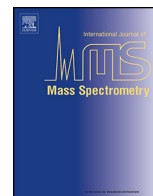




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Sector instruments for chemical analysis and research

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ABSTRACT

When the last chemical elements were successfully measured by mass spectrometry its use for the characterisation of isotopes declined, but its use for chemical analysis and research grew. This new field of activity was aided by the emergence of commercially manufactured sector mass spectrometers designed for the analysis of oil refinery gases. Although the 1940s saw the use of mass spectrometry dominated by the petroleum industry it also saw many developments in its application to chemical analysis. By the early 1950s heated inlet systems were allowing spectra of all kinds of volatile organic compounds to be obtained. The 1950s saw the development of accurate mass measurement of organic molecules as a means of determining their elemental composition. This led to a demand for higher resolution double focusing instruments. Two types of design competed for this application, each with their perceived advantages and disadvantages. It was another decade, following the application of computers to high throughput accurate mass measurement, before one of these came to dominate. Double focusing sector instruments also enhance the information afforded by “metastable” ions, allowing identification of precursor and product ions. This led to the developments of Collision Induced Decompositions, MIKES and “linked scans”. The mass range demanded of mass spectrometers jumped to new levels with the development of Fast Atom Bombardment (FAB). This led to new sector designs incorporating innovative new magnets. The success of FAB as a soft ionisation technique meant it produced little fragmentation and structural information. This led to a growth in the use of tandem MS/MS instrumentation as a tool for determining structures. This paper recounts these and many other developments which kept magnetic sectors at the centre of major new developments in mass spectrometry for chemical analysis and research for so long.

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1. Introduction

Following Thomson's famous experiments with positive rays [1], leading to the discovery of isotopes, it soon became evident that he had found a means of accessing a wealth of new information. It was equally evident that there would be much to be gained from improving the quality of the data. This has led to a century of continuous new developments and innovations in mass spectrometry instrumentation, and for the first half of that century that instrumentation was almost exclusively magnetic sector instrumentation.

In the years leading up to World War I work with positive rays was continued by Aston at the University of Cambridge, and Dempster at the University of Chicago. Aston used a discharge bulb as a source of ions and his mass spectrograph [2,3], comprising an electric field followed by a magnetic field, was designed to provide

velocity focusing to cope with the wide spread in ion velocities. He relied on collimation to restrict the peak broadening associated with the directional spread in ions emitted from the ion source. On the other hand Dempster obtained ions from salts on heated filaments and by electron bombardment of vapours emitted from these filaments. The ions from his ion sources had relatively little kinetic energy and, by accelerating the ions prior to mass analysis, they had a relatively small proportional spread in velocities. Consequently Dempster was able to use just a magnetic field with 180° deflection [4] which provides directional focusing of the ions.

Aston's discovery of the deviation of the mass of isotopes from whole numbers led to an interest in measuring the mass of ions to higher accuracy, and this in turn led to a need to develop instrumentation with higher mass resolution. In 1931 Bainbridge, at the Franklin Institute (later Harvard University), added crossed electric and magnetic fields before a Dempster type mass spectrograph [5] to provide velocity filtering of ions prior to mass analysis. In the mid 1930s, in separate overlapping developments, Dempster [6] and Bainbridge [7] each independently built new instruments combining electric sector and magnetic sectors to provide both directional

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focusing and velocity focusing of ions of a single mass, whilst at the University of Vienna Mattauch and Herzog [8,9] combined electric and magnetic sectors in such a way as to provide both directional and velocity focusing for all masses. Dempster's instrument comprised a 90° electric sector followed by a 180° magnetic sector, whilst Bainbridge used a 127.3° (i.e. $\pi/2^{1/2}$) electric sector followed by a 60° magnetic sector. Both used photographic plates for recording spectra, although simultaneous directional and velocity focusing was only truly achieved at one point along the plate. Mattauch and Herzog combined a 31.8° (i.e. $\pi/2^{5/2}$) electric sector and 90° magnetic sector, in an arrangement not dissimilar to that used by Aston, such as to achieve both directional and velocity focusing for all masses recorded simultaneously on the photographic plate. Sector instruments that provided both directional and velocity focusing became known as double focusing instruments.

In 1935 the last of the elements, Platinum and Iridium, were successfully measured by Dempster using ions created in a high voltage, high frequency spark. Aston is reported to have commented that mass spectroscopy had served its purpose and would die away as a field for research. However, by this time the mass spectra of organic compounds were already being recorded by Tate and co-workers at the University of Minnesota and by Bleakney and co-workers at Princeton University [10–12]. As the use of mass spectrometry for the characterisation of isotopes declined its use for chemical analysis and research grew.

2. Commercial manufacture

This new field of activity was aided by the emergence of commercially manufactured mass spectrometers from Consolidated Engineering Corporation (Pasadena, California) and Westinghouse Electric Corporation (Pittsburgh, Pennsylvania), designed for the analysis of oil refinery gases and low-boiling liquids. The subsequent developments and discoveries that laid the groundwork for mass spectrometry as a tool for the study of the structures and gas phase ionic reaction mechanisms of organic compounds took place chiefly in the laboratories of the petroleum industry.

Consolidated Engineering Corporation (CEC), later known as Consolidated Electrodynamics Corporation, was set up in 1937 by the United Geophysical Company to design electronic instruments needed by United in its geophysical operations. The CEC team borrowed an abandoned mass spectrometer built at the California Institute of Technology for the analysis of refinery streams. Interest in soil gas analysis waned, but the instrument was successful in analysing refining gases and low-boiling liquids [13]. Their first model, the CEC Model 21-101, was a Dempster type single focusing 180° magnetic sector with a 5" radius, and the first instrument was installed in late 1942 at the Atlantic Refining Co. in Philadelphia. Over the next 25 years the Model 21-101 was superseded by the 21-102, 21-103 (A, B and C) and 21-104, all retaining the original 5" radius, 180° sector geometry.

Over the decade from 1944 to 1954 the majority of mass spectrometer users were in laboratories of the oil companies and other companies with closely allied interests. The instruments were used almost entirely for quantitative analysis of gaseous mixtures, (i.e. light hydrocarbons and fixed gases), and selected fractions from low temperature fractional distillations of hydrocarbon streams. Initially the reproducibility of spectra of organic molecules, even simple hydrocarbons, was insufficient to adequately quantify the components of a mixture. CEC undertook the development of mass spectrometry to analyse mixtures of hydrocarbon gases, initially with the goal of seeking petroleum deposits by analysis of the gases evolved from the ground. The problems of obtaining reproducible spectra were at length resolved, but the analysis was found to be of little value in petroleum prospecting. However another urgent

problem in hydrocarbon analysis was found. The problem of C-1 to C-4 hydrocarbon mixture analysis, and particularly the butane isomer analysis in the catalytic cracking process for the production of aviation fuel, was a critical problem in the war effort [14]. Since compositions were calculated with solutions of simultaneous equations, reproducibility of fragmentation patterns was essential.

Although this decade saw the use of mass spectrometry dominated by the petroleum industry it also saw many developments in its application to chemical analysis and research. These included the establishment and distribution of the first reference calibrating compounds and libraries of reference spectra, labelling experiments (e.g. deuterium labelling, and studies using stable isotopic tracers), measurements of ionisation and appearance potentials, and their interpretation in terms of ion structures and decomposition processes. In the early 1950s heated inlet systems were becoming available, and spectra of volatile organic compounds of all kinds were being obtained.

In 1943 the Westinghouse Electric Corporation introduced the Type LV mass spectrometer for analytical purposes in the synthetic rubber development effort. This was a Nier-type magnetic sector, with a 90° sector angle. In 1940 Nier had introduced a single focusing sector field instrument with a 60° magnetic sector [15]. With the smaller sector angle the source and detector are positioned out of and away from the magnet. This allows the magnet to be reduced in size and weight. The Westinghouse instrument was also used in basic research, for example in the measurement of appearance potentials, and in the first studies of ion/molecule reactions at elevated pressures, which in turn led to the discovery of chemical ionisation [16–18].

Unlike the CEC Model 21-101, the Westinghouse Type LV 90° magnetic sector instrument had so called 'field-free' regions between the ion source and magnetic sector, and between the magnetic sector and the detector. As a consequence this instrument exhibited weak, unusually broad peaks in the mass spectrum, usually at non-integral m/z values. Hipple and his associates at Westinghouse established the origin of these peaks that we now know as 'metastable' peaks [19,20]. Unstable ions that have left the ion source may decompose before reaching the magnetic field and the product ions may be observed as broad peaks with an apparent m/z value different to that of either the unstable precursor ion or the product ion. These 'metastable' peaks could provide valuable information about the pathway of a particular molecular decomposition and the structure of the intact molecule itself. This also explained the origins of the diffuse, asymmetric background signals that were sometimes observed on the CEC Model 21-101 instrument.

After a few years Westinghouse withdrew from the instrument business and General Electric (GE) in Schenectady, New York, stepped in with a Nier-type 60° magnetic sector instrument that it had supplied for use as gas leak detectors in the Manhattan Project. GE re-engineered this instrument and began manufacturing it for general use.

In 1944 the UK Government had decided to develop its own atomic bomb, for which it needed mass spectrometers to investigate its success in separating the uranium 235 and 238 isotopes. The Metropolitan Vickers Company (Manchester, UK) was contracted to supply three mass spectrometers for the isotopic analysis of UF₆ gas to a specification then in the hands of James Chadwick at Liverpool University, where his team had built a prototype instrument [21,22]. Metropolitan Vickers (MV or MetroVick) was a large UK electrical engineering company that also had a vacuum engineering division. Before the war it had developed the first high-boiling petroleum oil derivatives, known as Apiezon oils, to replace mercury in high vacuum diffusion pumps. The mass spectrometer, known as the MS1, had an electron impact ion source and a 6" radius, 90° magnetic sector. The first instrument was delivered to Chadwick at Liverpool University in 1946, and the second and

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