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Radio frequency quadrupole technology: Evolution and contributions to mass spectrometry

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In recognition of the centenary of Sir J.J. Thomson's monograph "Rays of Positive Electricity and Their Application to Chemical Analyses", published October 4, 1913, the International Journal of Mass Spectrometry will publish two Special Issues, a Physics-centred issue and a Chemistry-centred issue; the latter issue will focus on the explosion of instrumentation and techniques that occurred approximately 50 years ago, and how these have blossomed into the mass spectrometry of today.

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ABSTRACT

Just as 2013 marks the centenary of the birth of mass spectrometry through the publication of Thomson's classic book '*Rays of Positive Electricity and Their Application to Chemical Analyses*', it is also exactly six decades since Paul and Steinwedel filed their first German patent 'Verfahren zur Trennung bzw. Zum getrennten Nachweis von Ionen verschiedener spezifischer Ladung' ('Method for separating or separately detecting ions of different specific charges') on 24th December, 1953. This patent described the quadrupole mass filter (QMF) and the three-dimensional quadrupole ion trap (3D-QIT), both of which operate by confining ions mass-selectively through the application of radio frequency quadrupolar potentials to appropriate electrode structures. In the ensuing 60 years since the initial description of these devices the impact of quadrupole technology upon mass spectrometry as a whole has been truly remarkable, especially when combined with chromatographic separation methods and/or other types of mass analysers. This retrospective article will aim to trace the principal milestones in the evolution of transmission quadrupoles (the QMF, quadrupole beam guides, and triple quadrupole tandem instruments) and of trapping quadrupoles (the 3D-QIT and, the more recent, linear quadrupole ion trap (LQIT)), both as stand-alone instruments and in various hybrid configurations. Recent research advances into quadrupole technology itself will be discussed; an account of ion trapping in the Kingdon trap and the Orbitrap™ mass spectrometer is included in the Supplementary Information for comparison.

1. Introduction

The 1950s in England was a period of discovery and excitement, especially for two young teenage boys 'R' and 'J', who had yet to meet each other. At 25 years of age, Princess Elizabeth ascended to the British throne in February, 1952, and was proclaimed Queen Elizabeth II by a succession of Privy Councils. In the late 1952, the windows of candy shops, filled miraculously with sweets and chocolates rationed no longer, were ablaze with lights turning night into day. The coronation was delayed for more than a year, supposedly to allow an adequate period of mourning following the death of King George VI, but possibly due to the enormity of the tasks of manufacturing sufficient television sets for the majority of the UK population and of televising for the first time a coronation ceremony, which took place on June 2, 1953. With a new Queen, ample chocolate, and the technical advances of television, a new form of sanity appeared following the end of WWII. Other technical advances in the United Kingdom were being made simultaneously by the Metropolitan Vickers Co. of Manchester. Robert Craig had joined MV in 1950 and was involved in the development of several mass spectrometers including the MS3, which was a scaled-down version of the MS2 magnetic sector instrument and, in 1955, the MS5 which used for the first time in a commercial mass spectrometer an electron multiplier ion detector [1]. For further information on the development of sector instruments, see the

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section on 'Sector Instruments' by R. Bateman in this Special Centenary Issue. By this time, the two boys mentioned above had entered the Honours Chemistry program at Leeds University where the Bragg father-and-son team had earlier carried out studies of X-ray diffraction. The Nobel Prize in Physics in 1915 was awarded jointly to Sir William Henry Bragg and William Lawrence Bragg *"for their services in the analysis of crystal structure by means of X-rays"*; to date, at the age of 25, Lawrence Bragg was the youngest Nobel Laureate in Physics.

R and J continued with their undergraduate studies blissfully unaware that Professor Wolfgang Paul, working with Helmut Steinwedel at the University of Bonn, had disclosed the operating principle of the quadrupole mass spectrometer (as the quadrupole mass filter, QMF, was described initially) in a patent filed in 1953 [2] and in a further patent by Paul et al. [3] filed in 1958. Despite suggestions that Paul and Steinwedel were long-time collaborators, the German and US Patents cited in Reference [2] and one earlier paper [4] were their only joint publications. Paul's discovery of the principle of confining ions by means of strong-focusing electric fields arose as he and the members of his group were designing a new high-energy accelerator that was to be constructed under the streets of Bonn. Once he had established the fundamental characteristics of quadrupole devices and built his accelerator, Paul's immediate interest in quadrupole mass spectrometry disappeared. Only when he was preparing his Nobel Lecture in 1989 did Paul discover, to his amazement, what remarkable things analytical chemists were doing with 'his' invention![2] Wolfgang Paul was awarded the Nobel Prize in Physics in 1989 along with Hans Georg Dehmelt and Norman F. Ramsey for introducing the concept of confining ions in "traps without material walls" [5]. While similar ideas had been proposed by others [6], Wolfgang Paul and his colleagues in Bonn recognized the principle of using strong focusing fields for mass analysis [4] and the first detailed accounts of the operation of a 3D quadrupole ion trap, 3D-QIT, appeared in the thesis of Berkling [7] in 1956 and by Fischer in 1959 [8]. The 1956 German patent, '900', and the 1960 US patent, '952', are quite remarkable as they are the sole patents that reveal the operating modes for both the QMF and the 3D-QIT. Among a variety of radio frequency spectrometers advanced during the period 1948–1955, only the QMF and the 3D-QIT have survived to this day. To this pair of quadrupolar devices must be added the linear quadrupole ion trap (LQIT) that appeared more recently.

Other members of this family are the cylindrical ion trap (CIT), rectilinear ion trap (RIT), and digital ion trap (DIT). The story of the development of the family of devices that utilize path stability as a means of separating ions is fascinating because it is a departure from the development of sector instruments that were pioneered by Thomson [9] in 1913 and others. Yet, despite the entrenchment of sector instruments in mass spectrometry, the quadrupole mass filter and the quadrupole ion trap have brought about a revolution in this field during the past quarter of a century as the forerunners of the class of mass spectrometers that utilize the confinement of ions. In the account that follows we consider the first two two-dimensional mass analysers, the quadrupole mass filter and the monopole mass spectrometer, followed by a discussion of the three-dimensional quadrupole ion trap, the cylindrical ion trap and the digital ion trap. Finally, we consider three variants of the relatively new 'linear quadrupole ion trap', as well as the 'toroidal' and 'halo' ion traps. In addition, an account of the physical principles behind the Kingdon trap and the Orbitrap™ mass spectrometer is included in the Supplementary Information in order to provide a comparison with the underlying theory of quadrupole technology.

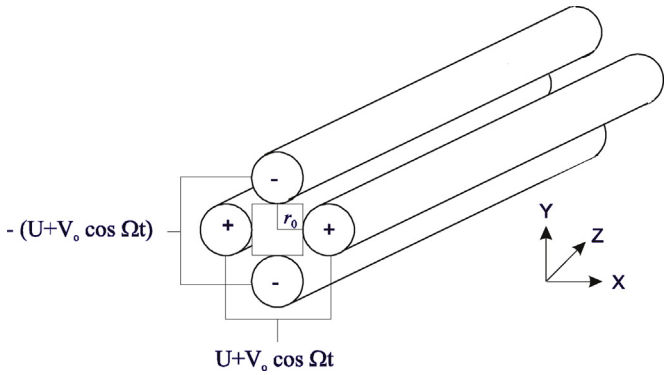

Fig. 1. Quadrupole mass filter. The ions enter and travel in the *z*-direction, while oscillating in the *x*–*y* plane. The oscillation is controlled by the DC (*U*) and RF (*V*) potentials applied to each pair of rods. Only those ions with stable trajectories at the selected *U* and *V* values will travel the length of the quadrupole mass filter and be detected. (Reproduced from R.E. March, J.F.J. Todd, (Eds.) Practical Aspects of Trapped Ion Mass Spectrometry: Vol. IV, Theory and Instrumentation, CRC Press, Boca Raton, FL, 2010. With permission from CRC Press.)

2. The Quadrupole mass filter

The quadrupole mass filter comprises a square array of four accurately-machined and aligned conducting rods where the distance of each rod from the central axis is r_0. This array is interposed between an ion source and a detector, usually an electron multiplier of some type, as shown in Fig. 1. Opposite pairs of rods are coupled together and an electrostatic radio frequency potential applied between the pairs.

In addition, the opposite pairs of electrodes may be biased with equal and opposite DC potentials, applied positively in the *x*-direction and negatively in the *y*-direction. The intention is to create equal but opposite quadrupolar potential distributions in each of the *x*- and *y*-directions, taken with respect to the central axis (*z*-direction) as being the origin. Ideally the inner surfaces of the rods should be hyperbolic in cross-section in order to maintain the correct quadrupolar shape of the potential distribution.

2.1. The QMF with round rods

Arrays of round rather than hyperbolic electrodes are used in most modern instruments to simplify construction and to reduce costs. Historically [2], it was considered that a good approximation to a quadrupole field can be obtained when the radius *r* of each round rod is chosen as 1.148× the selected r_0 value [10]. Recently, this assertion has been questioned by Gibson and Taylor [11] who claimed that the best performance is obtained not with a single value for r/r_0 but rather with a value in the range $r = 1.12 \times r_0$ to $r = 1.13 \times r_0$ because QMF performance is influenced to a small extent by the ion beam form upon entering the QMF.

Let us consider initially the case where the DC bias applied between the *x*- and *y*-pairs of electrodes is set to zero. When a positive ion is injected (at energies of a few electronvolts) from the source so that it moves through the electrode array (but not precisely along the *z*-axis itself), it will be subjected to electrical forces acting orthogonally to the direction of motion along the axis. The ideal quadrupolar potential distribution will result in these forces varying linearly with the displacements of the ion in the *x*- and *y*-directions, and the three components of the motion of the ion (that is, *x*, *y*, and *z*) can be considered independently. Thus, with the application of a sinusoidally-varying RF potential between the

[2] W. Paul, Personal communication to JFJT.

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