A 180° Mass Spectrometer Tube and its

Performance

A Thesis

Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science in the Department of Physics of McMaster University

by

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September, 1948.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance and encouragement of Dr. H. G. Thode under whose direction this work has been done. Thanks is also due to Dr. F. P. Lossing, Mr. R. B. Shields, Mr. T. Bryden and Mr. J. Macnamara for their assistance.

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INTRODUCTION

There is a great need for high precision mass spectrometers for the purpose of making accurate determinations of small variations in isotopic abundances that occur due to differences in thermodynamic properties of isotopes. With this in mind, a new 180° mass spectrometer tube has been designed and constructed, and techniques of measuring isotopic abundances investigated. This thesis describes the tube, its operation, and the results obtained.

The concept of isotopes first evolved about 1913, and since then it has been a matter of great interest to determine the isotopic content of the elements, the isotopic weights, and the relative abundances. The mass spectrometer is the most satisfactory instrument for determining relative abundances, which with the isotopic mass values from spectrographic measurements, are used to establish a set of physical atomic weights based on the defined atomic weight of 0^{16} as 16. The chemical atomic weight scale previously used was based on the assigned atomic weight of 16 for the mixture of the oxygen isotopes, and since the relative abundance of these isotopes may vary from sample to sample, the chemical scale is not reliable and should be abandoned for all accurate work.

The applications of the mass spectrometer have increased with the development of research involving isotopes in the fields of physics, chemistry, biology, and geology. The expansion of nuclear

physics and chemistry has made mecessary the identification of the fission product isotopes, which can be done quickly and precisely with very small samples in a mass spectrometer. The same type of analysis is necessary in work with artificially-produced radioactive isotopes to determine half-lives and concentrations for tracer work. Fission product Kr and Xe has already been done by Thode and Graham (1), and the half-life of Kr⁸⁵ determined from the isotopic abundance data.

The interest in early isotopic work lay in the identification of isotopes and the determination of their relative abundances which was considered to be more or less fixed. However recent work by a number of investigators has shown that variations occur in the isotopic content of naturally occurring elements.

Nier and Gulbransen (2) demonstrated variations in the isotopic content of carbon. Murphy and Nier (3) showed that variations occur in the isotopic content of oxygen in nature. Recent work by Thode, Menamara, Lossing and Collins, (4) with samples of boron from natural sources showed variations of the order of 3% in the relative abundance of the boron isotopes. Further work (5) on variations in the relative abundance of the sulphur isotopes in nature showed differences of 3% in the relative abundance of S³⁴.

Urey and Grieff (6) showed thermodynamic considerations that the isotopes of the light elements differ in chemical properties, and that these differences result in some fractionation of the isotopes in natural processes. Isotopic exchange constants for the isotopes of

carbon, nitrogen, oxygen, and sulphur, have been calculated by the methods of statistical mechanics and the results checked by experiment.

The work of Urey and Grieff (6) demonstrates clearly that some fractionation of the isotopes of the light elements may be expected in nature, and it has been shown experimentally that variations in isotoppic abundances occur in the case of the elements studied so far. Mass spectrometers on mign precision are needed for the accurate determination of small differences in isotopic ratios. Nier, Ney, and Inghram (7) have designed such an instrument for this purpose which makes use of the simultaneous collection principle. In this scheme two ion currents are collected simultaneously on separate collectors, amplified separately, and then one balanced against the other, first for one sample, and then for the other any deviation from the balance point is carefully measured, giving the difference in isotopic ratio between the two samples. This method is most elegant, as all factors which affect the two isotopes the same do not affect the ratio. Further, the isotopic ratio is obtained quickly, and in one step.

It is important for high precision that analyses be done as quickly as possible, thus minimizing time changes due to temperature variations in the source and drift in electronic units. One useful technique for speeding up analyses when two samples are being compared is the double sample line, where either sample may be introduced very quickly by a magnetic valve arrangement.

An alternative method was employed in this work to obtain high precision. Two samples to be compared were contained on the sample line

and could be introduced with a time lapse of about five minutes between samples. Ion currents were measured with a speedomax pen recorder (8), using a manual shunt selector system. 4

Early Mass Spectrometers

The mass spectrometers in use today have developed from the positive ray parabola work of Sir J. J. Thompson (9) who in 1913 reported a line corresponding to mass 22 which at that time could not be identified with any known gas. In 1919 Aston (10) obtained proof that the mass 22 observed by Thompson was actually an isotope of neon. Aston used his newly-contructed positive ray instrument which he called the mass spectrograph (Fig. 1) for his analysis.

In the succeeding years Aston analyzed a large number of elements, showing that most of them consisted of two or more isotopes. He calculated isotopic weights and obtained relative abundance values from his data. Many of his early values are still good today, to the precision given.

For most relative, abundance measurements it is more satisfactory to use a modification of the mass spectrograph, called the mass spectrometer, which was first pioneered by Dempster (11) shortly after Aston built his first instrument. Dempster's mass spectrometer is shown in a schematic diagram (Fig. 2), illustrating the 180 degree focussing method used by Classes (12) in determining e m for electrons. Positive ions were produced by heating filaments coated with salts of the elements to be examined, or by volatization of atoms from a pure metal or compound; the vaporized atoms were ionized by electron bombardment from a secondary heated filament. The positive ions were then accelerated by an electric field between the source and the entrance slit into the analyzer tube where they were bent in a semicircle by a magnetic field perpendicular to the plane of the tube, and focussed on the exit slit according to the focussing method employed by Classen. The ions were collected on a plate, and the current measured by an electroscope. Dempster used a constant magnetic field, and focussed ions of different mass on the collector slit by varying the accelerating electric field.

The first major change in design was Bleakney's (13) 180 degree instrument using a uniform magnetic field produced by a solenoid. The magnetic field was not shielded out of the source, as in previous instruments, but on the contrary was used to line up a beam of electrons moving parallel to the magnetic field; the controlled electron beam produced the ions to be analyzed from gas or vapour introduced into the source. A weak electric field served to move the ions through the first slit into the strong electric field region where the acceleration took place. The electric field was varied to scan across a mass range. The entire assembly was enclosed in a glass envelope which could be evacuated and baked to remove residual gasses. Bleakney's instrument has served as a model for most of the mass spectrometers constructed since 1932.

In 1937 automatic recording was used by P. T. Smith, Lozier, L. G. Smith and Bloakney (14), enabling them to make faster and more precise analyses.



Schematic diagram of Aston's first mass spectrograph.



Schematic diagram of Dempster's mass spectrometer. Dimensions are those given by Dempster in a paper published in Phys. Rev. 11, 316 (1918).



. Spectrometer used by Tate, Smith, and Nier. [Copied from Nier's paper, Phys. Rev. 50, 1041 (1936).]

Tate and P. T. Smith (15) and later Nier (16) constructed a mass spectrometer which was really only a short section of the Bleakney instrument, but with a large radius of curvature for high mass work, and which could be placed between the pole faces of an electromagnet so that stronger magnetic fields could be easily obtained. The instrument design is shown schematically in Fig. 3. The types of mass spectrometers not already mentioned are of secondary interest in this paper, and so will be tabulated bery briefly here. 7.

The magnetic lens type, designed primarily for the collection of finite amounts of pure isotopes, was first reported in 1934 by Smythe, Rumbaugh and West. (17).

The crossed field type, employing the well-known principle of crossed electric and magnetic fields, which permit only the ions of one isotope to pass through undeflected, was reported by Oliphant, Shire and Crowther (18) in 1934. This instrument is useful for isotope mass determination, not for abundance work.

The sector type of mass spectrometer, which employs the principle that a diverging beam of charged particles entering and leaving a magnetic field normal to the edges of the pole faces, is refocussed on the line extended from the source through the center of curvature of the charged particles in the magnetic field. Fig. 4 illustrates the principle, and shows the 180 degree spectrometer as a particular case. Nier (19) in 1940 reported the first sector-type mass spectrometer, and because of the relative low cost of these instruments, they are used extensively at the present time.



TUBE CONSTRUCTION

The new mass spectrometer tube which has been constructed, shown schematically in Fig. 5, replaces the one reported by Thode, Graham, and Ziegler (20). The electronic units used were reported previously, (21) by Graham, Harkness, and Thode, with the exception of the magnet current stabilizer which was described by Shields (22).

The old tube (20) and the new one differ in several respects. The source and collector are the same, but in the new tube they are attached directly to a stainless steel analyser tube, by carefully machined fittings. The alignment may be done very accurately, since it is completed before installing in the glass envelope which serves only as a vacuum chamber and no part of the tube construction depends on glass. In the old tube the source and collector assemblies were fitted to glass collars inside the envelope, which made alignment very difficult, and depended on the rigidity of the glass to maintain the position of the assemblies. The large uniformly shielded ion path is an improvement over the narrow path in the old tube which was shielded by an irregular stovepipe spiral of Nichrome V strips. The source plates have a tilt of 1° 30' with respect to the 180° line, and a shutter has been introduced at the 90° point to determine the position and intensity of the ion beam. The shutter is adjustable under vacuum by means of the assembly shown in Fig. 7. THEORY OF OPERATION

The operation of the tube shown in Fig. 5 is as follows: The gas to be analysed enters the source #8 which floats at 1500 volts positive, and the ions are formed in the electron beam #6 which is emitted from a heated filament, accelerated, and collimated by two



slits as shown; the magnetic field perpendicular to the plane of the tube and parallel to the electron beam, tends to keep the electrons lined up. The positive ions formed by electron bombardment of the gas molecules in the electron beam are repelled by a weak electric field of 1 volt/cm and some of them pass through slit #5. On passing through slit #5 the ions are accelerated by a strong electric field of 3000 volts/cm throught slit #4 into the analyser tube, where they are bent through 180° according to their e/m value.

If m is the mass of a positive ion produced in the source, e the charge carried by the ion, and V the accelerating voltage, we have

 $Ve = \frac{1}{2}mv^2 \qquad v--velocity$ The deflection in the magnetic field is given by the equation $\frac{mv^2}{R} \qquad R--radius \text{ of curvature}$ E--magnetic field strength

Combining these two equations, we obtain the equation for the ion path,

Hence for any given values of V and H, ions with the same charge but different masses will have different radii of curvature, so that the ions of only one isotope will arrive at the exit slit.

The ions passing through the exit slit of the analyser tube strike the faraday cup #12 giving up their charge, which is amplified by a linear feedback D. C. amplifier, and appears on the chart of a Leeds and Northrup recorder. By changing either the accelerating voltage or the magnet current in a continuous fashion, ions of different isotopic masses are focussed on the exit slit, and a spectrogram



recorded on chart paper.

THEORY OF DESIGN

The geometrical focussing in a 180° mass spectrometer involves the motion of charged particles in a magnetic field, and is similar to that used by Classen (12) in determining the e/m value for electrons. This focussing is dependent on the fact that charged particles with the same mass charge, and velocity, describe circles with the same radius of curvature in a uniform magnetic field. When these charged particles are collimated by slits to form a beam with a small angle of dispersion, then bent through 180°, they focus sharply at a point on a line joining the entrance slit into the magnetic field and the center of curvature of the path. These conditions must be satisfied in a mass spectrometer. In the design of the new tube two focussing problems arose.

The first was concerned with the angle of dispersion of the ion beam as it left the entrance slit into the analyser tube. To obtain good focussing with high ion currents, the dispersion angle must be small. By using narrower slits in the source, the dispersion angle may be made smaller, but the ion current is reduced. In an attempt to obtain sharp focussing without reducing the ion current excessively, a new focus goint was selected by placing the exit slit from the analyger tube at the 178^{10}_{2} point instead of the 180° , and introducing a shutter to cut off part of the ion beam. This scheme is shown in Fig.6. The shutter was adjustable while the tube was in operation.

The second problem was concerned with having the ion beam leave the entrance slit into the analyser tube normal to the 180° line jointhe the entrance slit and the center of curvature of the ion path.



FIG. 7

Since the ions in the source are accelerated in a magnetic field, a certain amount of bending will occur, and the ion beam will not leave the source normal to the last plate which contains the entrance slit into the analyser tube. By tilting the source the direction of the beam may be made normal to the 180[°] line, thus satisfying the focusing conditions. To obtain the numerical value of the tilt necessary, the equation of the ion path in the source must be calculated.

A schematic illustration of the ion source is shown in Fig. 9. The path of the ions in a mass spectrometer source of the type shown in Fig. 9 has been discussed fully by Jordan and Coggeshall (23) and by Coggeshall (24). In our case because of the very weak field in the ionization region, 1 volt/cm, the ions may be considered as having zero velocity at the slit in plate A, so that the equation of the ion path between plates A and B may be calculated directly.



The force equations for the motion of a charged particle in electric and magnetic fields may be set up at once.

In an electric field, Ee = ma E - electric field strength $= \frac{d^2x}{dt^2}$ m - mass a - acceleration

integrating, $x = \text{Eet}^2$ 2π

In a magnetic field, Hev = ma

$$=$$
 m $\frac{d^2y}{dt^2}$

Assuming dx/dt much greater than dy/dt

$$r = \frac{dx}{dt}$$

On integrating, after substituting for dx/dt, we have

$$y = \frac{\text{He}^2\text{Et}^3}{6m^2}$$

On eliminating t we have

$$y^2 = 2H^2 ex^3$$

 g_{mE}

And since the mass spectrometer equation $e/m = \frac{2V}{H^2R^2}$ holds in

this region, we may substitute for e

$$y^2 = \frac{4Dx^3}{9R^2} \quad (1) \quad \nabla$$

V - accelerating voltage
R - radius of tube

since
$$\frac{\mathbf{v}}{\mathbf{D}} = \frac{\mathbf{E}}{\mathbf{D}}$$

From this equation, (1), the horizontal displacement y may be found, which is the amount by which the slit in plate B must be

H - magnetic field strength v - velocity displaced with respect to the slit in plate A. Also the angle 0 which represents the amount of tilt of the source with respect to the 180° line that is necessary so that the ion beam will leave the source normal to the 180° line, may be found from the same equation. Since the equation (1) is general for any source with a weak electric field in the ionization region, a useful table of data has been included in Table I.

D	y(x10 ⁻³ cm.)	0		
0.3 cm.	4.0	1°8* 46'		
0.4	7.0	1°30* 1°		
0.5	11.0	1055 10 16'		
0.6	16.0	2°18, 1° 30'		
0.7	21.8	2°40 1° 47'		
0.8	28.4	3°4° 2° 2'		
1.0	44.5	3°49, 20 33'		

D = plate separation

y = displacement

2%

0 = deviation from normal

TABLE 1

EXPERIMENTAL

OPERATION

As mentioned in the section on tube construction, a shutter was installed at the 90° point in the mass spectrometer analyser tube to determine the position and intensity distribution of the ion beam. By making spectrograms with the shutter at different positions, it was found that the center of the ion beam was about 4 mm. below the geometric center of the tube, as shown in Fig. 8. A simple calculation shows that the ion beam was really following a 180° path, and not 1781° as had been expected.

A series of spectrograms with different shutter positions to determine the effect on peak shapes of cutting off part of the ion beam, showed a slightly sharper focusing on one side of the peaks, but made the peak tops sloping instead of flat. This could be expected since the shutter position was fixed while the ion beam moved during scanning, and since the focused ion beam at the collector was narrower than the width of the exit slit from the analyser tube, it was evident that during scanning the total ion beam was moving across the exit slit, resulting in sloping peak tops.

Since flat topped peaks are highly desirable, the shutter was completely removed from the analyser tube, even though the tube was not designed to give best focusing under these conditions. However, the focusing obtained was quite satisfactory. (See Fig. 11) This result is in agreement with the deduction made above, that for some reason the ions are following a 180° path even though the

source is not tilted 2018' as determined from Table I for D = 0.6 cm. The explanation appears to be that the source is a weaker magnetic field than the analyser tube, so that the larger radius of curvature of the ion beam in the source compensates for the lack of tilt. Since the magnet pole face radius is 8" and the pole gap 2", it follows that the region of non-uniform magnetic field extends into the pole gap a distance of approximately 2", as is well known from experience. Hence if a 6"radius tube were placed symmetrically between the pole faces, the entire ion path would be in the nonuniform region. To avoid this complication, the tube was placed between the pole faces as shown in Fig. 10 (scale 1:2), so that all the ion path was in a uniform magnetic field, with the exception of the source and collector. Since the weaker magnetic field in the source bends the ion beam less than the stronger uniform field, no tilt of the source is necessary to make the ions follow a 180° path. This has been found to be true for the tube discussed in this thesis. The focusing is not affected by this arrangement when the pole gap is large, since the region of non-uniformity is not sharply defined and the ion beam at both the source and collector is narrow, the greatest spreading taking place in the 90° region which is in a uniform field.



CURRENT



RESOLUTION

The theoretical resolving power may be calculated as follows: For the 180° ion path, $\frac{e}{m} = \frac{2V}{H^2R^2}$ (1) e = charge m = mass W = accelerating voltage H = magnetic field strength R = radius of eurvature $\frac{e}{m} = \frac{2V}{H^2(R - \Delta R)^2}$ (2) $\frac{(1)}{(2)}$ ratio is $1 - \frac{\Delta m}{m} = 1 - \frac{2\Delta R}{R} - \frac{\Delta R^2}{R^2}$ $\frac{(\Delta R^2)}{R^2}$ is negligible) R^2

ightarrow R = width of entrance slit + width of exit slit 2

Substituting the numerical values, we have

i.e. 1 mass unit in 232 would be resolved theoretically. The actual resolution from spectrogram measurements is given by

The discrepancy between the theoretical and actual resolution could be easily accounted for by the slit width measurements, which were not accurate to three figures.

SPECTROGRAMS

Three spectrograms have been included to illustrate the mass spectrometer performance in the different mass ranges. The first is of CO₂ with a 6% C¹⁴ content, resulting in a high mass 46 peak. This spectrogram is shown in Fig. 11. A manual shunt system was used to vary the input signal to the recorder, so that effectively the sensitivity of the recorder was changed according to the magnitude of the ion current. The shunts were arranged so that no ion current would produce less than 1/3 scale deflection on the recorder. By the use of the manual switching arrangement, the desired sensitivity for the next ion current to be recorded was selected at a point midway between the peaks. This technique permitted the recorder pen to draw the zero signal base line for the sensitivity used in recording each ion current; the peak height could then be measured directly without any extrapolation to determine the base line, as was the case with the automatic shunt selector reported by Lossing, Shields, and Thode (8). Fig. 11 illustrates the use of the shunt selector in the recording of ion currents of different orders of magnitude. The wellresolved, straight-sided peaks with flat tops, indicate good focusing. There is very little scattering, as the sharp base of mass 44 shows.

Figs. 12, 13, show spectrograms of normal krypton and xenon, which have been included to demonstrate the resolution obtained in high mass ranges.



MASS

NUMBER





PRECISION ABUNDANCE MEASUREMENTS

To determine accurately small variations in the abundance of isotopes that occur in nature, it is necessary to compare each sample with a standard. Although mass spectrometer abundance ratios vary by \pm 0.5% over a period of time, a relative precision of \pm 0.1% has been obtained by comparing the samples to a standard. In the analysis of a series of samples, one sample was arbitrarily selected as a standard, and the analysis was carried out by comparing each sample to the standard. The procedure was to analyse the standard, the sample, and the standard again. If the two standard analyses checked, then a comparison between the sample and the standard was established within the limits of the precision obtained.

A typical set of abundance data has been included in Table 2 to illustrate the method of measurement and the determination of precision. The sulphur was analysed as SO_2 , the ratio of mass 64/mass 66 being determined. The contribution of $S^{33}O^{16}O^{17}$ is negligible. Hence any variation in the 64/66 ratio from sample to sample will be due to variations in the S^{34} content.

Since the pressure in the sample line of a mass spectrometer slowly decreases with time, the ion currents will also decrease in direct proportion to the change in pressure. Hence one single spectrogram may not be taken as a true measure of the relative isotopic abundance. In order to compensate for this gradual decrease in ion current, each ratio appearing in Table 2 was determined from the average of two spectrograms, Set #1 made by scanning up in mass, and Set #2 scanning down in mass. This technique averages out any decrease of the ion current with time.

TAHLE 2.

Mass Shunt	Peak Height		x	Ratio	Deviation		
	<u>Set # 1</u>	<u>Set ∦ 2</u>	Average	Factors			
64	5	13.06	13.00	13.03	1320.7	2044	5.C.1
66	2	21.41	21,40	21,41	64.508	20.47	0.02
64	5	13.00	13.02	13,01	1318.7		
66	2	21,40	21,43	21.42	64.538	20.43	0.02
64	5	13.00	12.95	12.98	1315.7		
66	2	21.35	21.36	21.36	64.358	20.44	0.01
64	5	12.98	12.98	12.98	1315.7	e ognis :	
66	2	21.30	21.40	21.35	64.328	20.45	0.00
64	5	12.95	12.97	12.96	1313.6		
66	2	21.32	21.35	21.34	64.297	20.43	0.02
64	5	13.00	13.01	13.01	1318.7		
66	2	21.36	21.38	21.37	64.388	20.48	2 0.03

AVERAGE RATIO 20.45 ± 0.007

The result of the data shown in Table 2 was determined by taking the average or mean of the six independent values of the ratio. The reliability or precision of the mean was taken as the deviation of the mean, A. D. The probable error of the mean, not shown in Table 2, is 0.0076. It should be stressed here that the precision given is the internal precision of a set of data with no reference to external or residual errors which may be quite large.

In a mass spectrometer, the isotopic abundance value obtained for a sample may change from day to day by as much as \pm 0.5%. However, two analyses of a sample obtained with a time lapse of 45 minutes between them will differ by only \pm 0.1%. Since the relative isotopic abundance of a sample is only as precise as the reproducability of two standard analyses, the limiting precision depends on this variation.

The causes of changes in the isotopic abundance value of a sample are due to temperature variations in the source, changes in the characteristics and position of the filament, in the constants of the D. C. amplifier, etc., and, since these changes are a function of time, they may be minimized by reducing the analysis time.

DISCUSSION

DISCUSSION

The present technique used in the analysis of samples is to have the two samples to be compared contained on the sample line, so that either may be quickly introduced into the mass spectrometer. The first sample is analysed, the second, and then the first again. One hour is required for the above procedure. The possibility of installing a double sample line with magnetically operated valves has been considered as a means of changing quickly from one sample to another, and thus cutting down the time required for the comparison of two samples.to possibly 40 minutes. The shorter analysis time would minimize time changes in the mass spectrometer, especially since the gas flow in the source would be continuous.

At present, the filament which produces electrons for ionization of the gas molecules, is heated by rectified D.C. with a 40% A.C. component. Since the filament is in a strong magnetic field the A.C. component of the filament current gives rise to vibrations in the filament. These vibrations produce variations in the ionizing electron beam, and hence in the position and intensity of the ions formed. Since these ions are the ones that make up the ion beam, it is desirable to have the conditions under which they are formed as constant as possible. To correct this condition, a new emission control designed by Mr. R. B. Shields is being constructed to supply rectified D.C. with only a 3% A.C. component to the filament. The installation of this unit is expected to improve the stability of the instrument.

By means of these changes, it is hoped that the maximum precision obtainable will be improved considerably.

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