MASS SPECTROMETRY

The Role of Kratos

The magnetic sector mass spectrometer equation shows that for a given radius of curvature a particular ion mass can be brought to a focus at the collector slit by varying either the ion accelerating voltage or the magnetic field. Hence if the ion accelerating voltage is held constant, and the current flowing through the coils of the electromagnet is scanned in some known manner, then the ion species emerging from the source can be scanned successfully across the collector plate. The arrival of an ion beam at the collector gives rise to a flow of positive current through the measuring resistor to earth, and the magnitude of this current is a direct measure of the number of ions of the particular species leaving the ion source. The voltage developed across the resistor is measured electronically and can be displayed on a meter, an oscilloscope, or as a deflection of the trace on a pen recorder, or UV recorder; alternatively it may be digitised and stored in a data system. In this manner the relative abundances of the isotopic constituents of a particular gas, or the chemical compounds of an unknown mixture can be determined and mass spectrometers were used initially for this application.

Nier was amongst the first mass spectroscopists to use a mass spectrometer for the analysis of mixtures, instead of solely for the study of masses or relative abundances of isotopes. This work was seen to open up a new field of application of the mass spectrometer, particularly in the petroleum industry. The manufacture of mass spectrometer on a commercial basis was begun in the USA around 1940 by the Consolidated Electrodynamics Corporation (CEC); those instruments were of the 180 degree deflection type and were designed for the chemical analysis of hydrocarbon mixtures.

In 1940, with the entry of the USA in the second World War, Nier and his co-workers at the University of Minnesota began the design and manufacture of a number of sector field instruments for the analysis of isotopically enriched uranium in connection with the Manhattan Project. Approximately 40 of these instruments were subsequently produced by the General Electric Corporation in the USA also for use in the atomic bomb project.

MS1

The Metropolitan Vickers (MV) Research Department was approached by the Directorate of Tube Alloys of the Department of Scientific and Industrial Research in connection with the manufacture of mass spectrometers for the British part of the same project. A contract for four 90^{o}, 6 inch radius sector instruments, based on Nier's design information which had been released to the British Government, was signed in 1944. The instruments were ordered for the analysis of uranium hexafluoride for the determination of the isotopic concentration of uranium samples produced in the making of fissionable materials for atomic weapons. The design of the mass spectrometer was under the direction of Mr J Blears of the Vacuum Physics section of the Research Department and the first of the instruments was delivered to the Physics Department of Liverpool University in March 1946: this was the first mass spectrometer to be built commercially outside the USA.

The manufacture of 41 MS1 instruments allowed Metropolitan Vickers to extend the skills in vacuum engineering and the production of precise electrostatic and magnetic field which had been developed earlier in connection with the high voltage oscilloscope, and the electron microscope.

MS2

The design of an improved mass spectrometer, the MS2, was begun in 1946, and a prototype was completed in 1949, the first production instrument being delivered to the Chemistry Department of Oxford University early in 1950.

The instrument employed a 6 inch radius, 90^{o} magnetic sector analyser, but the glass vacuum envelopes used in the earlier MS1 series for the source and collector regions were replaced by an all metal analyser tube to which the source and collector housings, diffusion pump and cold trap, were attached by rubber gasketed metal flanges. This feature facilitated the removal of the source either for cleaning or for replacement of the electron emitting filament.

The metal sample handling plant for uranium analysis, used on the MS1, was replaced by a more versatile glass system which required a 1 cm^3 sample for a full analysis. The performance and reliability of the vacuum system was improved by the use of oil diffusion pumps and a stainless steel cold trap in which either liquid nitrogen or solid carbon dioxide could be used as the coolant.

The performance of the electronic stabilisers of the magnetic and electrostatic fields was improved, as was the reliability of the electronic circuitry in general. Particular advances were made in the ion current display system with the result that the tedious procedure of measuring each beam of the mass spectrum separately by means of a sensitive galvanometer was replaced by a more rugged amplifier and recorder which enabled the spectrum to be plotted as a series of peaks on a 10 inch wide paper chart. A unique feature of the recorder was its range changing system which automatically reduced the sensitivity of the electrometer amplifier in discrete steps if the ion beam was large enough to drive the recorder pen to full scale deflection on the most sensitive range. This range changing method allowed ion beams with amplitudes in the range of 10,000 to 1 to be easily measured from the recorder chart; the smallest detectable ion current was 3×10^{-15} amp.

The refinements in the design of the MS2, compared with its predecessor, made it suitable for the routine analysis of mixtures of hydrocarbon gases, as well as for isotope ratio measurements. A total of over 120 MS2 instruments was manufactured.

MS3

The almost universal usage of mass spectrometry for the analysis of low molecular weight gases in the early 1950's generated the need for a smaller and simpler instrument for isotopic analysis of gases and the analysis of lighter petroleum fractions. The MS3 was evolved to meet this requirement, the first instrument of this type being completed in 1952. The sample inlet system, 90^{o}, 4 inch radius magnetic analyser, vacuum pumping plant and electronic control and measuring circuits were contained in one cubicle. The single unit therefore contained the apparatus required for routine isotopic analysis of gases, e.g. nitrogen and oxygen, which are used as isotopic tracers in biochemical studies. An accessory unit containing a pen recorder and magnet current scanning system was available to make the MS3 suitable for the analysis of gas mixtures.

Accurate Mass Measurement

The development of the Gas Liquid Chromatograph as a gas analyser in the mid 1950's provided a cheaper and simpler alternative to the mass spectrometer in routine analysis of hydrocarbon gas mixtures, e.g. in refinery quality control work, with the result that mass spectrometers moved from the routine analytical field to more specialised fields of application. One of these applications was the detection and identification of small quantities of impurities found in nominally pure materials and the recognition of the importance of accurate mass measurement by Dr J Beynon, ICI Dyestuffs Division was of major importance in extending the technique into this area. In 1956 the first commercial double focussing mass spectrometer for organic analysis, MS8, was delivered to Dr Beynon's laboratory and provided a resolution of 10,000 and an accuracy of mass measurement of 10 ppm. The delivery of this instrument represented a major advance in instrument capability greatly extending the usefulness of mass spectrometry to the organic chemist.

The value of this approach to chemical analysis can be understood from a consideration of atomic masses; when expressed on the scale $^{12}C = 12.0$, the masses of the isotopes of any element are found to be very nearly equal to whole numbers, for example, the atomic mass of hydrogen is very nearly equal to 1, oxygen 16, and nitrogen 14. In the spectrum of a mixture or compound containing these 4 elements, 4 combinations can give rise to ions having an approximate mass of 28 atomic mass units i.e. CO, N_2, CH_2N, and C_2H_4. In the case of a mass spectrometer having aresolution of the order of 100, these ions would be indistinguishable from each other without further evidence from their breakdown, or cracking pattern. The smallest mass difference between any two of the four ions mentioned is 1/2500 of their mean mass, hence an instrument having a resolution of 2500 is required to separate the 4 components; in order to effect an analysis it is also necessary to measure the mass of the ion with the same order of precision by comparing the unknown mass with a known standard, for example the mass of oxygen.

Double Focussing

The resolution and mass measurement accuracy of a mass spectrometer employing only a magnetic sector are limited by the energy spread of the ions emerging from the source, since the width of the image formed by the ion beam at the collector slit is determined not only by the width of the ion beam at the source but also by an aberration term including a factor dependent upon the ion energy. The energy spread of the ions from a practical source is finite, hence some manner of reducing the energy aberration of the mass spectrometer must be found if the resolution is to be improved. The use of an electrostatic analyser preceding the magnetic analyser provides a practical solution to the problem of reducing energy aberration, and the combination of two sectors can be made to give both angular and energy focussing, hence 'double focussing' as was the case in the instrument built by Bainbridge in 1934.

MS8

The MS8, built in 1956 for Dr Beynon's laboratory, was the first commercial double focussing mass spectrometer to be built for use in the analysis of organic materials; the instrument, based on the theory of Nier and Roberts, gave a resolution of up to 10,000 and allowed ionic masses to be measured with an accuracy approaching 1 part in 100,000. These figures represent a considerable improvement over the performance of a magnetic sector, or 'single focusing' instrument and allowed Beynon and Williams to extend their pioneering work in the application of mass measurement techniques in the analysis of organic materials.

MS8 - continued

The MS8's geometry comprised a cylindrical 90^{o} sector electrostatic analyser of $7\frac{1}{2}$ inch mean radius, and a 90^{o} sector 6 inch radius magnetic analyser. In this form of double focussing instrument the aberration suffered by the ions in their path through the electrostatic analyser is compensated by the aberration arising in the magnetic sector.

MS9

Only one MS8 was built, and the experience gained in manufacture and operation of the instrument formed the basis of the design information for the MS9. The first production MS9 was supplied to the Shell Laboratories in Amsterdam in 1962, and during its life-time nearly 200 instruments were shipped.

The radii of curvature of the 90^{o} electrostatic and magnetic analysers are 15 inches and 12 inches respectively. The use of larger analysers than in the MS8, and of the comparatively high ion accelerating voltage of 8kV, together with an electron multiplier detector allows a relatively high sensitivity to be attained, while permitting operation at high resolution. A notable feature of the MS9 was the versatility of the sample inlet systems which allow gases, liquids and many organic solids to be admitted to the instrument for analysis. In particular, the direct insertion vacuum lock system allows solid samples to be inserted directly within the ionization region of the source without breaking the source vacuum; this method of sample handling permits solids to be inserted speedily and analyses can be carried out when only very small quantities of material (down to 10 nanograms) are available.

The original guaranteed resolution of the instrument was 25,000, but during its lifetime this was steadily increased until the MS902S offered a 100,000 resolution capability; to date only the MS50 has exceeded this level of performance. Mass measurements could be carried out with an accuracy of 1 or 2 parts per million. This order of performance was the highest demonstrated by any commercial instrument and was achieved only when the requisite mechanical tolerances and high stability of the fields were met in the electrostatic and magnetic analysers; for example the 15 inch radius cylindrical condenser plates forming the electrostatic analyser had to be parallel to within 0.0001 inches, and the field of the electromagnet stable to 1 part in a million. The mass measurement system employed a decade resistance box for the comparison of voltages to a precision of 1 part per million; the largest resistors used in this box are manufactured to a specification almost equal to that of international resistance standards.

MS12

The MS12 was a development of the MS9, being a single focussing instrument using the magnetic sector of the latter. The instrument was developed primarily for the analysis of samples emerging from a gas liquid chromatography, though the use of the versatile sample inlet systems developed on the MS9 allowed the MS12 to solve those problems or organic analysis which required neither a resolution greater than 2,500, nor an accurate mass measuring system.

MS5

The application of mass spectrometry is not concentrated solely on the solution of problems in the range of organic analysis and instruments outside this range have found a ready market.

The MS5 was developed in conjunction with AERE, Harwell, in 1955 for the isotopic analysis of solids by the thermal ionization process. A novel feature of the MS5 was the provision of a sliding bar vacuum lock. The source filament assembly, on which the salt of the sample is painted, can be loaded into the lock at atmospheric pressure, while a second sample is being analysed. The time required to change from one sample to another is reduced to about 15 minutes by the use of the vacuum lock. The MS5 enabled the hitherto unprecedented figure of up to 20 one-microgram samples of uranium to be analysed in one day, while samples as small as 10 nanograms can be analysed without difficulty.

MS7

It was in 1955 that work was started in the MV Research Department on a prototype double focussing mass spectrograph for the impurity analysis of solids. The MS7 was the first commercially built double focussing instrument in the world. The geometry chosen was that of the design of Mattauch and Herzog. The MS7 employs a spark source in which two small rods of the sample material are used as the electrodes in a spark gap within the vacuum system. The application of a pulsed voltage or the order of 30 to 100kV causes a spark discharge to occur between the electrodes, and ions representative of the sample material are used as the sample material are formed directly in the discharge and accelerated into the analyser system. A 2 inch by 10 inch photoplate is used as the ion current detector, and a rack mechanism operating through the vacuum system walls allows the photoplate to be moved sideways above the magnet gap so that up to 30 separate exposures can be made on one plate.

The vacuum spark source has a particular advantage for the analysis of mixtures of solids namely that the relative sensitivities of all the solid elements are very nearly the same, while the photoplate detector is particularly favoured for impurity analysis because of its ability to integrate simultaneously ions from all the solid elements present in a mixture.

A second prototype MS7 was built for the Research Department of British Thompson Houston Co (BTH) at Rugby; it was installed in 1956 and was in regular use until it was replaced by a production MS7 in 1963. The first production instrument was installed at the laboratories of the Mond Nickel Company at Birmingham in 1958. The design of the production instrument included many refinements conceived as a result of experience gained with the prototype; simplicity and ease of operation were factors which rated highly in the design, and the very considerable improvements in the vacuum system resulted in a greatly improved detection limit in impurity analysis.

The all metal vacuum system is bakeable to greater than 250^{o}C and employs gold gasketed flange joints in the source and analyser regions; this refinement in technique allows pressures of 10^{-8} torr or better to be maintained in the analyser system, and in turn permits very high detection limits to be achieved, for example 1 part of boron in 1000 million parts of silicon can be detected. This detection limit is equivalent to detecting a grain of sugar in a lorry load of sand. The MS7 was the only mass spectrometer in the world to achieve such a detection limit, and the foresight of the Company in allowing the prototype to be built was amply justified by the sale of approaching 150 MS7 series instruments.

MS4

The MS4 mass spectrometer was manufactured in 1959 to fill the need for a rapid gas analyser for use in medical research in the field of respiratory problems. The instrument was the first to be marketed specifically for respiratory gas analysis, and follows the design of Dr K T Fowler of the Medical Research Council. The inlet system of the MS4 samples continuously from atmospheric pressure, and the 2 inch radius 180^{0} analyser scans through its mass range at a rate of 25 scans per second; the intensities of the ion beams reaching the collector are displayed as vertical peaks on the oscilloscope screen. The collector current signal is also fed to a 4 channel selector circuit which allows any 4 peaks within the mass range of the instrument to be displayed as meter readings and as deflections on the trace of a 4 channel recorder.

The sample inlet tube is connected to the subject's breathing mouthpiece and a small fraction of the inspired or expired air in the mouthpiece flows almost instantaneously into the mass spectrometer. The gases usually displayed on the recorder are nitrogen, oxygen, carbon dioxide and either argon or helium. The high speed of response of the instrument enables it to detect changes in the concentration of any of these gases occurring in times of less than 1/25 second, so that changes in gas concentration in times much shorter than one expiration can be measured. The use of the MS4 in medical research made a significant contribution to the understanding of lung functioning, and to the development of some rapid tests of value in the diagnosis of certain respiratory diseases.

MS10

Kratos' smallest, though largest selling, mass spectrometer is the MS10 which employs a 2 inch radius 180^{0} deflection analyser somewhat akin to that of the MS4. The mass range covered by the instrument is 2 to 200 making it suitable for the analysis of gases and some low molecular weight liquids.

The instrument is manufactured in a number of forms; the basic analyser and control unit is used for the detection and analysis of residual gases in vacuum systems, the analyser being mounted directly on a port in the vacuum system walls. The analyser is designed to be baked to a temperature of up to 300^{0}C, so that the MS10 does not contribute to the background gases existing within the system to be examined. The instrument has a low detection limit, being capable of detecting partial pressures of most gases down to the region of 10^{-10} torr.

Conclusion

In the 70 years which have elapsed since the first mass spectrometer was constructed for use in the study of atomic structure, the field of application has widened to include many aspects of chemical analysis and during the 35 years in which the Company has been manufacturing mass spectrometers, Kratos has designed and developed a wide range of these instruments which has enabled the Company to achieve and maintain a position as a world leader in the science of mass spectrometry.

Current Products

At this point the mass spectrometer product range becomes more recognisable with the appearance of the MS30, MS50, MS25 and MS80. A number of innovations are incorporated in these instruments, in particular, the development of the double-beam mass measurement; the incorporation of hexapoles into the single-beam instruments for improved performance at high resolving power; the development of the alternate CI/EI (ACE) technique; and most recently, the development of revolutionary magnet technology that incorporates a fast scan capability with a high mass range. No other Company can match this history of innovation, a feature of Kratos that will continue.

Mass Spectrometer Data System

In parallel with the developments in ion optics, we have pioneered the application of computers to the acquisition and processing of mass spectral data; in this area Kratos can boast many first and fundamental patents, the most fundamental of which are the connection of a computer to a mass spectrometer collector for on-line acquisition and the development of the high resolution data acquisition technique for the assignment of accurate masses to an entire scan.

DS10

It was soon obvious that high resolution mass spectrometers could generate a vast amount of data and that the only way to overcome this was to use a computer based data acquisition system. This led, in 1967 to the introduction of DS10 based upon a PDP8 central processor. The DS10 could acquire high resolution scans, calibrate, determine accurate masses and calculated elemental compositions. DS10 was the first commercial mass spectral data acquisition system.

DS20

Essentially DS20 was an extended version of DS10 that incorporated a larger memory size and had back-up storage on disk; it was released in 1970 and was based on the PDP8.

DS30

With the growing demand for gc-ms came the need for a data system that could acquire, process and store even greater amounts of data; this led to the introduction, in 1971, of DS30. A further facility within DS30 was double-beam data acquisition developed in conjunction with the double-beam MS30. With this technique it became practical to obtain accurate mass data from fast scanning gc-ms experiments performed at relatively low resolutions.

DS50

Improvements in the performance of mass spectrometers continued to demand corresponding increases in the capability of the data system. After only two years of life it became apparent that even DS30 required significant improvement. Unfortunately, the PDP8, with its slow memory and 12 bit architecture, used in this system could not offer the required performance and when the DS50 series was introduced, in 1973, it was based on the best scientific minicomputer available, the Data General Nova 2. The selection of the Nova series has proved a wise choice as continuous development has maintained its leadership. DS50 offered faster acquisition rates with real-time reports, an unlimited back-up storage capability, and a wide range of peripherals and software.

DS50 - continued

DS50S was developed in order to exploit fully the facilities available within the newly released Nova 3. It was an extension to DS50S, and existing DS50 users could upgrade to DS50S without needing to replace any of their existing hardware; this policy is a fundamental feature of the design of the DS50 series.

Once again, DS50S made available increases in acquisition and operational speeds, and bulk storage capacity.

DS55

The latest member of the DS50 series was introduced with the Nova 4 and although it was associated with all the traditional improvements in performance, a novel data acquisition interface was developed to meet the always growing requirements of mass spectrometry.

GC-MS, especially capillary gc-ms, demanded even greater acquisition rates and dynamic range, especially with the new generation of fast (100 milliseconds per decade scan capability), laminated magnets. To meet these demands, the Fast Pre-Processor data acquisition was developed, with its 10^6: 1 (per sample) dynamic range capability and 200kHz sampling rate it matches these requirements.

Development of the DS50 series does not stop here; a large team of experienced programmers continues to keep Kratos' data system ahead of anything available.