AN ON-LINE MASS SPECTROMETER

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ABSTRACT

A mass spectrometer has been interfaced to a computer for rapid data acquisition and analysis. The spectrometer, a Nier-type instrument, with a sixty degree sector magnetic field and six inch radius of curvature, is set up for gas analysis. The computer is a PDP-9 manufactured by Digital Equipment of Canada, Limited. The system avoids the expense of conventional on-line mass spectrometers by replacing the digital-to-analog-to-digital signal processing system with one utilizing direct digital data acquisition. The system has been used to measure the ratio of mass 46 carbon dioxide to mass 44 carbon dioxide, the ratio of ^{202}Hg to ^{200}Hg and the ratio of ^{82}Kr to ^{86}Kr.

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INTRODUCTION

The events with which experimental physics is concerned are quantal events. This fact is no less true in mass spectroscopy than in nuclear physics, but the types of detection apparatus used in the two fields have for some time been different in kind.

The mass spectroscopist has taken advantage of statistics in his detection apparatus. Aware that he can construct his spectrometers so as to deal with orders of magnitude larger numbers of events than can the nuclear physicist, he has constructed detection equipment which, in general, acts as a digital to analog converter, producing voltage levels or currents which are proportional to the rate at which detectable events are occurring in his apparatus, or proportional to the total number of such events which have occurred. While such apparatus may not detect one event, it will be able to detect some lowest number of such events, if they occur close enough to each other in time that the integrating effect of the detection device will add them together to produce a detectable change from the null condition.

This approach vastly simplified data analysis, for now it was possible to measure mass differences or isotopic ratios simply by measuring peak positions or relative peak heights, either on a strip chart, or in a more recent development, with an Enhancetron, an electronic device which digitizes the analog signal and

stores it, very much in the manner of a multi-channel analyzer in the scale mode.

The advent of the electronic computer has induced mass spectroscopists, as it has most other physicists, to attempt to utilize the speed and accuracy of computers in the analysis of the output data of a mass spectrometer. By somehow feeding the analog output signal of the spectrometer to the computer, it was expected that properly written programs should be able to detect peak centres, separations, and relative peak heights, more reliably and with less bias than could a human operator, and thus could produce, in a very short time, a complete analysis of the data, including statistical computations which would require many hours of human labour to duplicate. The advantages in terms of saving man-hours were obvious, and many mass spectroscopists were quick to take advantage of them.

The most common detection devices which are utilized in mass spectroscopy are the vibrating reed electrometer, and the combination of electron multiplier and electrometer. Both of these devices produce output voltage levels which are analogs of the rate of detection of ions. For chart recording these levels are fed directly to the recorder. In the most common method of making this information useful to a computer, these levels are fed into a digital voltmeter, the output of which is coded and punched onto tape which can then be fed either directly or indirectly into the computer. Alternatively, it is possible to code the digital voltmeter output for

direct access to the computer. These two processes are known as off-line and on-line applications respectively.

But, as has been pointed out in the opening paragraph, the basic output of the mass spectrometer is inherently digital. It is not necessary, therefore, to utilize a three-step process in which digital information is converted to analog which is then reconverted to digital and fed into the computer. Instead, it should be possible, indeed, it may even be preferable, to utilize directly the digital output of the spectrometer, bypassing the two conversion steps, because of the inevitable approximations involved in digital to analog conversion, e.g. the statistical fluctuation in electron multiplier output for single-mass, monoenergetic ions, and the further approximations involved in the analog to digital conversion. If these approximations could be avoided, the quality of information should be substantially improved.

The purchase of the PDP-9 computer from Digital Equipment of Canada, Limited, by the University of Manitoba, Department of Physics, has made it possible to attempt to put a mass spectrometer on-line, and to utilize digital techniques in data-acquisition. At the suggestion of Dr. B. G. Hogg, I have constructed the necessary electronics hardware to interface the spectrometer to the computer, and have written a program for the acquisition, analysis and subsequent output of the data. This will describe the system, and some of the results achieved with it.

II GENERAL THEORY

A charged particle, moving in a magnetic field, is subject to a force which is dependent on the sign and magnitude of its electric charge, its velocity and on the strength of the magnetic field. Mathematically, it is expressed as $\underline{F} = q\ \underline{v} \times \underline{B}$ 1)

where $\underline{F}$ is the force vector, q the charge, $\underline{v}$ the vector velocity, and $\underline{B}$ the magnetic field strength. The vector product of the velocity and the field strength is denoted by X.

If we impose constraints upon the motion of the particle, and upon the shape of the field, we can specify a particular direction for the action of the force. We therefore specify that the particle enter the magnetic field at right angles to both the field direction, and to its boundaries, which we assume to be discontinuous. We further impose the condition that the field be uniform. Under these contitions, the vector product has the magnitude of the algebraic product and a direction perpendicular to both the velocity and the field direction. Since the force acts at right angles to the instantaneous velocity, it does not affect that velocity, but provides a component of momentum at right angles to it. This force is therefore a central force, the magnitude of which is given by elementary mechanics as mv^2/r, where m is the particle mass, and r is the radius of curvature of its circular

path. Thus,

$$qvB = mv^2/r \qquad 2)$$

or,

$$r = mv/qB \qquad 3)$$

and we have established a condition in which the path followed by a singly charged ion in a uniform magnetic field depends only on its momentum. The result of passing a beam of such ions of no particular mass or energy through a magnetic field in this manner would be a momentum spectrum. A doubly charged ion would act like one of half the momentum, a triply charged ion like one with a third of the momentum, and so on.

If we now specify that these ions are to be produced in a source and accelerated by falling through a potential drop, they will all have the same energy,

$$\tfrac{1}{2}mv^2 = qV \qquad 4)$$

where V is the potential drop. Solving for v in equation 3) and substituting, we have:

$$\tfrac{1}{2}m(qBr/m)^2 = qV \qquad 5(a)$$

or,

$$\tfrac{1}{2}qB^2r^2/m = V \qquad 5(b)$$

or,

$$m/q = B^2r^2/2V \qquad 5(c)$$

or,

$$r = (2Vm/q)^{\frac{1}{2}}/B \qquad 5(d)$$

Now, for singly charged ions of identical energy, moving in a uniform magnetic field, the radius of curvature of the circular motion they follow will depend only on the ionic mass, and the momentum spectrum will have become a mass spectrum, when the constraint of mono-energetic ions is applied. This, then is the basic theory of a mass spectrometer.

As well as the dispersion effect discussed above, magnetic fields possess focussing properties which enable them to provide momentum and mass spectra of divergent beams of ions whereas the discussion above is restricted to single ions or beams with strictly identical paths for all ions. The refocussing property of magnetic fields was first used for mass analysis by Dempster in 1918. It was not until 1934, however, that a general analysis of this property was published by Herzog. He was able to show that the semicircular magnetic field of Dempster was a special case of the general sector magnetic field, the refocussing properties of which had recently been demonstrated by Barber and Stephens.

He considered the problem of a divergent beam of mono-energetic ions impinging on a homogeneous magnetic field with sharply defined boundaries. The beam is produced at point P_1. Herzog found the condition for first-order refocussing of this beam at a point P_2 to be:

$$r \sin\phi + L_1 \frac{\cos(\phi-\varepsilon_1)}{\cos\varepsilon_1} + L_2\left[\frac{\cos(\phi-\varepsilon_2)}{\cos\varepsilon_2} - L_1\frac{\sin(\phi-\varepsilon_1-\varepsilon_2)}{r\cos\varepsilon_1\cos\varepsilon_2}\right] = 0 \qquad 6)$$

where r is the radius of curvature of the beam in the magnetic field, L_1 the distance from P_1 to the point where the central ion ray strikes the boundary of the magnetic field, L_2 the distance from the exit point of the central ion ray on the boundary of the magnetic field to the focussing point P_2, ϕ the angle of deviation of the central ion ray in the magnetic field, ε_1 the angle

which the central ion ray makes with the field boundary at the point of incidence, and ξ_2 the angle which the central ion ray makes with the field boundary at the point of emergence.

If we restrict ourselves to the case where the beam strikes the boundary at right angles, $(\xi_1 = \xi_2 = 0)$, and in which the distances L_1 and L_2 are equal, i.e. the case of the symmetric spectrometer, the condition for refocussing at P_2 to first order may be reduced to

$$L = r(\cot\phi + \operatorname{cosec}\phi) \qquad 7)$$

where $L = L_1 = L_2$. This is the mathematical statement of Barber's Rule, which specifies that the object point, image point, and centre of curvature of the ion orbit, lie on a straight line. This rule applies to asymmetric as well as symmetric spectrometers.

This refocussing is, however, not perfect. From simple geometric considerations, one can see that a diverging beam entering a uniform magnetic field will suffer a spherical aberration of $2r(1 - \cos\alpha)$ resulting from the non-uniqueness of the centre of curvature for different ions in the beam, where α is the half-angle of divergence. Where α is small, the focussing error may be expressed as $r\alpha^2$ to first order in α. This is the formula for a symmetric instrument, which is derived from a more general formula deduced by Stephens for the total spread S, measured normal to the central ray at the position of

best refocussing, which is given by

$$S = (r\alpha^2/2)(((l_2^2 + r^2)/(l_1^2 + r^2))^{\frac{1}{2}} + (l_1^2 + r^2)/(l_2^2 + r^2)) \quad (8)$$

Examination of the reduced first-order focussing condition reveals that it demands that the source point, the apex of the magnetic field, and the image point must lie on a straight line. Deviations from this condition result in further aberrations. Aberrations are also produced by the non-discontinuity of the field boundaries, field inhomogeneities, space charge effects (negligible in this instrument because of the low currents at which it is used), and deviation from the condition of monoenergetic ions.

The resolution of a mass spectrometer will naturally depend on the extent to which such aberrations can be avoided or corrected for. An expression for the resolution of the instrument may be derived as follows. Two beams of ions, one having ions of mass M, and the other having ions of mass $M + dM$, will be completely distinguished only when the dispersion is equal to or greater than the sum of the collector slit width plus the total image spread. If the source slit width is given by S_1, let the collector slit width be given by S_2. Since most of the aberrations are functions of the radius r, we will denote the image widening by $A(r)$, and the total image width will then be given by $S_1 + A(r)$. The resolution is then found from

$$r(dM)/M = S_1 + A(r) + S_2$$

The theoretical limit to the resolving power in the case of no aberrations is then:

$$M/dM = r/(S_1 + S_2)$$

This limit has a value of approximately 1000 for a 6" radius instrument. The resolving power is usually measured by measuring the separation, at the base line, of the two peaks. It is often convenient, however, to make this measurement at the half-maximum of the peak, where the actual location of the base line is in doubt. This second method has been the one used for this instrument, and naturally gives a somewhat larger figure for the resolving power than does the other.

The limiting value of resolution stated above corresponds to 0.003" slits which is the practical limit of adjustment for the source slits in this instrument. For a 6" radius of curvature, and an α of 0.02 radians corresponding to such slits, $r\alpha^2$ is 0.003", representing a broadening of the beam by an amount equal to its width. In the face of such large first order effects, higher order aberrations are unimportant, and all together probably do not contribute more than an additional 0.001" of broadening. These are minimum values, for optimum slit widths, and the first order aberrations will increase slightly faster than linearly with the slit width.

III THE SPECTROMETER

The spectrometer is a Nier-type unit, which was constructed partly in Winnipeg and partly in Dr. Nier's laboratory in Minneapolis. It has a six inch radius of curvature and a sixty degree sector magnetic field. The source is of the type developed by Nier for gas analysis. The sample is admitted to the source as a gas and passes through the ionization region where it is bombarded by electrons boiled off a filament carrying a current of 4.5 A. This current is adjustable and is supplied by a 6 V. lead-acid battery. These electrons have an energy in the neighbourhood of 135 V. in the ionization region. This is obtained by the use of three 45 V. dry cells placed in series, with the positive terminal of the combination connected to the shield which provides the positive high tension for ion acceleration. The negative terminal is connected to the positive terminal of the 6 V. battery. Thus the filament battery and filament are held at -135 V. with respect to the shield. The electron trap, a small metal box placed across the ionization region from the filament, and isolated from the shield, is held 45 V. positive with respect to the shield by means of another battery and collects electrons which make their way across the source region. The ions are repelled by the shield, usually held at 2100 V. above ground potential. The shield is connected to ground by a series combination of ten 270 K. ohm resistors and a 11 Megohm resistor, which form a voltage divider. The ion beam passes through a series of collimating slits, into the

beam pipe and towards the magnetic field. One such slit consists of two semi-circular plates which tap into the voltage divider network which supports the shield voltage. They can be adjusted with respect to ground by means of a double stepping switch whose two contacts always span two 270 K. ohm resistors. This means that the voltage across the two contacts is 85 V. The lower contact can move from 1675 V. to 2015 V., and the upper contact is always 85 V. higher, when the shield is at 2100 V. The two plates are further isolated from each other (see Fig. 3, contacts J_1 and J_2.) by means of a pair of 1 Megohm potentiometers which are cross connected and then attached to the terminals of the double stepping switch. This arrangement permits the mean voltage of the plates to be varied in 85 V. steps from approximately 1720 V. to nearly 2070 V. Further, the relative voltage between the two halves of the slit can be adjusted from -85 V. to 85 V. This provides a means for centering of the inn beam.

To provide the maximum possible resolution, it is necessary that the ions be formed in as small a volume as possible, necessitating some focussing of the bombarding electrons. To this end, a pair of small permanent magnets is placed outside the beam pipe on a small U-shaped iron stand. The air gap between the pole faces of the two magnets is filled by the beam tube when the magnets are in position. The direction of the magnetic field produced by this pair of magnets is directed parallel to the filament-electron trap line. Thus, any electrons which have a component of momentum which does not lie on this line

will experience a force tending to bend them back towards the line. The off-axis motion will then be converted into a circular motion, and the electrons will move in a helix through the sample gas. Thus, an electron which has a component of momentum corresponding to one-third of its kinetic energy perpendicular to the axis will move in a helix of radius approximately 0.4 cm., centered on the axis. Without the magnet it would strike the far side of the shield box about 1 cm. from the axis. Clearly this magnet can provide a great improvement in the focusing of the electron beam. If the ions are produced as nearly as possible in the same region, the effects of field gradients in the source can be minimized, with consequent improvements in the energy distribution of the ion beam. In practice it has been found that, the best resolution attainable when no particular attention was paid to source magnet position was on the order of 250. When the spectrometer was focussed on the ^{40}A peak, and the source magnet adjusted to provide for maximum beam it was found that it was possible to increase the beam intensity by nearly two orders of magnitude, and the resolution by a factor of four. It is not, however, necessary for the trap current to be a maximum for these optimal conditions.

The magnet was constructed in Winnipeg by the Dominion Bridge Co., Ltd., Winnipeg. The pole faces are made of mild steel, as the flux densities are relatively

low, on the order of 3 kG. for focussing of mass 45. The dimensions of the pole faces and yoke are shown in Fig. 2.

The beam pipe was constructed in Minneapolis and is made from 2" O.D. stainless steel pipe. The portion which passes between the pole faces has been pressed to form a pipe of mearly rectangular cross-section. The source is mounted on a flange which has a short length of this pipe on its upstream end. This pipe is sealed with a glass plug and the electrical feedthroughs to the source are made through this glass. The gas inlet to the source is through a hole drilled radially into the flange itself. Inside the flange a glass tube takes the gas from a small pipe protruding from this hole, to the ionization region. There are four other distinct components in the beam pipe. First, the curved flattened portion which passes between the pole faces of the magnet. Secondly, a 2 and 3/16 inch long spacer which has been included in the design so that the spectrometer may be adapted for double focussing operation by the addition of an electrostatic analyzer, and by the removal of this spacer. Thirdly, the detector slit and detector housing assenbly, and fourthly, the detector itself. The detector slit is adjustable by means of a spring-loaded push rod, driven by a second push rod, which itself moves in response to a motion of the threaded knob in which it is seated. The two push rods are separated by an aluminum diaphragm for vacuum sealing. The detector is mounted on a blank flange, and

all connections to the detector are made through insulated feedthroughs on the blank face of the flange. The detector is a ten-stage DuMont SPM. It is customarily operated at -3400 V. at the target dynode. A suppressor grid prevents secondary emission electrons released at the target from proceeding back up the beam tube towards the source. It normally provides a gain of the order of 10^5.

The magnet mount is provided with wheels and can be rolled along a horizontal line at right angles to the source slit-detector slit line. The entire beam tube is thus exposed. An asbestos box has been constructed which encloses the entire beam tube with the exception of the detector, and which has a length of heating element suspended from its inner surface, which permits baking of the vacuum system at temperatures of the order of 200 degrees C. Unfortunately, the present arrangement does not permit proper baking of the inlet system.

Vacuum is maintained by three pumps. Two of these are mechanical Duo-Seal Vacuum Pumps, capable of pumping at 33.4 litres/min. @ 300 r.p.m. The third is a VacIon pump by Varian Associates, which is rated at 8 litres/sec. One mechanical pump operates on the inlet system, and is in continuous operation. The other mechanical pump acts as a roughing pump, pumping on the beam tube to bring its pressure down to the point where the VacIon pump, which can be sealed off by a valve, is capable of