A THIRD PHASE IN THE DEVELOPMENT

OF A MASS SPECTROMETER

Ву

RICHARD D. BARRON Bachelor of Science Oklahoma Agricultural and Mechanical College Stillwater, Oklahoma

1948

Submitted to the Faculty of the Graduate School of the Oklahoma Agricultural and Mechanical College in Partial Fulfillment of the Requirements for the Degree of MASTER OF SCIENCE 1950

OKLAHOMA AGRICULTURAL & MECHANICAL COLLEGE LIBRARY JUL 31 1950

A THIRD PHASE IN THE DEVELOPMENT OF A MASS SPECTROMETER

RICHARD D. BARRON MASTER OF SCIENCE

1950

THESIS AND ABSTRACT APPROVED:

rbin S 20 lesis

Representa

Dean of the Graduate School

PREFACE

Recently Truman Franklin constructed a mass spectromotor of the Nior type for this department. Subsequently this instrument was assembled and made ready for operation by Wm. Lull and Edward O'Mealey. It had been the original plan to produce ions by electron bombardment of sample gases admitted to the instrument through a controlled leak Mr. Franklin had included in the design. This is standard practice, but the ion current produced by electron bombardment is small and difficult to detect. Also, the controlled leak is certain to increase the vacuum problems. Consequently, for testing and adjusting the instrument it was decided to produce ions by thermionic emission from coated filaments. As a result the writer's work was divided into two parts;

1. Determining suitable methods of preparing the filaments.

2. Utilization of these filaments in the mass spectrometer for prelimiary tests.

TABLE OF CONTENTS

| PART | I | |
|------|--|----|
| | Requirements Imposed by the Spectrometer | 1 |
| | Filament and Coating Materials | 5 |
| | Coating Techniques | 8 |
| | Test Equipment | 10 |
| | Test Methods | 13 |

PART II

| Prepa | arat | tion | oſ | the | Spectrometer | 16 |
|-------|------|-------|------|-------|--------------|----|
| Test | Equ | ijpme | ent. | | | 18 |
| Test | of | the | Spe | ectro | ometer | 20 |

| BIBLIOGRAPHY | 21 | 4 |
|--------------|----|---|
|--------------|----|---|

Requirements Imposed By The Spectrometer

A consideration of the mass spectrometer and its characteristics indicates certain requirements these filaments must satisfy. From the familiar equations,

Hev
$$= mv^2/r$$
, (1)

and

$$mv^2/2 = pd x e, \qquad (2)$$

we get

$$m = eH^2 r^2 / 2 \times 10^8 V gms.$$
 (3)

In this equation m is the mass of the ion, e its charge in electro-magnetic units, H the magnetic field strength, r the radius of arc described by the ion, V the accelerating potential, v the velocity of the ion, and pd the accelerating potential expressed in electro-magnetic units.

The mass of an ion is usually referred to in mass units; the mass unit being 1.66×10^{-24} gms. Then

 $m = eH^2 r^2 / 3.32 \times 10^{-16} V$ mass units. (4)

Consideration of the preceding equation shows the most accurate determination of mass will be made by adjusting the accelerating potential. Changes in the accelerating potential may have an effect upon the emission current, but it is probable that these will be small since field emission is negligible for the accelerating potentials used. In any case the emission current may be kept at a fixed value by controlling the filament temperature. The Nier mass spectrometer utilizes a V-shaped magnetic field. The apex of the V lies upon a line connecting the defining slits. The angle subtended by the field is such that the ion beam enters the field normal to it and at a distance of r cms from the apex. In the field the beam describes an arc with radius of r cms about the apex and leaves the field normal to it on the other side of the V. When these conditions are satisfied it is shown by Nier¹ that the resolution is,

$$S = A \alpha^2/2 \text{ cms},$$

where A is the distance from the source to the apex of the V, and \triangleleft one half the total angle filled by the ion beam. Since A is essentially a constant \triangleleft largely determines the resolution. Since \triangleleft will be determined by the width of the defining slits, and the geometry of the filament, it is desirable that the filament be as narrow as consistent with emission requirements in order that line source conditions may be closely approximated.

In the literature 2,3,4,5,6 all writers agree that ions

1 A. O. Nier, <u>Review of Scientific Instruments</u>, 11, 212 (1940)
2 J. P. Blewett and E. J. Jones, <u>The Physical Review</u>, 50, 464 (1936)
3 R. Hayden, <u>Physical Review</u>, 74, 650 (1948)
4 J. L. Hundley, <u>Physical Review</u>, 30, 864 (1927)
5 C. H. Kunsman, <u>Science</u>, 62, 269 (1925)
6 K. T. Bainbridge, <u>Journal of the Franklin Institute</u>, 212, 317 (1931)

produced by thermionic emission are singly ionized. Then equation h may be written,

m = k/V gms,

where

 $k = eH^2r^2/3.32 \times 10^{-16} = mV$ mass unit-volts. This equation indicates that k is a function of the magnetizing current. Then if the spectrometer is adjusted for an ion of known mass, the product of it's mass and the accelerating potential will equal k. So long as the magnetizing current is not changed k will remain constant, and V may be varied to determine other masses in this vicinity. By changing both V and the magnetizing current, so that the same current peak remains in focus, a wide range of values for k may be found with but one known mass. This suggests making a plot of k against the magnetizing current to get a convonient calibration curve for the magnet. Thus when any unknown ion is located a value of k corresponding to the magnetizing current being used can be found from the curve. Then by observing V and applying the equation,

m = k/V mass units,

the mass of the ion can be calculated.

The question arises as to the number of known ions required to plot a sufficient number of points for such a curve. A preliminary study of the problem suggests that three ions of approximately 5, 25, and 250 mass units will provide sufficient points for such a plot. For extremely accurate determinations of mass this method will not suffice. The slight variations in the magnetic field due to the hysteresis of the iron core renders methods based on current regulation⁷ inadequate for an absolute determination of H. This limitation would not exist if k were determined in terms of the flux as measured by a flux meter.

7 Hipple, Grove, and Hickam, Review of Scientific Instruments, 16, 69 (1945)

Filament and Coating Materials

The first filaments tried were tungsten spirals 15 nm long made of 5 mil wire. It was difficult to produce these with sufficient uniformity. Further, between the diameter of the spiral and the warping that occurred in most of them, line source conditions could not be approximated. It was decided to use a platinum ribbon 0.050 inches wide, 0.001 inches thick, and 1 inch long. Subsequent to the arrival of the platinum ribbon a nickel ribbon of the same dimensions that was available in the department was tried and found to be satisfactory except for the fact that it melted at currents of approximately 4.0 amperes. Later the platinum ribbon proved capable of sustaining currents as high as 6.0 amperes without melting.

The initial problem was to determine if the spectrometer would operate. Since no estimate could be made of the number of ions that might reach the Faraday chamber, it seemed desirable to have a source capable of very large emission. Assuming the original adjustment of the spectrometer to be poor, it should be possible to find some indication of the ion beam by using an extremely sensitive current detector. Then as adjustments improved the resolution of the ion beam it should be possible to use ion sources whose emission was less copious.

For the first tests it was decided to use either

spodumene or pollucite, since both are reported¹ to have large emission currents. For further work, particularly adjusting and testing the resolution, it will be desirable to have several sources of ions in addition to the three mentioned in section one. After some consideration of the results reported by Hayden² and Elewett and Jones³ several coating materials were chosen for test. These are listed in table 1 with the ions emitted.

1 J. P. Blewett and E. J. Jones, <u>Physical Review</u>, 50 464 (1936) ² R. Maydon, The Physical Review, 74, 650 (1948)

3 J. P. Blewett and E. J. Jones, The Physical Review, 50, 464 (1936)

| | TABLE 1 | |
|--------------------|--------------|------------------------|
| Coating Material | Ions Emitted | Mass Numbers |
| Nacl | Na | 53 |
| | MazCl | 81, 83 |
| KCL | | 39, 401, 41 |
| | K201 | 113, 115, 117, 119 |
| Al ₂ 03 | A 1 . | 27 |
| BaO | Ba | 1301, 1321, 1342, 1352 |
| | | 136°, 137, 138 |
| U308 | τ | 2341, 2351, 238 |
| | υ ο | 2501, 2511, 2521, 2531 |
| | | 251, 255*, 256* |
| | υ ος | 2661, 2671, 2681, 2691 |
| | | 270, 2711, 2721, 2741 |
| Spodumene | t.1 | 6", 7 |
| | <u>A1</u> 34 | 27 |
| Pollucite | Cs | 133 |
| | Nav | 23 |
| | A1 * | 27 |

indicates ions weakly emitted.
indicates isotopes with an abundance of less than

1 per cent. Indicates isotopes with an abundance of less than 锊 10 per cent.

Coating Techniques

Blewett and Jones¹ reported coating their filaments with oxides using water as a binder. The writer's first coating was made with several drops of a 5 per cent suspension of Al_20_3 . Most of the coating came off as the filament was heated, and the emission from the remaining material was weak and erratic. Following a suggestion of Bainbridge² it was found that strong stable emission was most consistently secured from a very thin uniform coating.

Al₂0₃, BaO, U₃O₈, spodumene, and pollicite were all coated in the same manner. They were first ground until they were extremely fine, and then one part of each was mixed with one hundred parts of water, by mass. A drop of this suspension was pipetted onto the filament and evaporated by gentle heating with a 2.0 to 2.5 ampere current. This was repeated until the desired coating had been formed. This thickness was characterized by a lightly powdered appearance that only slightly dulled the sheen of the platinum.

Since NaCl and KCl are soluble in water they are more difficult to coat. The writer was never able to secure surfaces that appeared as uniform as those made with suspensions. When the material was in solution the procedure was the same

¹ J. P. Blewett, and E. J. Jones, <u>The Physical Review</u>, 50, 464 (1936)

K. T. Bainbridge, Journal of Franklin Institute, 212, 317 (1931)

as that for suspensions, except that the current used to aid in evaporation did not exceed 1.6 ampores. More rapid heating than this caused the coating to disintegrate.

Test Equipment

The filaments were tested for emission in a diode connected to a glass vacuum system. The system used a mercury diffusion pump backed by a mechanical fore pump. Pressures were read by a McLeod gauge. A dry ice freezing trap was placed between the system and the diode to prevent Hg vapors from reaching the diode. A drying flask filled with P_2O_5 was located between the diode and the freezing trap. When in use and opened but briefly to atmospheric pressure the system was capable of pressures of the order of 10^{-5} mm Hg within forty minutes after pumping started. During tests the pressure generally rose to the order of 10^{-4} mm Hg. By longer outgassing lower pressures could have been maintained during the tests, but this was not essential since the minimum mean-free-path permissable was 1 cm.

The diode was constructed from a pyrex flash to which a ground glass joint had been scaled to permit a convenient means of removing the filament for coating. The plate of the diode was made of sheet nickel bent to form a section of a cylinder. This was welded to a tungsten rod that was then scaled through the end of the pyrex flash. The filament was 1 inch long and was welded to nickel supports that also served as conductors. These supports were welded to tungsten wires introduced through scale in the removable section of the ground glass joint. The nickel supports had been so fashioned that when the ground glass joint was closed and rotated the

filament could be brought to the center of the cylinder formed by the plate.

The filement current was supplied by an eight volt storage cell and controlled by two wire-wound variable resistors connected in parallel. The course control had a total resistance of 22 ohns, and was rated as 4.4 amperes. The fine control had a resistance of 86 ohns and was rated at 2.2 amperes. These were mounted on a board with a switch and meter so they might be moved from the test dick to the spectrometer.

The negativo plate potential was supplied by a 1080 volt battery consisting of 16 No. 167 Eveready dry batteries. This was regulated by using as many cells as needed. The maximum current that this battery could draw without voltage losses due to internal resistance was not known, but since 50 μ a was the largest current drawn, with the average usually of the order of 10⁻⁷ amperes, it is unlikely the potential was ever below the emf of the cells.

The emission current was read by a standard wall galvanomotor with a sonsitivity of 10^{-9} amperes/mm. The instrument was zeroed at the extreme end of the scale to permit readings of 0 to 0.5×10^{-6} amperes without the use of a shunt. For higher values of current it was necessary to shunt the instrument. With a potential of 1080 volts leakage of the order of the emission currents could easily occur. By insulating all parts of the circuit and keeping the glass of the diode dry and clean the leakage was reduced to 10^{-8} amperes (1 cm

deflection) or less. This could easily be corrected by changing the zero of the galvanometer.

Test Methods

It was estimated that when the spectrometer was finally adjusted ion currents of the order of 10-7 amperes should give currents at the collector that could be easily detected. Consequently all the coating materials vere tested with emission currents of this order, and spodumene and pollucite were also tested at currents as high as 10^{-5} amperes. When a filament was ready for test and the pressures had been reduced to the proper order the filement current was raised to 1.8 amperes, and several minutes were allowed for the temperature to reach equilibrium. The current was then advanced in 0.1 ampere steps with a few minutes between each change to allow the temperature to reach equilibrium. The filament current for which ion emission was first noted was recorded. Then the filament current was slowly raised until the particular current chosen for the test was reached. After this the filsment current was changed only as required to keep the ion current at this value. If the filament meintained this emission current for an hour and a half the coating was destroyed by increasing the filament current to 5 amperes. This was usually sufficient to eject the remaining ions in a short intense burst. Figure 1 is a graph of the filament current against time. These curves give a clear picture of the filament's performance, and also allows some means of estimating the probable life of the emission. These tests were made with an emission current of 10" amperes



using a potential of 540 volts on the plate. No two filaments of the same type were precisely alike, but there was close agreement so long as the coatings were thin, and reasonably uniform.

It had been noticed in some of the preliminary tests that turning off, or sharply reducing the filament current seemed to shorten it's life. Therefore in these tests if the chosen ion current was exceeded the heating current was not reduced, but the ion current was allowed to go as far below the set value as it had exceeded it. Thus, over the period of the test the average emission current could be kept at the desired value without ever decreasing the filament setting.

Below are listed other details concerning the various coating materials that could not be shown on the graph.

Pollucite was the strongest emitter of all the materials tested. Currents as high as 50 μ a were drawn from it for fifteen minutes after it had already been run three hours at currents between 0.1 and 0.5 μ a, 1/2 hour at 5 μ a, and 1/2 hour at 25 μ a. Even then it was capable of a steady emission at lower values. Emission started at approximately 2.1 amperes.

Spodumene was a very good source, but never as strong as pollucite. Emission started at approximately 2.5 amperes.

KCl proved to be an excellent source, and the most stable emitter tested. Emission started at approximately 2.1 amperes.

NaCl was quite short lived. Generally, it had become so erratic in its behaviour that the tests were concluded after 45 minutes. Emission started at about 2.2 amperes.

Ba0 was the poorest emitter tested. The highest currents emitted were of the order of 10^{-8} amperes. Emission started at 2.2 amperes and in the course of a twenty minute test it was necessary to raise the filament current from 2.9 to 4.5 amperes to maintain the weak emission mentioned.

Al₂0₃ was a good emitter for currents of the order of 10-7 amperes. At these currents it has been operated as long as three hours. It was very unstable if the coating was too thick. Emission started at about 2.2 amperes.

U308 was an excellent emitter and proved to be almost as stable as KCl. The material did not coat as evenly as the others, but it appeared to adhere better. It requires considerable outgassing before tests can be made. The emission started at approximately 2.8 amperes.

PART II

Preparation of the Spectrometer

The decision to use thermionic emission as a source of ions for the spectrometer tests had been made prior to the writer's joining in the work. Toward this end a new head plate had been constructed to replace the one that was part of the electron bombardment assembly. The insulators and filament supports were already in place so that it was only necessary to mount the filament and align it with the slit and the axis of the spectrometer tube.

When the filament was coated and aligned the instrument was closed, sealed, and exhaust started. The preliminary exhaust proved to be difficult since the instrument had been moved and a number of small leaks had developed. Further, it had been exposed to atmospheric pressure for several months, and the metal walls required considerable outgassing. Standard techniques were practiced in the outgassing¹ and leak hunting.^{2,3,4} Approximately three weeks were required to reduce pressures to the desired level.

For the ion beam to be appreciable it is necessary

| l ques, pp | S. Dushman, Scientific Foundations of Vacuum Techni- |
|---------------|---|
| 2 | S. Dushman, Ibid, pp. 370-386. |
| 3 | C. H. Bachman, Experimental Electronics, pp. 128-134. |
| 4 | S. Jnanananda, High Vacua, pp. 255-256. |

that the mean-free-path of the ions be approximately 60 cms. Calculations based on data drawn from several sources^{5,6} give values ranging from 600 to 900 cms for the mean-free-path at pressures of the order of 10⁻⁵ mm Hg. Pressures of this order assure the elimination of appreciable ion losses due to collisions. Pressures of this order were maintained through-out the tests.

5 S. Dushman, op. cit., p. 35
6 S. Jnanananda, op. cit., pp. 34-35

Test Equipment

The vacuum system of the spectrometer employed an oil diffusion pump backed by a mechanical fore pump. No freezing trap was used though the usual drying flask filled with P_2O_5 was employed. Pressures were read by a Pirani gauge and an ionization gauge. The Pirani gauge only served to indicate if the pressure was low enough to use the ionization gauge. The gauges were located at the most remote point of the system with respect to the pumps. Thus, the pressure differential of the instrument insured the existence of pressures considerably lower than those indicated by the gauges.

The filament current was read and controlled by the same instruments and equipment used in the emission tests. The emission current was also read by the same galvanometer, but provision had been made for the measurement and continuous regulation of the accelerating potential. The potential was read by an electro-static voltmeter with a range of 0 to 600 volts. If the potential exceeded 600 volts it was determined by reading the battery in parts and adding these parts. The potential was roughly adjusted by the number of cells used, and fine adjustments were made by means of a 250,000 ohm potentiometer connected across the first battery. The sliding tap of the potentiometer was used as the negative terminal of the supply.

The magnetizing current was supplied by a 12 volt storage

cell, and was regulated by three wire-wound resistors connected in series. Their resistances were 185, 22, and 8 ohms, while their current capacities were 1.5, 4.4, and 5.8 amperes respectively. The magnetizing currents employed in these tests ranged from 0.4 to 0.95 amperes.

The measurement of the very small currents that were found at the collector requires special methods and equipment. These are to be the subject of a report by J. J. Freymouth.

Test of the Spectrometer

After a number of attempts had failed to detect an ion beam it was decided to widen the slits at the filament and admit larger currents to the spectrometer. When this was attempted it was found these slits were improperly aligned. At the same time the Faraday collector was connected to the second defining slit so that all ions passing through the first defining slit were counted. As a result of these changes a weak ion current was detected at once.

In Nier's instruments^{1,2} the ion sources had been enclosed in a glass envelope that was sealed to the metal spectrometer tube. If the region beyond the slits was to be free of electric fields the metal spectrometer tube and the slits had to be maintained at the same potential. With this arrangement the only electric fields in the vicinity of the filament were between it and the slits. In our instrument the entire envelope was metal and at ground potential with respect to the filament. Under these conditions ions emitted by the filament were accelerated in all directions and only a small portion reached the slits. This was remedied by constructing a shield of sheet nickel for the filament as

1 (1940) 2 A. O. Nier, <u>Review of Scientific Instruments</u>, 11, 212 A. O. Nier, <u>Review of Scientific Instruments</u>, 18, 398 (1947) shown in Figure 2. This altered the field in the vicinity of the filament so that all the ions were accelerated in the direction of the slit. Before this change emission currents of the order of 5×10^{-5} amperes had given only weak ion currents at the collector. After it was installed emission currents of the order of 10^{-7} amperes gave strong ion currents at the collector.

In Figure 3 the mass numbers of the ions emitted by a filament coated with pollucite were plotted against the collector currents. The emission current was kept constant at 10⁻⁷ amperes. A calculation of the mass of the strong line using equation 4, with a value for H determined by standard methods³ and the observed value of V, was within 1.5 per cent of the accepted value for Cs. Pollucite was reported⁴ as a copious emitter of Cs with small traces of Na and Al present. No indication of the latter could be found. The impurities found in pollucite were known⁵ to vary with the sample and its source. The masses determined as 79.8 and 139 mass units agree roughly with a number of elements that might have been present as impurities. The mass at 289 if approximately correct seems to indicate the emission of a complex ion. Since the lines were several mass numbers

³ A. W. Smith, Electrical <u>Measurements</u> in <u>Theory</u> and <u>Application</u>, pp. 225-235.

4 K. T. Bainbridge, Journal of Franklin Institute, 212, 317 (1931)

J. P. Blewett and E. J. Jones, The Physical Review, 50, 464 (1936)

CUTAWAY DRAWING OF THE FOCUSING SHIELD





Glass Insulator On Negative Lead

Scale: 1cm =1cm

FIGURE 2



NI SOVIN

wide, the identification of these impurities was not possible. When further alignment and tests with other ion sources improve the resolution so that the abundance of the isotopes can be evaluated, such work will be possible.

The readings to determine the masses discussed above were taken in the following manner. First the accelerating potential was set at some value and the magnetizing current adjusted to bring the strong line to it's maximum value. As was shown earlier

k = m₁₃₃V₁ mass unit-volts,

where m₁₃₃ is the mass of the strong line. Then V was adjusted to focus the other line being investigated on the collector. Then,

 $m = m_{133}V_1/V_2$ mass units.

After this k was determined for another value of V and the line being checked was re-located. Since widely varying values of k and V resulted in close agreement for all the masses plotted it was felt that no large errors existed in the approximate values plotted on the graph.

The resolution obtained in these tests was poor, but it must be pointed out that all the requirements of good resolution had been sacrificed in favor of large currents. Further, the magnet was only roughly adjusted. In view of these facts the initial tests of the spectrometer appeared to be highly satisfactory. The agreement between the experimental determination of the mass of the single isotope of Cs and it's accepted value seemed to indicate that the orbit of the ion beam varied but slightly from the ideal, upon which equation 4 was based. Future tests with other ions will be required to see if similar agreement is to be had for other masses. Should these be successful and further adjustments improve the resolution the department will have a useful research tool at it's disposal.

The writer wishes to thank Dr. F. M. Durbin for the advice and assistance that had much to do with the success of the project. He also wishes to thank Prof. Snyder for suggestions concerning the electro-static shield, and J. J. Freymouth for his co-operation in the tests on the spectrometer.

BIBLIOGRAPHY

Books:

- Bachman, C. H. <u>Techniques</u> in <u>Experimental</u> <u>Electronics</u>. New York: J. Wiley, 1948.
- Cork, J. M. <u>Radioactivity</u> and <u>Nuclear Physics</u>. New York: D. Van Nostrand, 1947.
- Dushman, Saul. Scientific Foundation of Vacuum Technique. New York: J. Wiley, 1949.
- Hoag and Korff. <u>Electron and Nuclear Physics</u>. New York: D. Van Nostrand, 1948.
- Jnanananda, S. <u>High Vacua</u>. New York: D. Van Nostrand, 1947.
- Richardson, O. W. Emission of Electricity from Hot Bodies. London: Longmans, Green and Co., 1916.
- Smith, A. W. <u>Electrical Measurements in Theory and</u> <u>Application. New York: McGraw-Hill, 1934.</u>

Periodicals:

- Bainbridge, K. T. "The Isotopes of Lithium, Sodium and Potassium." Journal of Franklin Institute, 212, 317 (1931).
- Blewett and Jones. "Filament Sources of Positive Ions." Physical Review, 50, 464, (1936).
- Hayden, R. "Mass Spectrographic Mass Assignment of Radioactive Isotopes." Physical Review, 74, 650 (1948).
- Hipple, Grove, and Hickam, "Electronic Problems Involved in the Practical Application of the Mass Spectrometer," <u>Review of Scientific Instruments</u>, 16, 69 (1945).
- Hundley, J. L. "The Relative Intensities of Positive Rays from Lithium." The Physical Review, 30, 864 (1927).
- Kunsman, C. H. "A New Source of Positive Ions." Science, 62, 269 (1925).
- Nier, A. O. "A Mass Spectrometer for Routine Isotope Abundance Measurements." <u>Review of Scientific Instruments</u>, 11, 212 (1940).
- Nier, A. O. "A Mass Spectrometer for Isotopic and Gas Analysis." <u>Review of Scientific Instruments</u>, 18, 398 (1947).

Typist: Flora Hippe