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THE TRANSFORMATION OF A SINGLE FOCUSING MASS SPECTROMETER INTO A MASS ANALYSED ION KINETIC ENERGY SPECTROMETER [2]

An old single focusing mass spectrometer was transformed into a Mass Analysed Ion Kinetic Energy Spectrometer by adding an Electrostatic Sector after the Magnetic Sector. Details of the construction are given and the performance of the instrument is studied.

1 — INTRODUCTION

The interest in the kinetic energy of ions formed by electron impact in a mass spectrometer has been sustained for over a quarter of a century. Many methods are available and have been exploited from time to time, leading to the study of ions with high kinetic energy which where first detected by making negative the ion repeller in the source (1). Other methods include the analysis of peak shape (2, 3) and of the change in relative ion intensities with modifications of the accelerating voltage (4), which also influences the width of the beam at the collector (5).

The change in relative ion intensities with the voltage of the ion repeller has been investigated (6) and a study was made of the shapes and positions of ions with and without kinetic energy selected using the accelerating voltage and scanned by an auxiliary magnetic field (7). The metastable supressor placed between the magnet and the collector has been used for the same purpose (8-12). Some authors have employed deflecting plates immediately after the source (6, 13, 14). Electrostatic sectors were used both before (15) and after (16) mass analysis. Further, the kinetic energy of ions has also been studied using instruments based upon different principles such as the trochoidal path (17), the coincidence time of flight (18) and the time of flight (19) spectrometer. BEYNON (20) and his group have also started a series of investigations involving the relationship between the width of the metastable peak and the kinetic energy of the fragment ion, a method since then widely applied (21). In this case the excess kinetic energy measured corresponds to metastable transitions and as is to be expected (22), is smaller than for ions formed inside the ion source.

In the instrument here described the electrostatic sector was constructed to follow the magnetic sector, this geometry allowing the determination of the kinetic energy of the ions after mass analysis and also the study of the metastable transitions corresponding to each group of ions of a known

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mass-to-charge ratio. Instruments with this geometry have been built previously to study ion molecule reactions (16) and to improve the resolving power of a mass spectrometer (23) by reducing the number of scattered particles reaching the collector. Recently four papers (24-27) have been published reporting results obtained using alike sequence of sectors.

2 — DETERMINATION OF THE GEOMETRIC CHARACTERISTICS OF THE ELECTROSTATIC SECTOR

The basic instrument to which the electrostatic sector was to be attached was an MS2 (28) (Metropolitan-Vickers no. 11) single focusing 90° magnetic sector mass spectrometer. From the original instrument the Nier type source, the tube and the magnet were kept unchanged, the 2 kV circuit was replaced by a highly stabilized commercially available power supply ([1]) and all the other circuits were new solid state circuits manufactured in the workshops of the Department. The position of the defining slit of the collector of the MS2 was taken as the source of ions proceeding to the electrostatic sector.

To choose the dimensions of the electrostatic sector, the calculations made by H. Ewald and H. Liebl (29, 30, 31, 32) for a toroidal sector were followed.

As the energy resolution $E/\Delta E$ of the electrostatic sector is proportional to the velocity dispersion coefficient a study was made of the variation of this factor with the geometric characteristic of the torus considering the limited space available to place the sector in the apparatus. The torus being the surface generated by a circumference of radius R_e turning around an axis *z* at a distance a_e from the centre of the circumference, for $a_e = R_e$ the surface generated will be a sphere while for $R_e \to \infty$ it will be a cylinder. From the calculations made it prooved convenient to build a spherical sector which has a high velocity dispersion coefficient with the additional advantage of focusing both in the radial and axial direction.

The spherical sector is defined by the radius a_e and by the angle $\varnothing_e$ of deflection in a cylindrical system of coordinates r, $\varnothing$, z, z being in this case an axis containing a diameter of the sphere. It is also useful to define two other systems of cartesian coordinates with origin in the points $r = a_e$, $\varnothing = 0$, $z = 0$ and $r = a_e$, $\varnothing = \varnothing_e$, $z = 0$, where the z direction is parallel to the axis *z* of the sector and the *y* direction is in each of the two points the direction of the radius a_e of the sector.

A spherical sector has to satisfy the following lens equation:

$$(l_r' - g_r)(l_r'' - g_r) = f_r^2$$

where g_r is the distance of the object or image focal points from the corresponding sector boundary and is equal to $a_e \cot \varnothing_e$; f_r, focal length of the spherical electrostatic lens is equal to

$$\frac{a_e}{\sin \varnothing_e};$$

l_r' is the distance from the object to the respective sector boundary and l_r'' from the other boundary to the image.

The amplification (32) was made unity which corresponds to a symmetrical sector, that is, $l_r' = l_r''$. The chosen sector (fig. 1) is a 60° of arc sector and has a radius of 152.40 mm, $l_r' = l_r'' = 264.0$ mm. The distance between the two concentric spherical plates was set at 22.86 mm. This value was fixed considering the accuracy required in the construction, which has to be better than 1 in 1000 to permit a resolution of this order ([2]). The plates have radii of respectively 140.97 mm for the concave and 163.83 mm for the convex plate.

One ion entering the sector in the plane $z = 0$ and describing an orbit of radius a_e is submitted to a centripetal force (31) given by

$$\frac{M_0 v_0^2}{a_e} = -eE_0$$

where M_0 is the mass of the ion, v_0 its velocity, e its electrical charge and E_0 the intensity of the radial electrostatic field, between the plates for a radius a_e. The intensity of the field is given by

$$E_0 = -\frac{\Delta V}{2b}$$

where V is the potential difference between the plates

([1]) Oltronix 2.5-10 HR.

([2]) The sector was machined in non-magnetic stainless steel by Carrick Precision Tools, Stewarton, Scotland.

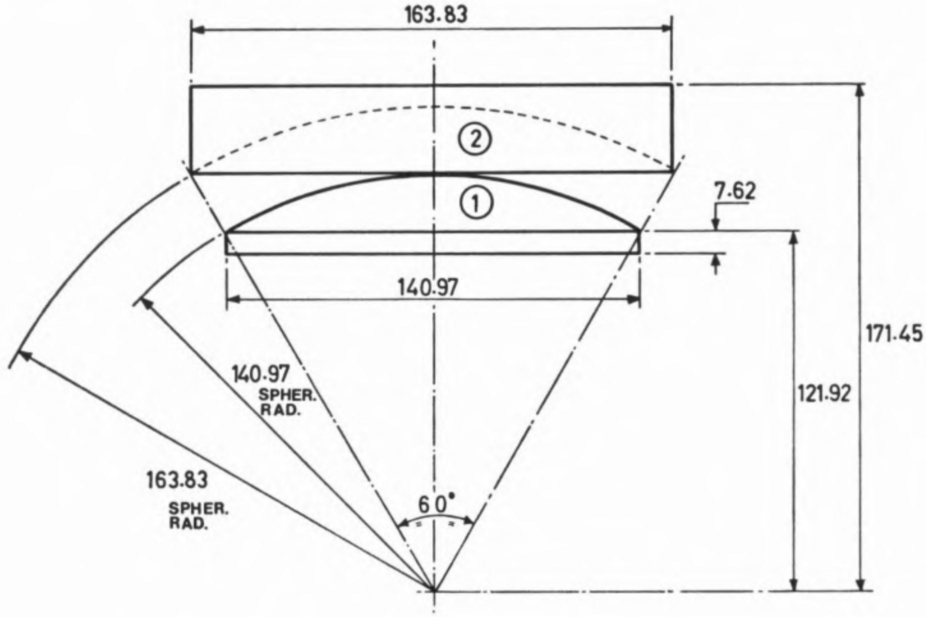

Fig. 1
Dimensions of the electrostatic sector plates.

and 2b the gap between the plates. For the chosen sector, ions with 2kev kinetic energy are focused for a voltage difference of 600 V between the plates, that is + 300 V to the concave plate and − 300 V to the convex.

As the field applied to the sector plates will not cut off abruptly at their boundaries, the analyser will in fact operate over rather more than 60° of arc. The effect of the fringing field was calculated approximately using Herzog's expression (33) for plane plates. Thin, grounded plates are placed near the field boundaries (34) to compress the fringing field region. The final adjustment to focus the beam was made experimentally by moving the two bellows (fig. 2) which are situated between the magnetic and electrostatic sectors, and the electrostatic sector and final collector.

The fringing field only shifts the focusing point so it was appropriate to calculate the second order aberrations of the image neglecting the fringing field. The increase in the width of the image and corresponding decrease of the energy resolution due to second order effects were deduced from the expression for the path of the beam after the electrostatic sector as determined by Ewald and Liebl (31). This also allowed the calculation of the maximum possible dimensions of the slits permiting to obtain the desired resolution.

Two groups of ions, entering the sector with different velocities will be distinguishable if the images they form can be separated. Half the size of the image is equal to the sum of half the width of the entrance slit, because the amplification is unity, plus the second order aberrations together with half the width of the collector slit, as the collection was made electrically (28).

To reduce the second order aberrations the entrance and exit angles of the ionic beam are made quite small by using the Herzog plates simultaneously as limiting slits. The spherical sector has focusing properties for one point only, so all the diaphragms

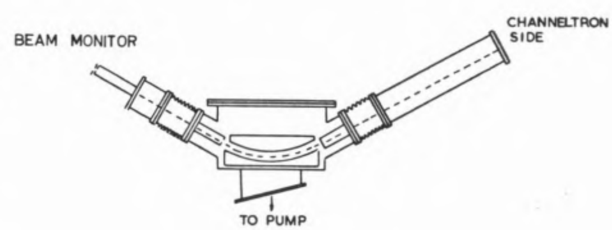

Fig. 2
Sector assembly.

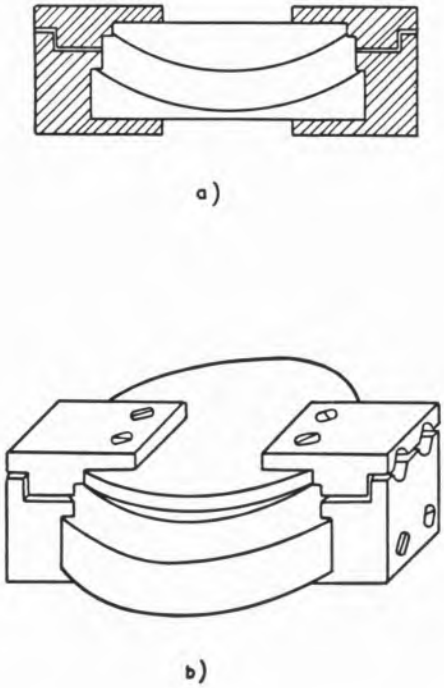

Fig. 3
Plates assembly: a) *vertical section;* b) *perspective.*

defining the path of the beams should have circular holes instead of slits. However to facilitate the detection of the beam as well as the initial setting up, slits have been used, their dimension in the *z* direction being reduced by means of another diaphragm. It would be easier to use adjustable slits but they were not available.

The use of rectangular slits makes the second order aberration in the *y* direction of the same order of magnitude of the image itself. The resolution in energy, theoretically calculated, is of the order of 0.8 in 10^3 and although this value could be improved by further reducing the second order aberrations it is within the limits of precision set in construction.

3 — ASSEMBLY OF THE INSTRUMENT

The two spherical plates are supported in position with pyrophillite parts machined to size and heat treated to get mechanical strength. Between the pyrophillite parts, attached to the top and bottom plates (fig. 3) are placed small brass rods to define the spacing. In spite of a slight contraction of the pyrophillite due to heat treatment the distance between the two plates has an error of less than 0.025mm as measured by a surface micrometer. The whole assembly is enclosed in a brass box, through which the potentials are applied by means of ceramic to metal seals (1).

The adjustment bellows are attached to each side of the box. They have the maximum length advised by the manufacturer (2), that is a length equal to the diameter. The length of the bellows was measured under vacuum before deciding the length of the rigid parts. A course adjustment is made by moving the box assembly relative to the handy angle structure while a fine adjustment is made by means of smalll angular movements obtained with the bellows. Fig 2 shows the box containing the sector, with mechanical connections. The base of the box makes an angle of 15° with the horizontal to permit the connection to the mass spectrometer.

Fig. 4 is the complete diagram of the instrument after assembling.

Besides the two vacuum systems of the original mass spectrometer a third vacuum system is used, formed by a rotary and a diffusion pump and a liquid nitrogen trap, this one being placed directly under the brass box. The pressure in the tube and sector varies from 0.267×10^{-3} Newton per square meter (2×10^{-6} Torr) to 1.3×10^{-3} Newton per square meter (1×10^{-5} Torr). The limitation in the vacuum obtained is due to the use of pyrophillite and brass parts.

Two collectors are used, one of them monitoring the beam going into the electrostatic sector. The top plate of this collector is held at − 72 V and has a slit 1 mm wide which limits the beam reaching the collecting plate and sets the resolution obtained here at a very low value. This plate also repels secondary electrons produced at the surface of the slit preventing them from reaching the collector. The next plate with a slit width of 0.20 mm defines the beam which goes to the electrostatic sector. This plate has the same position that was occupied by the defining slit of the Faraday collector in the conven-

(1) Supplied by 20th Century Electronics Ltd., King Henry's Drive, New Addington Croydon, Surrey, U. K.

(2) Supplied by United Flexible Metallic Tubing Co. Ltd., South Street, Ponders End, Enfield, Middlesex, U. K.

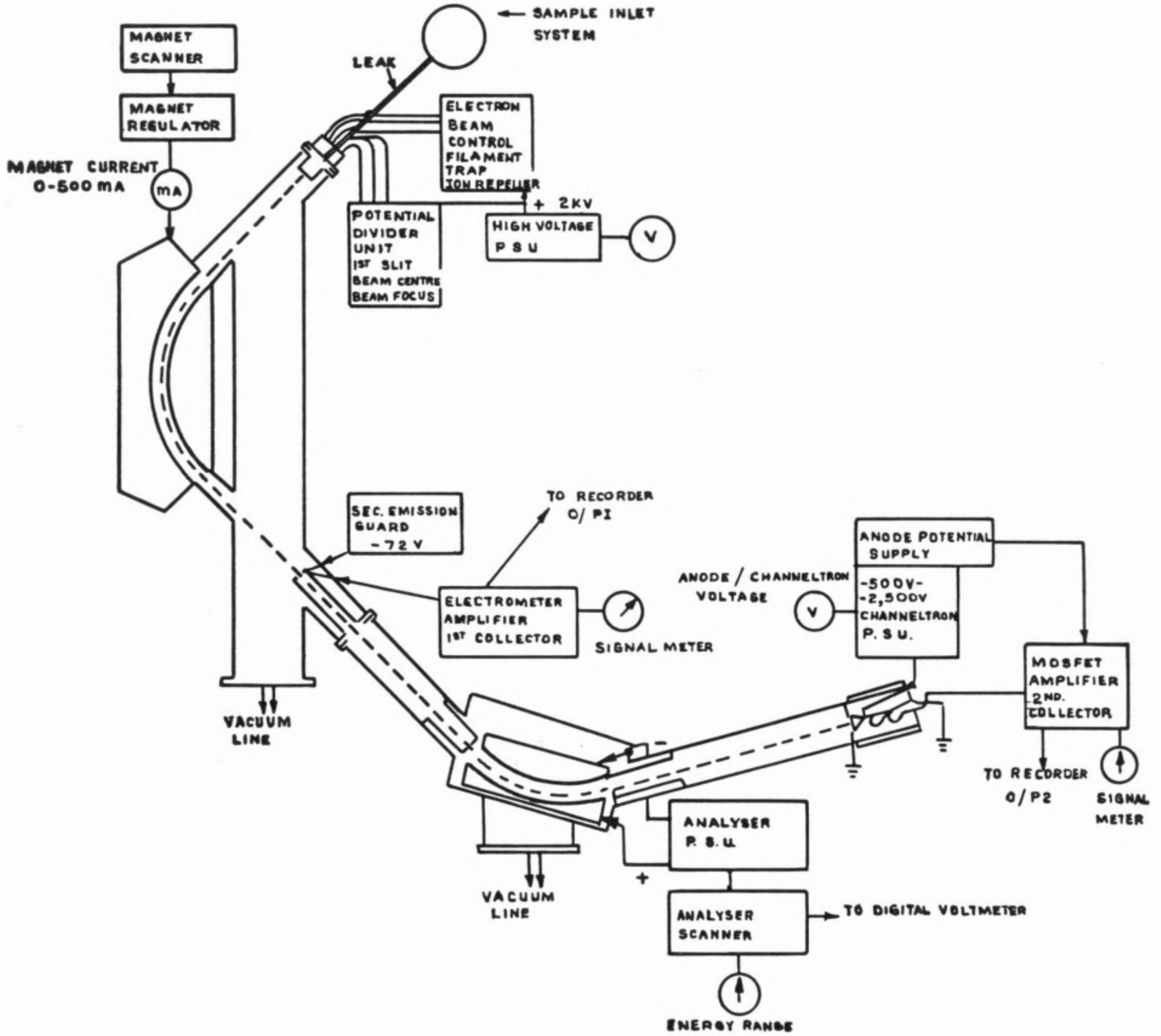

Fig. 4
Complete diagram of the Mass Analysed Ion Kinetic Energy Spectrometer.

tional MS2. All the ions passing through the 1 mm slit, but not through the 0.20 mm one are received on this plate which is connected to an electrometer amplifier. The momentum resolution

$$\frac{mv}{\Delta mv}$$

obtained in this collector is smaller than the resolution for the beam entering the electrostatic sector which was of the order of 150. A third plate cuts the dimension of the beam in the *z* direction to reduce the second order aberrations.

The end collector was a channel electron multiplier [1]. The «channeltron» assembly is represented in fig. 5. Once this assembly is attached to the system, the top plate (with a 0.02 mm slit) is situated at the image forming distance (l_r'') from the electrostatic sector plates. The «channeltron» itself was fixed with the cone about one millimetre away from the

(1) Mullard type B419AL No. 456.

plate. It was supported and simultaneously insulated from the two brass pillars by means of two teflon bands. In front of the opening of the positive end a small trap was also held in place. Electronic units supplied both the high voltage, which could be varied between − 500 V and − 2,500 V, to the «channeltron» and the voltage of + 50 V to the trap. The «channeltron» was used in the continuous current mode. The signal entering into the «channeltron» was very high particularly during the setting up of the instrument which had to be done using wide slits. The intensity of the signal made the «channeltron» to start loosing gain (35) after a relatively short time. This and mass discrimination against the lower masses (36) led to its replacement by a conventional electron multiplier.

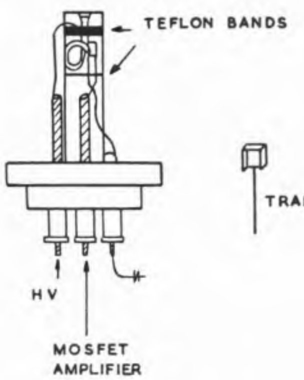

Fig. 5
«Channeltron» assembly.

A power unit provides − 300 V to the upper plate and + 300 V to the lower plate of the electrostatic sector. There is also provision for a small correcting voltage. The voltages are stable to ± 0.25 V and focusing has allways been obtained with the difference between the absolute values of the potentials in the plates lower than this. The ± 300 V can be scanned simultaneously, changing the voltage in both plates by the same amount but in opposite directions. The range of the scan can be varied from zero (fixed voltage) to three hundred volts. When convenient this scan is made automatically.

Both the ion accelerating voltage (~ 2 kV) and the voltages of the plates of the electrostatic sector are measured with a Solartron digital voltmeter which has a precision of ± 0.25 V in all its ranges up to 1000 V. A shunt is used to measure the 2000 V. Usually only the voltage of one of the plates is measured.

The signals from the two collectors are recorded either upon a Tektronix storage oscilloscope or a Watanabe multirecorder.

4 — APPLICATIONS

So far the work done with the instrument has been intended mainly to check its performance.

The resolution in energy is of the order of 1 in 2000 volts. It is limited mainly by the energy spread in the ion beam and may be improved by redesigning the source, modifying the slits or both.

This resolution permits the detection, for peak 14 of Nitrogen, of two groups of ions with respectively 1 eV and 3.5 eV of excess kinetic energy superimposed on a group of ions with a Gaussian distribution of energy. These ions have been previously detected (37-39). The group of ions with thermal energy only corresponds to the decomposition (39):

$$N_2^+ \ (D\ ^2\Pi_g) \rightarrow N(^4S^o) + N^+(^3P)$$

From the potential energy curves, and considering the translational energy of the ions, the ion with 1 eV was assigned to the process (39):

$$N_2^+(C^2\Sigma_u^+) \rightarrow N(^2D^o) + N^+(^3P)$$

while the ion with 3.5 eV was attributed to the coulombic repulsion of the two N^+ ions resulting from the decomposition of N_2^{2+} in a low lying state (40). After setting the mass spectrometer to detect an ion of a predetermined mass to charge ratio, lowering the potential difference of the plates of the electrostatic sector, all metastable transitions, ocurring in the field free region between the beam monitor and the electrostatic sector, are easily observed. This technique called direct analysis of daughter ions (DADI) (24, 25) permitted the detection of the metastable transition of N_2^+ giving N^+ (41, 42) and of all the metastable transitions of methane (43, 44) and methanol (45, 46) reported in the literature.

A further application consists in the determination of the kinetic energy released in the metastable transition by measuring the width of the corresponding peak (20, 21). For this geometry (47) and for the fields used (2000 volts in the accelerating field and $\pm$ 300 volts in the electrostatic sector plates for the stable ions) the peak width is given by

$$d(\text{volts}) = 26.83 \sqrt{\frac{m_2(m_1 - m_2)}{m_1}} \sqrt{T}$$

where m_1 is the mass of the metastable ion, m_2 the mass of the resulting fragment ion and T is the kinetic energy released. As can be seen the energy released in the center of mass of the ion is greatly amplified in this system of measurement. However due to the loss of sensitivity of the «channeltron» no quantitative results have been obtained yet.

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RESUMO

Um modelo antigo de espectrómetro de massa de focagem simples foi transformado num Espectrómetro de Massa com Análise da Energia Cinética dos Iões acoplando um sector electrostático a seguir ao sector magnético. São dados detalhes sobre a construção do sector electrostático e são estudadas as capacidades do novo instrumento.