of revolution. The dimensions were chosen to have z_o (the minimum distance from the center to one of the endcaps) equal to 1.3 cm. The electronics has an r-f frequency of 1 MHz, and a voltage of 5000 volts, peak-to-peak. The mass range is from 1 to 75 atomic mass units. Heavier masses can be stored in the spectrometer, but cannot be easily mass-analyzed with the present electronics. The ion storage properties of these units are extremely good. Ions were stored in the mass spectrometer for days at low pressures. An interesting property was observed that may be useful in ion storage experiments. The presence of a neutral light gas, such as helium, was found to make heavier ions much more stable. The ion densities that can be stored in the spectrometer were found to be somewhat higher than had originally been expected. A direct calibration measurement yielded a value of 5 x 10^8 ions in the spectrometer. A new phenomenon discovered in this work (self-ejection of ions due to ion plasma resonances) enabled an independent density determination to be obtained. This density was higher, being 6. 4 x 10^8 ions/cm^3 for mass 28 ions in some volume near the center of the spectrometer. [© General Electric Company, 1969.]

[2.30] 26. A simple mass spectrometer. *Rev. Sci. Instrum.* **40** (1969) 1444–1450. (P.H. Dawson, J.W. Hedman, N.R. Whetten). [25 June 1969; 6 August 1969].

A mass spectrometer of unusually simple construction is described. The three electrodes were hand formed from coarse stainless steel mesh. Despite the imprecise shape of the electrodes, the spectrometer has a half-height resolution of 75. The device is a three-dimensional quadrupole, or ion trap type of mass spectrometer. It is operated so as to store a single *m/e* species at a time. After a suitable storage time, the ions are pulsed out of the trap into an electron multiplier for detection. The optimization of operating parameters and the ion buildup characteristics for various gases are presented. The performance of the instrument is compared to that of a magnetic sector mass spectrometer. The cracking patterns are simpler than for the magnetic analyzer. In contrast with the magnetic analyzer, no extraneous peaks due to ion desorption from surfaces are present. The lowest measured partial pressure was about 10^{-12} Torr, and this was limited only by the minimum total pressure attained. Trace analysis capability of 1 part in 2500 was observed with little effort to optimize this property. [© American Institute of Physics, 1969.]

[2.22] 27. Fringing fields in the quadrupole mass filter. *Int. J. Mass Spectrom. Ion Phys.* **6** (1971) 33–44. (P.H. Dawson). [12 October 1970].

The mass filter is a dynamic mass spectrometer and its performance is very dependent on fringing fields at the entrance and exit. The influence of these fields was investigated by a computer calculation of ion trajectories. Entrance ramps, where the static and dynamic components of the field increase gradually to their full values, create a near equivalence of ion behaviour for all initial phases of the r.f. field. This leads to good resolution and good peak shape. In this sense, entrance ramps are preferable to perfect, abruptly beginning, fields. For coincident (d.c. and a.c.) ramps of less than about three r.f. cycles there is also a larger effective aperture than for the "perfect" field, but long ramps lead to small effective apertures. This may cause discrimination against ions of low velocity (high mass or low energy). Ramp effects have undoubtedly been present in many existing quadrupole mass filter designs. The "delayed" d.c. ramp proposed by Brubaker retains the near-equivalence of ion behaviour for all phases of the r.f. field and solves the aperture problem in the case of the slow ions. At the exit from the quadrupole, it is suggested that an advanced d.c. ramp may sometimes be advantageous to ensure total ion collection. [© Elsevier BV, 1971.]

[2.42] 28. Use of fringing fields in the monopole. *J. Vac. Sci. Technol.* **8** (1971) 263–265. (P.H. Dawson). [Conference date: 20 October 1970].

Previous computations of ion trajectories in the monopole mass spectrometer [P. H. Dawson and N. P. Whetten, *Rev. Sci. Instrum.* **39** (1968) 1417–1422.] for ion injection parallel to the instrument axis, have predicted asymmetric peaks with a tail on the low mass side and only 40% ion transmission. This is because an off-axis object cannot be completely focused at the exit from the analyzer. It is shown here that superior focusing at the analyzer exit, leading to symmetrical peaks, 100% ion transmission and, in some conditions, a reduction in the necessary rod-Vee Block spacing, and therefore in r.f. power, can be obtained by proper use of a fringing field at the monopole entrance. A simple linear entrance ramp, where ion trajectories are mathematically unstable, and which is apparently harmful to the quadrupole mass filter [W. M. Brubaker, Advances Mass Spectrometry. **4** (1967) 293], can be beneficial in the monopole. Examples of computed ion trajectories and peak shapes are given and various entrance ramps are compared. The chance use of an entrance ramp probably explains some of the high performance monopoles that have been constructed. [© American Vacuum Society, 1971.]

[2.10] 29. Quadrupole mass spectrometry, in: D. Price (Ed.), Dyn. Mass Spectrom., Vol. 2, 1971, 1-60. (P.H. Dawson, N.R. Whetten). [No submission date]

[Review, no abstract]

In this review, we shall attempt to present the general principles of operation of quadrupole mass spectrometers, to contrast their differences, and to relate their present performance. We make some predictions about possible future trends in this field. [© John Wiley & Sons, 1971.]

[3.10] 30. CS_2/O_2 Chemical lasers: chemistry and performance characteristics. *J. Appl. Phys.* **43** (1972) 1022–1032. (R.D. Suart, P.H. Dawson, G.H. Kimbell). [26 July 1971; 20 September 1971].

Experimental results from the CS_2/O_2 chemical laser system using both a flash photolysis initiated pulsed laser and a microwave discharge initiated continuous-wave laser were examined by computer simulation techniques. The comparisons between predicted and observed laser performance led to some conclusions concerning the chemical mechanisms operative in the laser. In particular, the laser pumping step is $O+CS\rightarrow CO+S$ followed by the chain carrying step $S+O_2\rightarrow SO+O$ which must be rapid, in agreement with the measurements of Fair and Thrush. The oxygen atom consuming reaction, $O+NO_2\rightarrow NO+O_2$, competes too strongly with the other reaction steps for the photolysis of NO_2 to be effective as a power improving technique in the flash photolysis laser. The cw laser operates on totally inverted vibrational level populations when cold CO is added to the reaction mixture. Some evidence was found to suggest that excess O_2 molecules may act as a vibrational energy sink in the cw system. The laser was operated at a power of 2.3 W cw exhibiting 0.92% and 0.64% chemical and electrical efficiencies, respectively. [© American Institute of Physics, 1972.]

[2.+22/2.42] 31. Fringing fields in quadrupole-type mass analyzers. *J. Vac. Sci. Technol.* **9** (1972) 487–491. (P.H. Dawson). [28 July 1971].

[No abstract provided. A comment is presented from paragraphs 2-3 of the Introduction.]

Fringing fields seem to be the key to the high performances achieved with the mass filter and with the monopole. The case of the “fringe-free” or abruptly beginning field applies to the three-dimensional quadrupole where the ions to be analyzed are created within the quadrupole field. In any evaluation of its properties in relation to the mass filter or monopole, the fringing fields of the latter must be considered. The importance of the fringing fields was recognised by Brubaker, after observation of the effect of ion entrance angle on transmission. He reported the first computations of the effects of fringing fields on amplitudes of ion motion. [© American Vacuum Society, 1972.]

[3.10] 32. Chemical lasers, in: L. Marton, C. Marton (Eds.), Adv. Electron. Electron Physics, Vol. 31, Academic Press, New York, 1972, 1–37. (P.H. Dawson, G.H. Kimbell). No submission date.

In this article we discuss first the necessary conditions for the achievement of chemical lasing action and then describe, in turn, the important processes involved in lasing systems such as (a) the vibrational transition which gives the emitted radiation, (b) the production of vibrationally excited species by reaction, and (c) the vibrational—vibrational and vibrational—translational energy exchanges which can cause depopulation of the excited levels. In order to achieve chemical laser action, the pumping reaction must be (i) exothermic, (ii) lead to product molecules in an inverted population, and (iii) be sufficiently fast to maintain an appreciable inversion in the system. Measurement of product energy distributions have generally been made by studying either infrared chemiluminescence or molecular beam techniques. The main effort in the exploration of theoretical approaches has been in the use of classical trajectory calculations of reaction dynamics, especially by Polanyi and co-workers. We give a qualitative account of such calculations for the three-body exchange reaction A+ BC → AB + C. Finally we describe some typical examples of chemical lasers to illustrate the progress achieved. Since the field of chemical lasers is evolving so rapidly, there is no attempt at comprehensive coverage of the achievements. [© Elsevier BV, 1972.]

[3.20] 33. Vibrational energy transfer in carbon monoxide. *Can. J. Phys.* **50** (1972) 889–897. (P.H. Dawson, W.G. Tam). [1 November 1971].

The role of V–V processes in vibrationally excited CO systems in the longitudinal and transverse flow chemical lasers is studied. Initial vibrational energy distributions of CO formed by the O + CS reaction are deduced from chemiluminescent data using calculated values of the vibration energy exchange probabilities. The time evolution of the population distributions is then obtained by computer simulation. The results are compared with experimental measurements. The effects of excess oxygen and of "cold" CO on the population distributions are also discussed. [© National Research Council, 1972.]

[2.50] 34. A high-resolution focussing “dipole” mass spectrometer. *Int. J. Mass Spectrom. Ion Phys.* **12** (1973) 53–65. (P.H. Dawson). [2 December 1972].

A high-resolution focussing “dipole” mass spectrometer is proposed and its properties are explored by the computer calculation of ion trajectories. The device has a field corresponding to half that of a quadrupole mass filter and consists of two hyperbolic rods and a plane grounded electrode. Low energy ions are injected transversely to the instrument axis. It is shown that by using the focussing properties of quadrupole fields, both a high resolution and a large mass range should be possible while preserving the usual advantages of quadrupole mass spectrometers. [© Elsevier BV, 1973.]

[3.20] 35. Evolution of the CO vibrational energy distribution in a transverse flow laser. *Can. J. Phys.* **51** (1973) 1026–1029. (P.H. Dawson). [7 December 1972].

Values of the probabilities of vibrational energy exchange among CO molecules are calculated using the long-range force theory and provide the basis for a computer simulation of CO vibrational energy distribution in a transverse flow chemical laser. A comparison with experimental data demonstrates the importance of the very rapid redistribution of energy among high-lying levels due to CO†–CO† interactions and of the role of the chemical by-product OCS in enhancing the population inversion in levels $v = 6$ to 10. [© National Research Council, 1973.]

[2.50] 36. High-resolution focussing dipole mass spectrometer, US Patent 3,925,662, Filed 25 March 1974; Issued 9 December 1975. (P.H. Dawson). [Also published as Canadian Patent CA973282A, Filed 20 July 1973; Issued 19 August 1975.].

The high-resolution focussing dipole mass spectrometer consists of two suitably spaced hyperbolic rods and a grounded plate electrode in a plane parallel to the rods. A voltage consisting of a constant voltage U and an alternating voltage $V \cos \omega t$ is applied between the rods. Low energy ions are injected into the field transversely to the rods, through an entrance slit in the plate. Ions of the particular mass are focussed by the field so as to leave the device through an exit slit in the plate. By using the focussing properties of quadrupole fields, both a high resolution and a large mass range is possible while preserving the usual advantages of quadrupole mass spectrometers. [© US Patent and Trademark Office, 1975.]

[2.22] 37. A detailed study of the quadrupole mass filter. *Int. J. Mass Spectrom. Ion Phys.* **14** (1974) 317-337. (P.H. Dawson). [15 February 1974].

The use of matrix methods to calculate ion displacements in quadrupole fields is applied to a detailed simulation of mass filter operation. Ion transmission is calculated for various scan lines and various apertures both with and without fringing fields. The experimentally observed tailing on the low mass side due to insufficient cycles of the r.f. field is explained and its avoidance investigated. Study of ion transmission as a function of initial phase shows that the optimum initial phase for maximising instrument aperture is associated with the necessity for a longer instrument. Conversely, the optimum phase for minimising instrument length has the poorest useful aperture. [© Elsevier BV, 1974.]

[2.30] 38. Pulse-out synchronization in the quadrupole ion trap. *Int. J. Mass Spectrom. Ion Phys.* **14** (1974) 339–347. (P.H. Dawson, C. Lambert). [27 February 1974].

Detailed observations were made of the dependence of the output signal of a quadrupole mesh ion trap on the r.f. phase and amplitude of the pulse which empties the trap. The behaviour is complex, but improved trajectory calculations qualitatively explain the observed results. Correct choice of pulse phase and amplitude may be very important in ion trap experiments. [© Elsevier BV, 1974.]

[2.24] 39. Higher zones of stability for the quadrupole mass filter. *J. Vac. Sci. Technol.* **11** (1974) 1151-1153. (P.H. Dawson). [24 July 1974; 10 September 1974].

Matrix methods based on phase-space dynamics are used to examine the feasibility of operating a quadrupole mass filter using one of the higher zones of stability. Ion transmission efficiencies are calculated for various modes of operation. By using lower rf, performance may approach that of the conventional mass filter under certain conditions, but instrument apertures are generally somewhat smaller. [© American Vacuum Society, 1974.]

[2.33] 40. A detailed study of the quadrupole ion trap. *Int. J. Mass Spectrom. Ion Phys.* **16** (1975) 269–280. (P.H. Dawson, C. Lambert). [30 July 1974].

The recent development of matrix methods, based on phase-space dynamics, allows the ready calculation of ion trajectory stability and ion displacements in quadrupole fields. Detailed studies have been made of the efficiency of ion trapping in the three-dimensional quadrupole field for various conditions of mass analysis. They include a comparison of axially and radially directed electron beams of various diameters, and the consideration of fragment ions formed with initial kinetic energies. [© Elsevier BV, 1975.]

[2.23] 41. The acceptance of the quadrupole mass filter. *Int. J. Mass Spectrom. Ion Phys.* **17** (1975) 423–445. (P.H. Dawson). [21 January 1975; 18 April 1975].

The acceptance of the quadrupole mass filter in the presence of realistic fringing fields is examined using phase-space dynamics. Parameters are obtained which characterize the ion transmission in terms of instrument radius, ion mass, ion energy and frequency of the applied field. These parameters can be used to evaluate ion-source designs or to optimize lens systems coupling ion sources to quadrupoles. Some examples are given. Consideration of the three-dimensional variation of the fringing fields shows that ion trapping and ion reflection are possible for slow-moving ions at both the entrance and the exit. [© Elsevier BV, 1975.]

[2.23/4.10(?)] 42. Quadrupoles for secondary ion mass spectrometry. *Int. J. Mass Spectrom. Ion Phys.* **17** (1975) 447–467. (P.H. Dawson). [21 January 1975].

The use of quadrupole mass filters in the secondary ion mass spectrometry (SIMS) of surfaces is analysed by means of mass-filter acceptances calculated using phase-space dynamics. The acceptance takes account of the fringing fields. The quadrupole is considered alone or coupled with various energy analysers. The instruments are characterized by the target areas and secondary ion angular distributions that are accepted. This enables the selection of the optimum design for a particular SIMS application such as static SIMS with high sensitivity, static SIMS with energy analysis, depth profiling or trace analysis capability. [© Elsevier BV, 1975.]

[2.32] 43. High-pressure characteristics of the quadrupole ion trap, *J. Vac. Sci. Technol*. **12** (1975) 941-942. (P.H. Dawson, C. Lambert). [21 January 1975].

Quadrupole mass analyzers are able to operate at relatively high pressures, but few detailed measurements of their behavior in this region have been made. The quadrupole ion trap was used to investigate the influence of added gases on the N_2^+ peak and to assess the importance of various collision processes. [© American Vacuum Society, 1975.]

[2.33] 44. Energetics of ions in quadrupole fields. *Int. J. Mass Spectrom. Ion Phys.* **20** (1976) 237–245. (P.H. Dawson). [2 July 1975; 2 September 1975].

The phase-space dynamics approach is used to calculate velocity distributions and mean kinetic energies of ions contained by quadrupole fields and to examine their dependence on the phase of the rf field. [© Elsevier BV, 1976.]

[4.20] 45. The oxidation of aluminum studied by SIMS at low energies. *Surf. Sci.* **57** (1976) 229–240. (P.H. Dawson). [8 December 1975; 26 January 1976].

The adsorption of oxygen by aluminum was studied using secondary ion mass spectrometry at low primary ion energies (⍰ 500 eV) and low primary ion fluxes (⍰ 5×10^{10} ions/cm^2/sec) in an ultrahigh vacuum system. The SIMS characteristics of a cleaned aluminum surface were measured and yield changes of positive and negative ions were measured as a function of oxygen exposure. The results strongly support a model of oxygen uptake in two stages, the first monolayer equivalent being mostly incorporated into the aluminum, probably in the second layer and the next half-monolayer equivalent being superficially chemisorbed. Selection of the correct model is important in calculations of the resonances in the electronic (valence band) structure of free-electron-like metals caused by oxygen adsorption. [© Elsevier BV, 1976.]

[2.22] 46. Experimental measurements of quadrupole mass analyser performance and comparison with theoretical predictions. *Int. J. Mass Spectrom. Ion Phys.* **21** (1976) 317–

332. (P.H. Dawson). [9 December 1975].

The performance of a quadrupole mass analyser with an offset ion detector was examined using a solid-state ion source of well-defined energy. The relationship between the transmissivity and resolution and its dependence on the axial ion velocity are compared with theoretical predictions. The lateral position of the source was adjustable so that the off-axis acceptance of the quadrupole filter could also be examined. [© Elsevier BV, 1976.]

[2.43] 47. Phase-space calculations of monopole mass spectrometer performance. *Int. J. Mass Spectrom. Ion Phys.* **22** (1976) 57–70. (R. Baribeau, P.H. Dawson). [9 February 1976].

The phase-space techniques recently developed for quadrupole mass filter calculations are applied to the monopole mass spectrometer. As an illustration, exact matching of the ion source emittance to the monopole acceptance is assumed and peak-shapes, resolution and relative sensitivity are determined as a function of the length of the monopole field in rf cycles. [© Elsevier BV, 1976.]

[4.10] 48. High performance SIMS system. *Rev. Sci. Instrum.* **48** (1977) 159–167. (P.H. Dawson, P.A. Redhead). [14 July 1976; 14 October 1976].

The performance of a high-sensitivity secondary ion mass spectrometer is described. The spectrometer is used for studies of gas–surface interactions and operates under ultrahigh vacuum conditions with a mass-analyzed primary beam of low energy. The secondary ion detection system incorporates a retardation/acceleration energy analyzer with a large acceptance angle and a central stop which improves the signal/noise ratio. The analyzer emittance was designed to match the acceptance of a quadrupole mass filter. A calibration procedure is used to correct for the velocity discrimination of the quadrupole mass analyzer. Some applications to SIMS and to electron-induced desorption are illustrated. [© American Institute of Physics, 1977.]

[4.20] 49. Sims studies of the adsorption of O_2, CO and CO_2 on titanium using low primary energies. *Surf. Sci.* **65** (1977) 41–62. (P.H. Dawson). [16 August 1976; 14 February 1977].

The influence of the adsorption of O_2, CO and CO_2 on secondary ion yields from titanium has been examined using 500 eV primary argon ions. Secondary ion energy distributions were also measured. Electron-induced desorption was used as an auxiliary technique. For oxygen adsorption there is agreement with measurements using other techniques and the adsorption process is shown to occur in two stages, an initial rapid chemisorption regime followed by an oxide regime. For carbon monoxide adsorption, the measurements suggest that dissociation does not occur significantly at room temperature. For CO_2, the results are more complex. Complete dissociation seems unlikely but there may be partial dissociation. Some tentative generalizations are made concerning the influence of adsorption on secondary ion yields. [© Elsevier BV, 1977.]

[2.23] 50. The quadrupole mass filter: design and performance, in: N.R. Daly (Ed.), Adv. Mass Spectrom. Vol. 7B, Heyden & Son, London, 1978, 905–912. (P.H. Dawson). [Conference date: 30 August – 3 September 1976.]

Since Baril and Septier demonstrated the usefulness of phase-space dynamics in calculations of the performance of quadrupole field devices, these techniques have been rapidly applied to the mass filter the quadrupole ion trap and the monopole mass spectrometer. They have also been used in the design of a combined energy and mass filter system for secondary ion mass spectrometry. This paper illustrates the application to mass filter design studies and compares some of the predicted results with recent experimental measurements. [© John Wiley & Sons, 1978.]

[4.20] 51. Oxygen adsorption on molybdenum studied by low-energy secondary-ion mass spectrometry and electron-induced desorption. *Phys. Rev. B.* **15** (1977) 5522–5534. (P.H. Dawson). [28 December 1976].

The adsorption of oxygen on molybdenum in the monolayer region was studied using a combination of secondary-ion mass spectrometry (SIMS) at low primary energies and electron impact desorption. By examining the ion yields during adsorption and desorption at various temperatures, it was possible to identify two strongly bound states with activation energies for desorption of 120 and 107 kcal/mole. At room temperature, these β states are populated first and afterwards there are at least two α states which are simultaneously filled. The desorption energies for the α states were estimated to be about 37 kcal/mole. One α state gives rise to electron-induced desorption of 0_2^+, the other does not. After only partial filling of the α states, a transformation of the state giving 0_2^+ could be observed at quite low temperatures (> 550°K). The rate of transformation was greater, the lower the degree of occupation of the α states. The β_1, β_2, and α states have quite different influences on the SIMS ion yields. The formation of the oxide produces characteristic changes in ion yields. Secondary-ion energies were also measured. The value of low-energy SIMS in characterizing different states of adsorption is demonstrated. [© American Physical Society, 1977.]

[2.10] 52. *Quadrupole Mass Spectrometry and Its Applications*, Elsevier Science Publishing, Amsterdam, 1976. (P.H. Dawson). [No submission date].

[Book; contains several chapters by PHD]

[2.32] 53. The effect of collisions on ion motion in quadrupole fields. *Int. J. Mass Spectrom. Ion Phys.* **24** (1977) 447–451. (P.H. Dawson). [3 February 1977].

Ions trapped in RF quadrupole fields may undergo changes in their velocities because of collisions with ambient atoms or molecules. This will lead to the stabilization of some ion trajectories but the destabilization of others. The ensemble of ions can be treated in phase space in order to calculate the percentage of ions remaining trapped after one or more collisions and the distributions of ion positions and velocities. [© Elsevier BV, 1977.]

[2.22] 54. Performance of the quadrupole mass filter with separated RF and DC fringing fields. *Int. J. Mass Spectrom. Ion Phys.* **25** (1977) 375–392. (P.H. Dawson). [18 April 1977].

A leaky dielectric material can be used at the entrance aperture of a quadrupole mass filter to achieve a delayed DC ramp effect. The acceptance of such a quadrupole is calculated theoretically using the phase-plane analysis approach and is compared with measurements of transmissivity versus resolution for ions of different velocities and with the off-axis acceptance of ions. There is good agreement between the theory and the experiments. Compared with a mass filter having coincident RF and DC fringing fields, the important changes are greatly improved transmission for low velocity ions (much less velocity discrimination) and greater symmetry between the *x*- and *y*-transverse acceptances. The achievement of high transmission through the entrance fringing fields produces problems due to inefficient ion collection at the exit and also reveals the intrinsic limitations of the particular mass filter. [© Elsevier BV, 1977.]

[4.20] 55. The adsorption of CO on molybdenum studied by low energy SIMS and EID. *Surf. Sci.* **71** (1978) 247–266. (P.H. Dawson). [15 July 1977; 25 August 1977].

The adsorption of CO on polycrystalline molybdenum was studied using a combination of secondary ion mass spectrometry at low primary energies and electron induced desorption. Auger electron spectroscopy was used as an auxiliary technique. By examining ion yields during adsorption and desorption at various temperatures, it was possible to identify several different states of adsorption in agreement with earlier flash desorption studies. There are two strongly bound states which fill simultaneously, followed by the occupation of a third state. Continued exposure to CO results in the formation of weakly held states. Electron induced desorption gives O^+ from one of these states but CO^+ from the most weakly bound state. A characteristic of the latter is the production of $MoCO^+$ on ion bombardment. The different states of adsorption have quite different influences on the secondary ion yields. The nature of the adsorption states and the significance of SIMS in characterizing them is discussed. [© Elsevier BV, 1978.]

[2.21] 56. Some distortions in quadrupole fields and their relation to mass filter performance. *Int. J. Mass Spectrom. Ion Phys.* **29** (1979) 269–299. (P.H. Dawson, M. Meunier). [22 June 1978].

The phase space acceptance for the mass filter of limited length is calculated and two-dimensional field distortions are treated as perturbations to the ideal case. The objective is to seek approximate relationships between mechanical or electrical errors in construction and the limits to performance (such as acceptance and resolution). Third-, fourth- and sixth-order distortions are examined in detail. Some simple guidelines for quadrupole mass filter construction are suggested. [© Elsevier BV, 1979.]

[4.20] 57. The interaction of oxygen with polycrystalline niobium studied using aes and low-energy SIMS. *Surf. Sci.* **81** (1979) 464–478. (P.H. Dawson). [28 June 1978; 25 September 1978].

The interaction of oxygen with polycrystalline niobium has been studied using both Auger electron spectroscopy and low-energy secondary ion mass spectrometry in the temperature range from 300–1250 K. At higher temperatures there is oxygen dissolution into the bulk but a preferential surface segregation on re-cooling. Between 300 and 1250 K, there is a rapid initial adsorption into a very stable state which is associated with increases in the Nb^+ and NbO^+ yields that are linear with coverage. At 1250 K, further changes are very slow. At 900 K, the initial stage is followed by the adsorption with a lower sticking coefficient (<0.1) as coverage increases from $\theta = 0.5$ to 0.7. This produces an additional larger increase in the yield of Nb^+ but a much smaller change in NbO^+. At 300 K, the sticking probability falls more slowly with coverage above $\theta = 0.5$ and the amount of oxygen continues to increase slowly with exposure. The SIMS spectrum shows dramatic increases in Nb^+, NbO^+ and NbO^{+2} yields and the successive appearance of small yields of ions such as Nb_2O^{+2} and Nb_2O^{+3} as oxide formation begins. The Nb^+ yield slowly decreases as further oxidation occurs. Each stage of oxidation has a characteristic secondary ion mass spectrum. [© Elsevier BV, 1979.]

[4.20] 58. A comparison of low energy SIMS and AES in a study of the interaction of oxygen with polycrystalline nickel. *Surf. Sci.* **81** (1979) 164–180. (P.H. Dawson, W.-C. Tam). [18

July 1978; 29 August 1978].

A comparison has been made between low-energy SIMS yields and AES intensities during the oxidation of polycrystalline nickel. The AES measurements are in good agreement with earlier work that indicated an initial rapid chemisorption, a plateau in oxygen uptake during which oxide nucleation occurs and the subsequent lateral growth of the oxide layer at its limiting thickness (of 2–3 layers). At 300 K, the SIMS yield data show two regions during the chemisorption stage. In the first, up to about 1 L exposure. Ni^+ and Ni^{+2} increase in a parallel fashion and Ni_2O^+ appears. In the second (1–4 L), the Ni^+ increases more rapidly and reaches a maximum at the beginning of the plateau of oxygen uptake after an increase of 120 times over the clean surface yield. During the surface transformation as the oxide nuclei form, the yields of all the ions decrease significantly and particularly that of Ni^{+2}. During the lateral growth of the oxide layer, there is a slow decline in all ion yields if the primary energy is in the range 150–500 eV but an increase in Ni^+ yields is observed using higher primary energies. Some evidence was found for the incorporation of hydrogen into the oxide layer. The primary ion density must be kept extremely low during the nucleation stage especially at higher temperatures (<1 ion striking the surface per 200 molecules of oxygen) to avoid interference with the oxidation process. Sputtering of the oxidized surface was also examined. [© Elsevier BV, 1979.]

[2.25] 59. Quadrupole mass spectrometer, US Patent 4,189,640, Filed 27 November 1978; Issued 19 February 1980. (P.H. Dawson). [Canadian Patent 1115429A1, Filed 17 September 1979; Issued 29 December 1981.]

The quadrupole mass spectrometer has four conventional rod-shaped poles symmetrically located about the ion injection axis. Opposite pairs of rods are interconnected and connected to an rf voltage source. A shield having a circular aperture is located at the output end of the rods to assure the stoppage of low mass particles. In addition, a stopping element also preferably circular is located on the axis at the output to assure the stoppage of heavy particles. A pair of grids incorporating the stopping element, are sequentially located at the output, normal to the axis, the first is connected to a dc voltage source to accelerate the remaining particles through the fringing field of the quadrupole and the second is connected to a dc voltage source to subsequently decelerate the particles. [© US Patent and Trademark Office, 1980.]

[2.10] 60. Radiofrequency quadrupole mass spectrometers, in: A. Septier (Ed.), Adv. Electron. Electron Phys. Appl. Charg. Part. Opt. Suppl. 13B, Academic Press, New York, 1980, 173–256. (P.H. Dawson). [No submission date, but ‘note added in proof’ saying that article originally prepared in 1978 and revised in 1979].

In this article the background to the design theory for all three types of quadrupole mass spectrometer [mass filter, monopole and three-dimensional ion trap] is presented first. This is the case of "perfect" quadrupole fields where ions spend many rf cycles. Each type of instrument then will be considered in some detail with a discussion of the problems and limitations imposed by real fields. The emphasis throughout is on the ion optical properties and the experimental evidence, which supports the present design approximations. In a concluding section, there is a brief summary of the present state of the art and a discussion of the kind of calculations and measurements that are still required to improve our understanding of quadrupoles. The questions of mechanical construction are not discussed here. Such details as are publicly available have been presented elsewhere [Current Ref. 52, Chapter 2]. [© Elsevier BV, 1980.]

[4.20] 61. The use of low energy SIMS to study the chemisorption of CO on Ni(100) and polycrystalline nickel. *Surf. Sci.* **91** (1980) 153-164. (P.H. Dawson, W.-C. Tam). [8 May 1979; 3 July 1979].

Adsorption of CO on Ni(100) has been investigated using secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy at 175 and 295 K. Interaction with polycrystalline nickel was examined at 295, 325 and 365 K. All the secondary ions, Ni$^+$, Ni^{2+}, NiCO$^+$ and Ni$_2$CO$^+$ show large increases in intensity as CO is adsorbed but there is no simple correlation of the secondary ion species with the sequence of linear and bridge-bonded CO species expected from electron energy loss spectroscopy. Adsorption of CO at 175 K on a hydrogen saturated Ni(100) surface, which is thought to permit only bridge-bonded adsorbed CO, does not result in any enhancement of Ni$_2$CO$^+$. The extent of increases in secondary ion yields after CO adsorption on the nickel surfaces are primarily related to the variations in the heat of adsorption as a function of surface coverage. The presence of more weakly-held species is important in enhancing secondary ion yields. [© Elsevier BV, 1980.]

[2.61] 62. Tandem mass spectrometer with synchronized RF fields, US Patent 4,329,582, Filed 28 July 1980; Issued 11 May 1982. (J.B. French, P.H. Dawson). [Canadian Patent 1134957A, Filed 3 August 1979; Issued 2 November 1982, also published as 1134957A1. German Patent DE 3066835D, Filed 8 January 1980; Publication date 4 December 1983. European Patents EP 0023826A1, Priority date 3 August 1979; publication date 2 November 1981; and EP 0023826B1, Priority date 3 August 1979; publication date 3 July 1984.]

A tandem quadrupole mass spectrometer system having first, second and third quadrupole sections close coupled in series with one another. AC-only is applied to the center section and conventional AC and DC voltages are applied to the two end sections. The AC applied to all three sections is synchronized in frequency. The AC phase shift between each section is of magnitude between 0 and 0.1 cycles in absolute value, preferably between 0 and 0.03 cycles in absolute value, and in the preferred embodiment the AC phase shift between each section is essentially zero. The sections are spaced apart longitudinally by a very short distance not exceeding r_o, the radius of the inscribed circle within the quadrupole rods. [© US Patent and Trademark Office, 1982.]

[2.25] 63. Studies of a radiofrequency-only quadrupole mass filter, in: A. Quayle (Ed.), Adv. Mass Spectrom. Vol. 8B, Heyden & Sons, London, 1980, 1629-1637. (P.H. Dawson, M. Meunier, W.-C. Tam). [Conference date: 12 – 18 August 1979].

[Conference proceedings, no abstract provided]

NOTE: This paper includes a reference #3 (to the filing of a patent application) in the list at the end, but #3 has not been cited in the text? The corresponding patent seems to be US Patent 4,198,640 (1980) (filed 27 November 1978) listed under Ref. No. 59.

[2.23] 64. Ion optical properties of quadrupole mass filters, in: L. Marton, C. Marton (Eds.), Adv. Electron. Electron Phys., Vol, 53, Academic Press, New York, 1980, 153–208. (P.H. Dawson). [No submission date].

The objective of this work is to make available for all, but particularly those who are interested in quadrupole performance for any application, the means by which design details may be calculated in order to optimize the coupling of source to analyzer and the inevitable trades-off in performance. This chapter is focused on describing the new design approaches commencing with elementary descriptions of phase-space dynamics and the use of matrix methods in ion optics. Calculation methods are discussed in detail. [© Elsevier BV, 1980.]

[2.23] 65. Ion optical design data for the quadrupole mass filter. *Int. J. Mass Spectrom. Ion Phys.* **36** (1980) 353–364. (P.H. Dawson). [17 March 1980].

Phase-space dynamics has proved to be very valuable in studying problems of ion optical design for the quadrupole mass filter. The calculation of ion acceptance involves the computation of (2 × 2) matrices representing (a) one full cycle of the field beginning at a chosen phase, (b) partial cycles of the field beginning at the same phase, and (c) the appropriate fringing field of some given length in r.f. cycles. It is shown that under the usual operating conditions of the mass filter, all the matrix elements have simple relationships to the (a, q) values. Algebraic relationships are tabulated for both x and y directions for the full quadrupole field and for linear fringing fields of one, two and three r.f. cycles. [© Elsevier BV, 1980.]

[2.61] 66. The use of triple quadrupoles for sequential mass spectrometry 1 - The instrument parameters. *Org. Mass Spectrom.* **17** (1982) 205–211. (P.H. Dawson, J.B. French, J.A. Buckley, D.J. Douglas, D. Simmons). [26 May 1981].

Triple quadrupoles are becoming widely used in sequential mass spectrometry. The observed spectra are very dependent upon the choice of instrument parameters such as the gas target density, the mode of operation of the central quadrupole, and the direct current levels of the quadrupoles (rod-offsets) which determine the collision energy and the maximum mass resolutions in each analysing quadrupole. The influence of each of the instrument parameters is discussed with examples of experimental measurements of performance, and the optimum choice of modes of operation is determined. [© John Wiley & Sons, 1982.]

[2.61] 67. The use of triple quadrupoles for sequential mass spectrometry. 2 - A detailed case study. *Org. Mass Spectrom.* **17** (1982) 212-219. (P.H. Dawson, J.B. French, J.A. Buckley, D.J. Douglas, D. Simmons). [26 May 1981].

A detailed exploration of the application of triple quadrupoles in sequential mass spectrometry has been carried out using dimethylmorpholinophosphoramidate as a case study of an ion of relatively high mass and complex structure. Both metastable ion decomposition and dissociation by low energy collision were examined. Variation of the basic instrument parameters allowed the investigation of the cross-section for dissociation as a function of collision energy, the change in fragmentation patterns with collision energy, the kinetic energy distributions of daughter ions and the overall kinetics of dissociation in a succession of ion decomposition sequences giving daughter and granddaughter ions. The daughter ions could also be produced in the source region and examined separately so that a genealogical tree could be established. [© John Wiley & Sons, 1982.]

[2.61] 68. The effective containment of parent ions and daughter ions in triple quadrupoles used for collisional dissociation. *Int. J. Mass Spectrom. Ion Phys.* **44** (1982) 195-211. (P.H. Dawson, J.E. Fulford). [25 September 1981; 12 November 1981].

Since triple quadrupoles are becoming widely used in analytical applications of low energy collisionally-induced dissociation mass spectrometry (MS/MS), a clear understanding of the role of the radiofrequency (r.f.) only quadrupole is of paramount importance. This paper presents experimental results, supported by theoretical calculations, which demonstrate how a well-designed system can be operated with very low ion losses so that quantitative measurements can be made. Ion containment was studied as a function of applied r.f. voltage and the effects of gas scattering and of the sudden change in ionic mass during ion fragmentation were evaluated. The results allow some insight into the problem of establishing standard operating conditions for collecting library spectra and emphasize the importance of some of the design-dependent variables. [© Elsevier BV, 1982.]

[2.62] 69. Determination of sulfa drugs in biological fluids by liquid chromatography/mass spectrometry/mass spectrometry. *Anal. Chem.* **54** (1982) 451–456. (J.D. Henion, B.A. Thomson, P.H. Dawson). [2 October 1981].

The technique of direct liquid introduction (DLI) liquid chromatography/ mass spectrometry/mass spectrometry (LC/ MS/MS) is implemented on an atmospheric pressure chemical ionization (API) triple quadrupole mass spectrometer. Experimental details are described. A series of sulfa drugs including sulfamethazine (SM), sulfisoxazole (SOX), sulfadiazine (SD), and sulfadimethoxine (SDM) are studied in the full scan LC/MS, full scan LC/MS/MS, and selected ion monitorlng (SIM) LC/MS/MS modes. Comparisons between the data are made. Full scan LC/MS/MS and SIM LC/MS/MS results are described for the analysis of a raw organic extract of racehorse urine and plasma containing residues of administered sulfadimethoxine . The method minimizes sample cleanup, protects the mass spectrometer from abusive exposure to high levels of endogenous materials that result from direct insertion probe sample introduction, and provides retention time information for the eluted components of interest. On-column full scan sample detection limits in the low microgram range were easily obtained using the DLI split effluent LC/MS/MS interface and could be increased by utilizing micro LC techniques and improved effluent desolvation techniques. [© American Chemical Society, 1982.]

[2.62] 70. The collision-induced dissociation of protonated water clusters studied using a triple quadrupole. *Int. J. Mass Spectrom. Ion Phys.* **43** (1982) 195–209. (P.H. Dawson). [9 January 1982; 8 March 1982].

The collision-induced dissociation of protonated water clusters $(H_2O)_nH^+$ with $n = 1–6$ has been studied in the energy range 0–50 eV. The collision gases are argon and methane. Cross-sections for dissociation have been determined and branching ratios for the loss of one, two and three water molecules estimated. Threshold energies expressed in the centre-of-mass system are in reasonable agreement with those expected from thermochemical data. The distributions of daughter ion energies have also been measured and these show that, at collision energies well above threshold, glancing angle collisions dominate in the dissociation process. The results have important implications for the operation of triple quadrupoles in analytical applications. [© Elsevier BV, 1982.]

[2.62] 71. Comparison of low-energy collisionally induced dissociation of *n*-butyl benzene ions with photodissociation. *Int. J. Mass Spectrom. Ion Phys.* **44** (1982) 51–59. (P.H.

Dawson, W.-F. Sun). [19 April 1982].

The collisionally-induced dissociation of *n*-butyl benzene ions to form $C_7H_7^+$ or C_7H_8+ fragments has been examined at centre-of-mass collision energies in the range 0–30 eV using a triple quadrupole. The target gases were methane, nitrogen, argon, propane and krypton. The ratio of the intensities of the fragment ions has previously been shown by photodissociation experiments to be a very sensitive function of the internal excitation energy of the parent ion. For all the target gases, the ratio of $C_7H_7^+$ to $C_7H_8^+$ rose almost linearly with centre-of-mass collision energy above the threshold for $C_7H_7^+$ formation, but the ratio reached a maximum at an energy of ∼ 9 eV and slowly declined at higher energies. The maximum ratio was target-dependent and a comparison with the photodissociation data suggests that slightly lower amounts of excitation energy are available when the target is polyatomic. The equivalent internal excitation energies are much higher than those found in high-energy collisional activation, indicating the efficiency of the direct translational to vibrational energy conversion that occurs at low collision energies. Measurements of fragmentation energy distributions show distinct differences between $C_7H_7^+$ and $C_7H_8^+$. [© Elsevier BV, 1982.]

[4.20] 72. Electron-induced desorption of O^+ ions from W, Mo and Cr. *Surf. Sci.* **122**(3) (1982) 588–598. (P.H. Dawson, M.L. Denboer). [15 June 1982].

We have studied the electron-induced desorption (EID) of O^+ ions from oxygen-covered polycrystalline W, Mo and Cr surfaces. As the incident electron energy is increased, desorption begins at about 25 eV, and increases dramatically at the binding energy major low-lying substrate core levels. In the range of electron energy studied, below about 200 eV, there are also other variations in ion yield not associated with known core levels. The peak ion kinetic energy is 7.8, 5.3 and 3.4 eV for W, Mo and C, respectively, and is independent of incident electron energy. These measurements imply that the desorption is initiated by a core level ionization event, although the subsequent electronic transitions leading to desorption apparently differ from those occurring on metallic oxide surfaces. [© Elsevier BV, 1982.]

[2.61] 73. Studies of the mechanism of collision induced dissociation at low energies using a triple quadrupole. *Int. J. Mass Spectrom. Ion Phys.* **47** (1983) 121–124. (P.H. Dawson, D.J. Douglas). [IMSC Vienna date: 30 August – 3 September 1982].

A greater understanding of the mechanism of the collision induced dissociation of ions at low energies (1–100 eV) is important in the application of triple quadrupoles to analytical problems. A well-designed triple quadrupole (ref.1) can itself be used to make quantitative measurements of (a) the kinetics of dissociation, which allow cross-sections to be estimated (b) the variations in ion yields with collision energy and the determination of threshold energies for dissociation and (c) the fragment in energy distributions which give information about the scattering angles involved. Illustrations are given for the dissociation of $(H_2O)_nH^+$, $C_2H_5OH_2^+$, $C_6H_6^+$ and $C_{10}H_{14}^+$ in collision with many different target gases, both monatomic and polyatomic. It is shown that by using collisions, energy can be deposited in polyatomic ions in a controlled manner. This adds another facet to the application of MS/MS techniques. [© Elsevier BV, 1983.]

[2.62] 74. A study of the collision-induced dissociation of $C_2H_5OH_2^+$ using various target gases. *Int. J. Mass Spectrom. Ion Phys.* **50** (1983) 287–297. (P.H. Dawson). [30 September 1982].

A triple quadrupole mass spectrometer was used to study the collision-induced dissociation of $C_2H_5OH_2^+$ using Ar, Kr, N_2, CH_4, C_2H_6 and C_3H_8 as target gases. The principal fragments were $m/z = 29$, 27 and 19. Approximate cross-sections were determined for each decomposition pathway. The products were examined as a function of collision energy up to 75 eV. Threshold energies in the centre-of-mass system were in reasonable agreement with thermochemical values. An extensive survey was made of the fragment ion energy distributions. The $m/z = 29$ and 19 fragments, which are easily formed, had relatively narrow distributions which also indicated small scattering angles. At the lower collision energies, the $m/z = 29$ ion, which has a higher threshold for its formation, had a very broad distribution indicating a wide range of scattering angles. For the $m/z = 29$ and 19 fragments, polyatomic targets gave consistently lower fragment energies than the rare gases. The data also suggest an inverse correlation between scattering angle and collision energy. [© Elsevier BV, 1983.]

[2.23] 75. An approximate method for determining the emittance of ion sources in quadrupole mass spectrometry. *Int. J. Mass Spectrom. Ion Processes* **54** (1983) 159–167. (P.H. Dawson, Y. Bingqi). [25 February 1983].

An approximate method of determining the emittance of an ion source coupled to a quadrupole mass spectrometer is described. The method combines the conclusions of recent phase space dynamics calculations of quadrupole acceptance and experimentally-measured transmission curves with the d.c. voltage set to zero. The calculation of source emittance is carried out in one dimension and assumes cylindrical symmetry. An exact solution for the emittance, while possible in principle, would be very time consuming and so an iterative approximation was used. The accuracy of the result can be tested by using the calculated emittance to regenerate ion transmission curves. The method described provides a basis for further study of the effective coupling of ion sources to quadrupoles and some improvements to its accuracy are suggested for future work. [© Elsevier BV, 1983.]

[2.62] 76. Collisionally activated dissociation of low kinetic energy ions, in: F.W. McLafferty (Ed.), *Tandem Mass Spectrometry*, Wiley-Interscience, New York, 1983, 125–148. (P.H. Dawson, D.J. Douglas). [No date].

[Book chapter, no abstract]

[2.61] 77. A round robin on the reproducibility of standard operating conditions for the acquisition of library MS/MS spectra using triple quadrupoles. *Int. J. Mass Spectrom. Ion Processes* **55** (1984) 155–170. (P.H. Dawson, W.-F. Sun). [16 June 1983].

As a preliminary to establishing standardised operating conditions (e.g. collision energy, collision target thickness) for the generation and interchange of library MS/MS spectra using triple quadrupoles, an international round-robin test of the reproducibility of a proposed operating procedure was undertaken by seven laboratories. Two ions were selected for study, *n*-butylbenzene, $C_{10}H_{14}^+$, and the protonated dimethyl phthalate ion $C_{10}H_{11}O_4^+$ with both argon and nitrogen as collision gases. These ions give various sets of daughter ions whose relative intensities are (a) not dependent on collision energy and target thickness, (b) dependent on collision energy but not target thickness and (c) dependent on both collision energy and target thickness. The data can therefore be analysed to verify independently the reproducibility of collision energy, target thickness and machine characteristics between different laboratories. Proposals are made to improve the definition of the standardised set of operating conditions. [© Elsevier BV, 1984.]

[2.62] 78. Chemical synthesis inside the collision cell of a MS/MS system: 1-formation of adduct ions between protonated esters and ammonia. *Org. Mass Spectrom.* **20** (1985) 269-275. (J.P. Schmit, P.H. Dawson, N. Beaulieu). [19 July 1983].

An evaluation of the TAGA 6000 tandem quadrupole MS/MS capabilities for the study of the formation of adduct ions is presented. It is shown that under chemical ionization conditions the protonated molecular ions of esters [current authors' note: this should read as 'protonated ester molecules'] react with neutral ammonia inside the collision cell of the instrument to yield adduct ions. Under the same reaction conditions the molecular ions obtained under electron impact conditions do not yield any adduct. Although it is not yet clear whether the adduct structure is of the cluster or covalently bonded type, the experimental results argue mainly in favor of the latter. The center-of-mass energy range usable for the formation of adduct ions is narrow and an order of magnitude lower than the energy required for collision-induced dissociation. However, despite the weak parent ion center-of-mass energies used, the spectra exhibit fragments characteristic of the adduct ion structures. Finally, by controlling the parent ion center-of-mass axial kinetic energy, the number of parent ions and the target thickness, it is possible to measure and control all the usual physicochemical parameters for adduct ion formation. [© John Wiley & Sons, 1985.]

[2.24] 79. The second stability region of the quadrupole mass filter. I. Ion optical properties. *Int. J. Mass Spectrom. Ion Processes* **56** (1984) 25–39. (P.H. Dawson, Y. Bingqi). [8 August 1983].

The quadrupole mass filter can be operated in a stability region at a much higher q value than that normally used. This requires a high r.f. voltage or a lower r.f. frequency and only a very small d.c. voltage. Details of the higher q stability region were calculated. Typical ion trajectories in the phase space were used to estimate ion acceptances both with and without fringing fields. The presence of any fringing field is not beneficial and transmissivity is almost an order of magnitude less than in normal operation. Good resolution is achievable with quadrupole fields in which the ions spend very few r.f. cycles and the effects of field imperfections which normally limit the ultimate attainable resolution might be minimised. [© Elsevier BV, 1984.]

[2.24] 80. The second stability region of the quadrupole mass filter. II. Experimental results. *Int. J. Mass Spectrom. Ion Processes* **56** (1984) 41–50. (P.H. Dawson, Y. Bingqi). [8 August 1983].

The quadrupole mass filter can be operated in a stability region near $a = 0$, $q = 7.547$. The resolution achievable was examined as a function of quadrupole field length for various r.f. frequencies and ionic masses. The limitations to performance were compared with those of the same quadrupole operating in the normal manner. With the particular ion source used, sensitivity at resolutions of a few hundred was an order of magnitude lower than in the normal operation. However, there was a length advantage of about fourteen times and resolutions of greater than 1000 could be achieved with ions of 300 V energy. Ultimate achievable resolution was only about 50% greater than in normal operation. [© Elsevier BV, 1984.]

[2.62] 81. Collisionally activated dissociation spectra of protonated methyl N-alkanoates studied using a triple quadrupole. *Org. Mass Spectrom.* **18** (1983) 396–401. (W.-F. Sun, P.H. Dawson). [23 November 1983].

The collisionally-activated dissociation (CAD) spectra of protonated methyl *n*-alkanoates $CH_3(CH_2)_nCOOCH_3$ with n = 1-9 were studied using a triple quadrupole. The influence of hydrocarbon chain length and collision energy on characteristic fragment ions such as those due to the loss of methanol was examined. It was found that most characteristic fragment ions became less important in the CAD spectra with increasing chain length of the esters and finally disappeared in the higher members of the series. Special care would have to be taken when trying to use such neutral losses in analysis for identifying the presence of a certain class of compounds. [© John Wiley & Sons, 1985.]

[4.20] 82. CO chemisorption on $Pt_{0.98}Cu_{0.02}(110)$: An ESD and low energy SIMS study. *Surf. Sci.* **145** (1984) 223–238. (V.S. Sundaram, P.H. Dawson). [7 December 1983].

The chemisorption of CO on an annealed $Pt_{0.98}Cu_{0.02}(110)$ surface was studied by a combination of secondary ion mass spectrometry and electron stimulated desorption. After adsorption at 300 K, the thermal desorption spectrum from this surface has two peaks at 543 and 380 K. Electron induced desorption gave both O^+ and CO^+ ions with the intensity of CO^+ being a factor of 2 greater than that of O^+. The intensities of both CO^+ and O^+ ions increased linearly with exposure up to about 0.45 L [The authors refer to both 'dosage' and 'exposure' in terms of the volume, in litres, of CO added to the system] which coincided with the appearance of the second peak in the thermal desorption spectra. For exposures > 0.45 L, CO^+ and O^+ intensities showed a plateau followed by a decrease, with the O^+ decline being more pronounced. Chemisorption measurements at 140 K showed the presence of states corresponding to CO adsorption on copper related sites. Using low energy ion bombardment only a small Cu^+ emission was observed from the clean surface. CO adsorption at 300 K resulted in an increase in Cu^+ intensity and a weak $CuCO^+$ signal but adsorption at 140 K resulted in large Cu^+ and $CuCO^+$ signals. The weakly bound states are highly active for both ESD and SIMS. [© Elsevier BV, 1984.]

[2.24] 83. Quadrupoles operating in the second stability region. Proc. 32nd ASMS Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, pp. 509-510 (1984). (P.H. Dawson, Yu Bingqi).

[No abstract provided] [Conference dates: 27 May – 1 June 1984].

[2.62] 84. The collision-induced dissociation of O_2^- studied using a triple quadrupole mass spectrometer. *Int. J. Mass Spectrom. Ion Processes* **61** (1984) 123–131. (P.H. Dawson, W.-F. Sun). [22 March 1984].

The collision-induced dissociation of O_2^- was examined using a triple quadrupole mass spectrometer. The cross-section for O^- formation reached a maximum at about 11 eV (centre-of-mass energy) and was estimated to be 2 $Å^2$, in good agreement with earlier measurements using a tandem magnetic sector instrument. The expected threshold of 4.1 eV was observed, with the cross-section above threshold rising with the square of the excess energy. The O^- energy distributions were interpreted in terms of scattering angles involved in the collision. The most probable scattering angle decreases as the energy rises above the threshold and is near 90° at the cross-section maximum. At a particular collision energy, only a relatively narrow range of scattering angles was observed. [© Elsevier BV, 1984.]

[4.20] 85. Oxygen on Pt(110): Thermal enhancement of electron stimulated desorption. *Surf. Sci.* **146**(2-3) (1984) L593–L600. (V.S. Sundaram, P.H. Dawson). [1 May 1984].

Adsorption of oxygen on Pt(110) at room temperature occurs in two stages, a rapid adsorption to about half the saturation coverage followed by a much slower adsorption. Electron stimulated desorption (ESD) produces a small yield of O^+ ions. If the saturated surface is heated above about 600 K, the ESD yield of O^+ can increase by as much as twenty times. The high yield condition produced by heating is then stable at lower temperatures. Complete desorption occurs on heating above ~ 900 K. If the exposure at room temperature is arrested after the initial rapid adsorption, the transition above 600 K is not observed. However, adsorption above 600 K on the clean surface gives directly the high O^+ yielding state. The observations relate to some activated surface re-arrangement but more studies are required to verify whether or not the platinum atoms are directly involved. [© Elsevier BV, 1984.]

[2.62] 86. Collisionally activated dissociation of O_2^+ in a triple quadrupole and the role of excited tates. *Int. J. Mass Spectrom. Ion Processes* **63** (1985) 305–314. (P.H. Dawson). [8 August 1984; 7 September 1984].

O_2^+ produced in an electron impact source of variable energy has been studied in collisions with argon atoms at low energies in a triple quadrupole mass spectrometer. The role of the long-lived metastable $a^4\pi_u$ state was examined. Thresholds for the ground and excited states were determined for both charge transfer and collisionally activated dissociation. Cross-sections for the excited state are an order of magnitude greater than for the ground state at a collision energy of 10 eV. The O^+ product is formed over an unusually wide range of scattering angles. [© Elsevier BV, 1985.]

[2.62] 87. Low-energy collision-activated dissociation of *n*-butylbenzene. Effect of the electron energy used during parent ion formation. *Int. J. Mass Spectrom. Ion Processes* **63** (1985) 339–341. (P.H. Dawson). [8 August 1984].

[Short Communication, no abstract provided]

[2.25] 88. Performance characteristics of an r.f.-only quadrupole. *Int. J. Mass Spectrom. Ion Processes* **67** (1985) 267–276. (P.H. Dawson). [29 April 1985].

The r.f.-only quadrupole is of interest because of its potential for (i) greater sensitivity than the normal quadrupole at good resolution, (ii) tolerance of the effects of contamination or errors in construction, and (iii) the absence of discrimination against high mass ions. The performance characteristics of one type of r.f.-only quadrupole were examined in detail with particular reference to peak shape, peak tailing and resolution as a function of ion velocity using various combinations of ion mass, ion energy and applied r.f. frequency. [© Elsevier BV, 1985.]

[2.20] 89. Quadrupole mass spectrometers: mass filter considerations and performance. *Vacuum*. **35**(12) (1985) 629-629. (P.H. Dawson). [Abstract from a workshop on calibration of residual gas analyser 7–9 May 1985, Gaithersburg.]

[2.20/2.30] 90. Quadrupole mass analyzers: Performance, design and some recent applications. *Mass Spectrom. Rev.* **5** (1986) 1–37. (P.H. Dawson). [No submission date].

This review describes the current state of knowledge concerning the relationship of performance to instrument design. It is clear that while a basic understanding of performance has emerged, there are many outstanding questions. The design theory and the computer simulations could be extended to more sophisticated models, but this is unlikely to be profitable in the absence of a body of experimental data of a more precise nature than is presently available. There are surprisingly few quantitative experimental measurements of performance carried out in a systematic manner covering the accessible range of mass and energy variations. There is only the one series of direct measurements of ion acceptance characteristics. Given the obvious importance of fringing fields and their various modifications in changing the effective acceptance of ions, such measurements are essential if performance is to be optimised. With the detailed knowledge that ion acceptance measurements would bring, ion source design could then, in turn, be optimized. The measurements are not simple to do but perhaps the demands for higher performance will encourage more efforts of this type. In the meantime, there will, no doubt, be a continued exploration of new modes of utilization of quadrupole fields in the search for operation with less dependence on geometrical perfection or to try to avoid some of the intrinsic limitations to performance in the conventional mode. With the increasing complexity of analytical problems, the use of tandem instruments of various types is likely to become routine. Quadrupoles, including the three-dimensional quadrupole ion trap, originally aroused interest because of their supposed simplicity. Now, an apt summary might be that they will probably continue to find widespread application despite their complexity. [© John Wiley & Sons, 1986.]

[2.62] 91. Dissociation of the benzene ion by low energy collisions. *Int. J. Mass Spectrom. Ion Processes* **70** (1986) 97–107. (P.H. Dawson, W.-F. Sun). [25 November 1985].

The dissociation of $C_6H_6^+$ ions in collision with gases such as argon and nitrogen was examined in the centre-of-mass energy range of 0–20 eV using a triple quadrupole mass spectrometer. For ions produced in an atmospheric pressure chemical ionization (APCI) source, the energy thresholds were dependent on target thickness and consistent with a two-step dissociation process at low energies via an excited state. For ions produced in an electron impact source, the dissociation cross-section at low collision energies depended strongly on the electron energy used to produce the ions, again indicating the importance of long-lived ions with some internal energy of excitation. Threshold energies for ground-state ions were determined from measurements on ions produced in the APCI source dissociating at low target thicknesses under single collision conditions. [© Elsevier BV, 1986.]

[2.25] 92. Quadrupole mass spectrometer, US Patent 4,721,854 , Filed 23 June 1986; Issued 26 January 1988. (P.H. Dawson). [Canadian Patent 1115429A, Filed 17 September 1979; Issued 29 December 1981.] [Canadian Patent 1251870, Filed 11 December 1985; Issued 28 March 1989.]

This disclosure presents an alternative, improved approach to the RF only quadrupole mass spectrometers. The ions whose masses place them near the stability limit for a given operating voltage and RF frequency, can be strongly influenced by the application of a very small dc voltage to the quadrupole rods. If this voltage is modulated at a low frequency (typically a few hundred hertz), the (a,q) values will pass alternately through the stability boundary and ions will be transmitted with the imposed frequency. The advantages of the new approach are two-fold (a) lock-in amplifier synchronous detection schemes can be used. These give improved signal/noise ratios. Background noise due to photons, soft X-rays or excited neutrals—often a problem in quadrupole mass filters---will not be modulated and will not be detected. (b) Higher resolution can be achieved. [© US Patent and Trademark Office, 1988.]

[2.22] 93. Quadrupole mass filters using modulated voltages. *Int. J. Mass Spectrom. Ion Processes* **70** (1986) 237–241. (P.H. Dawson). [17 December 1985].

[Short Communication, no abstract provided: **Conclusion:** This work has demonstrated how a.c. detection techniques can be very simply applied to rf-only quadrupoles. They may be advantageous in certain applications. With more complex circuitry the same approach could also be considered for the "normal" operation of the quadrupole near the tip of the stability region I.] [© Elsevier BV, 1986.]

[2.22/2.24] 94. Quadrupole mass filters with varying Mathieu parameter. *Int. J. Mass Spectrom. Ion Processes* **83** (1988) 295–309. (P.H. Dawson). [24 September 1987; 16 November 1987].

Quadrupole mass filters may have a q value (the Mathieu parameter) that varies as ions pass through owing to either non-parallel rods or to very rapid mass scanning either by voltage or by frequency variation. The acceptance of a mass filter of finite length is calculated under these conditions. Assuming full utilization of the available acceptance, peak shapes and peak positions are calculated. They are both functions of the rate of change of q. Varying q can lead to peak tailing. The orientation of the acceptance area in the phase plane varies for operating points near the stability boundary when there is a transition from stable to unstable conditions as the ions pass through the quadrupole. This could result in peak shape irregularities depending upon the matching of the ion source emittance to the analyser acceptance. [© Elsevier BV, 1988.]

[2.22] 95. Quadrupole mass filters with bent or bowed rod sets. *Int. J. Mass Spectrom. Ion Processes* **83** (1988) 295–309. (P.H. Dawson). [23 December 1987].

The acceptance of ions by quadrupole mass filters with small longitudinal distortions is calculated. The rod sets are assumed to be bowed out or bent in at the centre. It is shown that quite small geometrical deviations ($\delta r_0/r_0 \sim 10^{-3}$) can have significant effects for slow-moving ions under high-resolution conditions. Bowed rod sets tend to produce mass peakswith shoulders or satellites on the high-mass side and those bent inwards give structures on the low-mass side.The predicted characteristics are qualitatively similar to those frequently observed experimentally as performance is pushed to high levels. [© Elsevier BV, 1988.]

[2.22] 96. Source-analyser coupling in the quadrupole mass filter. *Int. J. Mass Spectrom. Ion Processes* **100** (1990) 41–50. (P.H. Dawson). [23 March 1990].

Transmission/resolution relationships in the quadrupole mass filter are calculated for sources of different emittance characteristics. The previously predicted regions of source limited and analyser limited operation are demonstrated. Some quantitative information is obtained about the resolution at which the transition occurs for a source of a given size of emittance. Contrary to previous qualitative predictions transmission under analyser limited conditions is proportional to $1/R$ rather than $1/R^2$. The effects of emittance shape and orientation in the phase plane are considered. Such changes might result from poor choice of focusing conditions between the source and the analyser. A “hollow beam” source is also examined. Some approximate information about peak shapes with various source configurations is obtained for ions passing many cycles in the r.f. field. [© Elsevier BV, 1990.]

[5.00] 97. A bibliometric view of the state of Canadian research in semiconductors and photonics, La Physique au Canada, July/August, **52** (1996) 151-158. (P.H. Dawson, R. Dalpé, B. Longpré, C. Caron). [31 July 1996]

Bibliometric tools for analyzing published research outputs are now readily available but they have been relatively little exploited in Canada. They can provide an illuminating view of international technology trends, national degrees of specialisation in various fields, the identity and positioning of the major research institutions and the linkages and networks that exist between them. This study examines the areas of physics and electrical engineering research in Canada in a general way and then provides a more detailed analysis of research outputs related to photonics and semiconductors. It reveals strengths and weaknesses in the Canadian effort. [© Canadian Association of Physicists, 1996.]

(TABLE 3)

APPENDIX II

Peter H. Dawson: Education and Employment History*

*The column labelled ‘WP’ denotes the ‘Work Place’ abbreviation shown in the spreadsheets presented in the *Supplementary Information*.

WP*	**Date**	**Employment**
	1955-1958	King’s College, University of London, England; B.Sc. Honours in Chemistry.
A	1958-1961	King’s College, University of London, England; Ph.D. in Physical Chemistry.
B	1961-1963	Post-doctoral fellow, Division of Chemistry, NRC, Ottawa.
C	1963-1969	Research Scientist, Electron Physics, General Electric Co., Schenectady, New York, U.S.A.
D	1969-1974	Research Professor, Université Laval, Quebec (and Defence Research Establishment, Valcartier).
E1	1974-1984	Research Officer, NRC Division of Physics.
E2	1984-1986	Section Head, NRC Division of Physics.
E3	1986-1990	Laboratory Director, NRC Division of Physics.
E4	1990-1998	(First) Director-General, NRC Institute for Microstructural Sciences.
	1998-2015	Chairman (formerly President), Iridian Technologies, Ottawa.