

Lawrence Berkeley National Laboratory

Recent Work

Title

MASS SPECTROGRAPHIC ANALYSIS OF TRANSURANIUM ELEMENTS

Permalink

<https://escholarship.org/uc/item/4hj3007b>

Author

Karraker, D.G.

Publication Date

1951-03-01

UNIVERSITY OF CALIFORNIA - BERKELEY

UCRL-1213

c.2

OFFICIAL USE ONLY

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

RADIATION LABORATORY

UCRL-1213
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

MASS SPECTROGRAPHIC ANALYSIS OF TRANSURANIUM ELEMENTS

D. G. Karraker

MAR 1951

Introduction

The instrument used in mass spectrographic analysis of transuranium elements at Berkeley is a 60° sector-magnetic field, Nier-type mass spectrograph, with a 20 cm radius of curvature, which was built under the supervision of F. L. Reynolds. A schematic diagram of the instrument is shown in Fig. 1. The ions are produced in the source assembly by thermal ionization; that is, positive ions are produced by heating the sample to a high temperature on a wolfram, tantalum or platinum filament. The ions are accelerated through a voltage drop of 8 kilovolts, and bent by the magnetic field so that when in focus they go through a slit and strike the collector plate. The charge from these ions is measured by a D. C. Voltmeter connected to a L & N recorder. To measure a different isotope on the collector, the magnetic field is adjusted to bring successive isotopes into focus. The high voltage may be adjusted instead, but because of the difficulty of control and effect created by potential changes, the magnetic field sweep is more satisfactory.

Vacuum System

A schematic of the vacuum system is shown in Fig. 2. There are no valves in the mass spectrograph proper, and all connections are made through a pumping manifold. In operation, the air inlet valve and the valve to the diffusion pump are closed and the valve to the rough pump opened. The rough pump (HI VAC mechanical Pump) pumps the

OFFICIAL USE ONLY

-2-

system down to about 20 mm Hg pressure (~ 30 minutes), at which pressure the rough pump valve is shut and the valve to the oil diffusion pump opened. In about 2 hours, the system is down to a vacuum of about 5×10^{-5} mm Hg, which is considered sufficiently low for operation. The vacuum system is all copper and brass tubing except at the steel magnet pole faces which form part of the vacuum system. The use of a manifold is to provide uniform pumping on the beam tubes, avoiding the necessity for pumping out one beam tube through the $1/4$ " magnet gap. The vacuum is limited by a number of factors, not the least of which is the difficulty of preventing leaks in a metal system where two orifices are opened often. It should be noted that there is no necessity for an extremely good vacuum except for high resolution operation at mass 200 or above. Gas scattering widens the mass peaks and lowers the resolution in isotopic determinations in the heavy region. The extent of the pressure dependence of the resolution is not known, but pressure broadening is suspected of being a major factor in the resolution obtained.

The frequency of use of the machine is dependent on the time necessary to pump to an operating vacuum. The Berkeley instrument can be used perhaps twice a day due to the time necessary for pumping after every sample change. The two or three hour pumping period can be cut to 30 to 45 minutes by isolating the source assembly from the rest of the vacuum system with some sort of a valve, which would not necessitate breaking the vacuum on the whole system to change samples. In this sort of arrangement, the source could be lowered to atmospheric pressure for changing samples. The majority of the vacuum system would be left

OFFICIAL USE ONLY

-3-

at high vacuum. It would be necessary only to pump out the source before the next run, instead of the whole machine.

High Voltage

The high voltage is applied to the ions in the source over a distance of 2 cm and is controlled to 8 parts in 10^5 . The usual accelerating voltage is 8 kilovolts, but other voltages in this range of 3 to 10 kv can be used when isotopic analysis is made by receiver current. The careful control of the accelerating voltage is quite critical to the resolution at high mass values, since the separation between masses is only 20 volts at mass 250. A small ripple in the voltage will cause appreciable widening of the image and consequent lowering of resolving power of the instrument. The distance over which the voltage is applied to the ions is not particularly critical--distance sufficient to avoid arcing is all that is necessary.

Magnet

Geometrically, the magnet is a sector of a 60° arc, with plane pole faces, designed only for first order focusing. The coils are wound on elliptical cores, but the pole faces are trapezoids. The magnet is capable of a field of 14 kilogauss with a magnet current of 250 ma but is limited to a maximum field of 14 kg by the saturation of the iron magnet yoke. The magnet gap is approximately $1/4$ " wide and 2" high, but is collimated so that the ion beam sees only an area $1/8$ " wide and $3/4$ " high. The beam area is diminished to avoid inhomogeneities in the magnet field. The pole faces are separated by brass spacers, and the spacers and pole faces are hard-soldered in one rigid

piece which forms part of the vacuum system. This design has the difficulty that the beam tubes cannot be adjusted until the best focus for the beam is obtained. Happily, the Berkeley instrument seems to focus well enough that further adjustments were not necessary.

Control of the magnet current supply is not too critical, although the current supply should be stable over a period of 10 minutes or so. Control to 1 part in about 13,000 is used at Berkeley and has been quite satisfactory when the magnet current is of the order of 100 ma. Since the magnet current is varied during isotopic analysis, it is convenient to have a motor-driven magnet sweep over small ranges in magnet current which will give a uniform variation of magnet current with time.

Source

A schematic diagram of the source is shown in Fig. 3. The principle of the thermal ionization source is quite simple. The ions are produced by heating the filament and then accelerated by the potential drop between the plates, passing through the defining slits. The slit size may be varied, depending on the geometry and resolution desired. An electrometer connected to slit plate serves to indicate the presence of an ion beam. To obtain high resolution, a small slit is desirable, while to get a high geometry, a large slit is desirable. The slits used on the Berkeley instrument are 1.1 cm in the horizontal dimension and 0.010 inches in the vertical dimension. These, together with the slit on the source side of the magnet, determine the half-angle of the incident beam on which the resolution depends.

Insulation of the metal parts at the source in high potential is accomplished by Mkrcy studs, which have been quite satisfactory. When operating as a thermal source, some arcing is encountered in the first few minutes of filament heating. This is perhaps due to the large amount of gas freed in the source assembly by initial heating of the wolfram filament, and the consequent rise in pressure. Under such conditions, arcing is sometimes encountered. After the initial surge of gas, the insulation and the pressure should be sufficient to maintain the potential without arcing.

The filaments used in the thermal production of ions are made of wolfram, tantalum, or platinum ribbon 30 mils wide and 1 mil thickness bent into a U-shape and spot-welded rigidly to a frame. Samples for analysis are evaporated on the filament from solution. Precipitates are placed on the filament as a slurry and then dried. The amount of sample necessary to provide a sufficient quantity of ions for isotopic analysis varies with the element, and depends further on the impurities present on the filament. The usual sample size for plutonium and higher transuranium elements is approximately 10 μg . The ionization of the sample from a filament has the advantage that the background of the mass spectrometer is not a problem. The only substances that can produce ions are materials on the filament, so the use of a new filament for each determination avoids completely the possibility that samples from previous runs of the machine might influence the results.

The chemical form of the sample is responsible in some degree for the efficiency. The transuranium elements show the best efficiency

when run as the fluorides, either by a slurry of the fluoride on the filament, or by precipitating the fluoride directly on the filament. The explanation of this effect may be found by considering the Langmuir-Saha equation for ionization from a filament

$$\frac{N^+}{N} = C e^{\frac{(\phi-I)}{KT}}$$

C is an empirical constant

N is total No. of atoms

N⁺ is No. of positive ions

φ is the work function of the filament

I is the ionization potential
of the metal

K gas constant

Considering the exponential term, it may be seen that for a maximum production of ions we wish for a high work function on the filament, and a low ionization potential for the sample material.

The equation has little utility in practice, since there is virtually no data on the ionization potentials of metals from their compounds, and the work function of the filament is usually not known. The work function for pure wolfram is 4.52 ev, but for the ordinary filament, coated with oxides, (or fluoride, if the filament is treated with HF) the work function is usually higher, 8 or 9 ev. Unfortunately, this is not completely predictable, and small amounts of impurities may have the property of cleaning up the filament, thus lowering the work function and decreasing the efficiency of ion production. The usual experimental practice involves drying a few drops of HF on the filament to create a fluoride surface.

Large amounts of sample do not usually lead a greater production of ions, since the excess sample apparently falls off the filament when the temperature is increased, and no more ions are produced than when a smaller amount of sample is used. The presence of masses of foreign salts, such as NH_4Cl decreases drastically the number of ions produced, both by samples falling off the filament, and by decreased ionization efficiency.

The production of ions from the filament is quite temperature dependent, and seems to be governed mainly by volatility considerations. Each metal appears to produce ions at a characteristic temperature, below which no detectable ions appear. Increasing the temperature increases the ion current first, but then the current slowly decreases as the temperature is further increased. The sample is expended more quickly at high filament temperatures than at lower temperatures, and with a decrease in efficiency. Most efficient ion production is obtained from the sample if the filament temperature is raised to a temperature slightly above the threshold temperature and allowed to stay constant as long as an ion beam appears. This produces a steady ion current with very little fluctuations in intensity. Best results are obtained for plutonium by adjusting the temperature until ions are just emitted, then reducing the filament temperature quite a bit below what was necessary to start emission. Plutonium will supply a steady, even ion current if run in this manner.

The efficiency of ion production varies widely from element to element and is usually expressed as loss factor, meaning the ratio of ions collected at the receiver to the atoms of sample placed on the filament. For transuranium elements, the loss factors are of the

magnitude of 10^5 to 10^6 . This factor includes the geometry of the instrument -- about 1% -- but it is a measure of the efficiency of ionization of these elements. Americium has the lowest loss factor, followed by plutonium and curium in that order. It should be specified that these loss factors apply to the elements only when run as their fluorides.

Receiver

The receiver assembly has arrangement for two types of detection -- a photographic plate or a Faraday cup to collect the ions. The Faraday cup is placed behind a slit, arranged to be parallel to the magnet face at the true focus of the instrument. The photographic plate is placed horizontal and in the same vertical position as the source slits. Use of the photographic plate is limited in isotopic analysis, since it involves standardization of developing procedure and of plate response to ions. It is far simpler to use the Faraday cup receiver for isotopic analysis. The current from the Faraday cup is amplified by a DC voltmeter connected to an L & N recorder.

The voltmeter is quite critical for proper measurement of the intensity of mass peaks. The D. C. Voltmeter used was designed by Hugh Farnsworth of the electronics group, and is a 100% inverse feed back type, with linear amplification over a range of 10^5 in ion current. It is capable of measuring electrometer currents of the order of 10^{-10} - 10^{-15} amps. A great deal of care is necessary for the proper construction of this voltmeter, but once operating, it is quite rugged and has few troubles.

Health Precautions

Early in the course of analysis of a large number of plutonium samples, it was observed that the accumulated alpha activity of plutonium constituted a dangerous health hazard, which might be spread throughout the installation unless preventative measures were taken. Accordingly, a Berkeley box was fitted about the source to prevent spread of radioactivity from that orifice of the instrument. Investigation of the receiver apparatus showed very little activity in that general area, and lead to the decision that enclosing the receiver was not necessary from a health standpoint, since almost all the sample, after volatilization from the filament, remains in the source box.

The Berkeley Box fitted around the source is designed so that all operations are carried on within the box from the point where a sample is presented for analysis. The sample is introduced in a sealed tube through a door in the box, and the apparatus within the box permits spot-welding filaments, evaporating samples, as well as assembling and disassembling the source apparatus. Entrance to the source can be obtained only through the Berkeley box.

The Berkeley box is maintained at a slight negative pressure with respect to the room by an exhaust fan. It is estimated at the present time that the source and the Berkeley box together enclose about 10^{10} alpha counts per minute, with only very minor contaminations of the room.

Operation

In operation of the mass spectrometer the accelerating voltage is set at a constant value and the magnetic field set at approximately

the correct field. The filament current is increased until the electrometer at the source detects a sizeable ion current. Minor adjustments of the magnetic field are made until the deflection of the L & N recorder connected to the receiver electrometer indicates that ions are observed. The field is then varied slowly and uniformly 10 or 12 times over the mass range covered by the element to be analyzed. The ion currents are recorded on the L & N recorder. The height of the deflection of the recorder is directly proportional to the number of ions collected for each isotope. From the recorder data the isotopic composition of the element is easily determined. During each different sweep, care must be taken to assure a constant ion beam, otherwise the ion currents will reflect changes in ion production as well as differences in isotopic abundance. This limits the length of time that can be allowed for determination of the ion current of each individual isotope. The isotopic ratios obtained at Berkeley are expected to be correct to better than 1%, in samples where the isotopic ratios are approximately equal. When the sample contains two isotopes in a ratio of about 20 to 1, the accuracy of the isotopic abundance of the less abundant isotope is only about 5 or 10%. In the high mass region, the individual mass peaks are not perfectly resolved, so that each peak carries over into the neighboring mass numbers.

This is a serious limitation on the accuracy of the results, and an instrument designed to obtain the isotopic ratios of transuranium elements with high accuracy should be designed with sufficient resolving power to obtain clear definition of the masses.

Suggested Improvements

The dispersion, or distance between line centers, for a mass spectrograph is given by the equation

$$d = 2r \frac{\Delta m}{M}$$

d is dispersion

r is the radius of curvature of the normal beam

M is the mass

and, for a 60° sector field the width of the line is given by

$$S = r\alpha^2 + W + \text{terms of 2nd order.}$$

W is the width of the slit

α is half-angle of entrance to the magnet

The resolution is given by

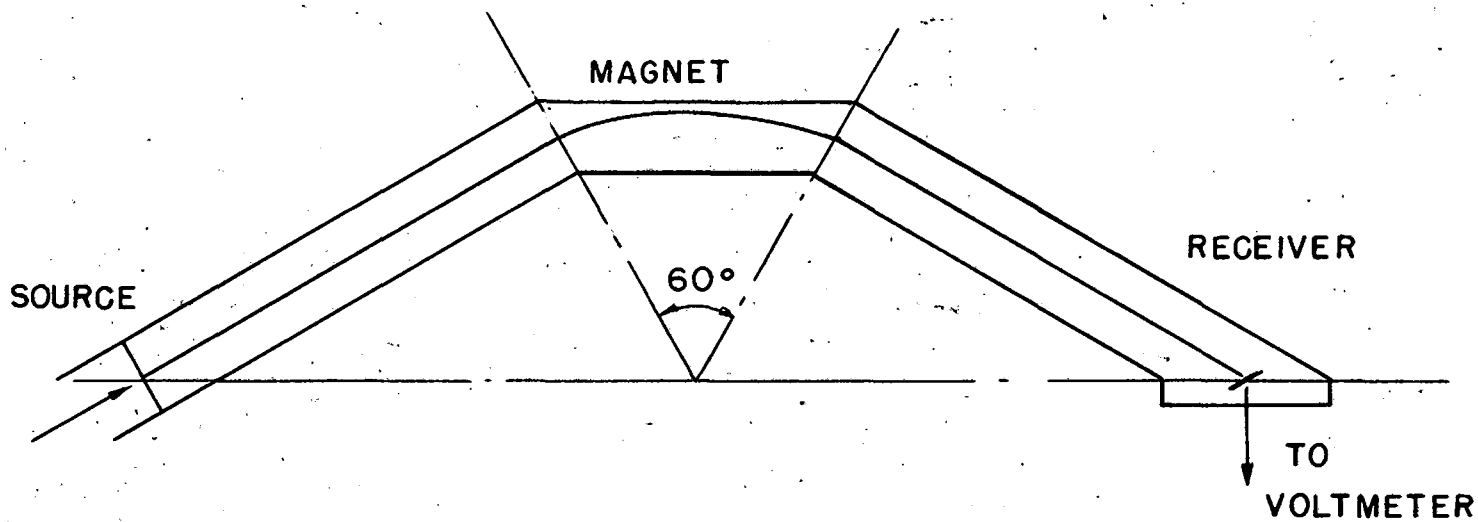
$$R = d/s$$

A consideration of the effects of a larger radius of curvature show that it can be effective in increasing the resolving power of the instrument only if the $r\alpha^2$ term in the equation of the spread can be considered small. This means in practice, that the resolution can be improved by increasing the radius of curvature, but at the expense of the geometry.

The practical value of the spread is not equivalent to the theoretical value, since other effects tend to increase the spread. Gas scattering and defocusing of the fringing field are perhaps the two most important factors in increasing the spread of the line. The line width at optimum operating conditions approaches the calculated value within a factor of 2, and with efforts made to reduce other factors, might be improved further.

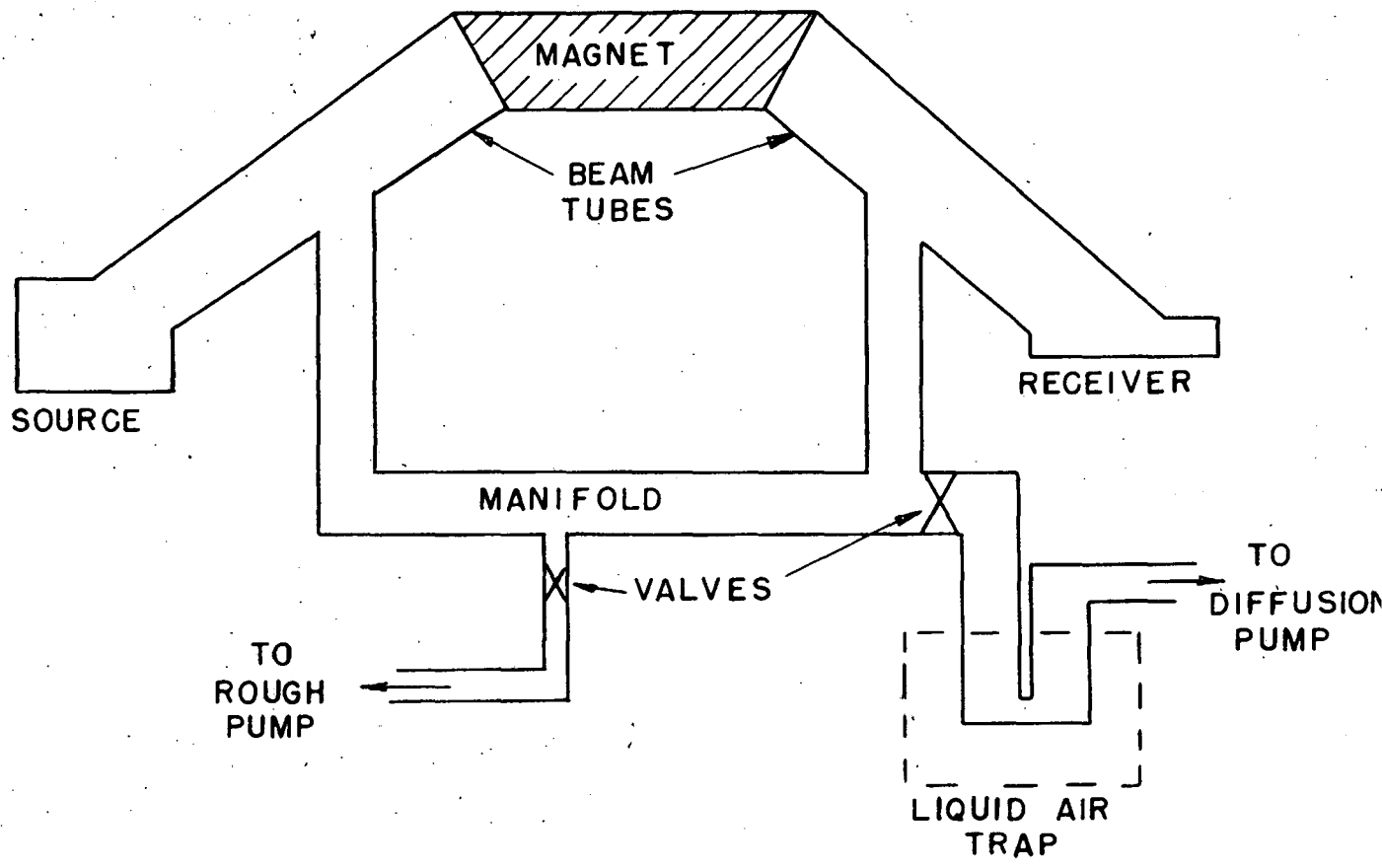
An instrument embodying a larger radius of curvature, a higher operating vacuum, and an adjustable beam tube for best focusing would be expected to have better resolution than the instrument described herein.

In conclusion, for isotopic analysis of plutonium, this instrument is not the best attainable, and could be considerably improved. However, it has the virtues of operating simplicity, and adaptability for a variety of uses. It has been used with considerable success in isotopic analysis, photographic detection of radioactive isotopes and isotopic separation. It is felt that the thermal ionization methods used in this instrument may be relied on for ionization of transuranium elements. For an instrument designed solely for plutonium analysis, suggested improvements are (1) vacuum lock that permits sample changing without completely opening the system to the atmosphere, (2) a larger radius of curvature for increased resolution and (3) a beam tube which is free from the pole faces of the magnet, and capable of adjustment for the best focusing.



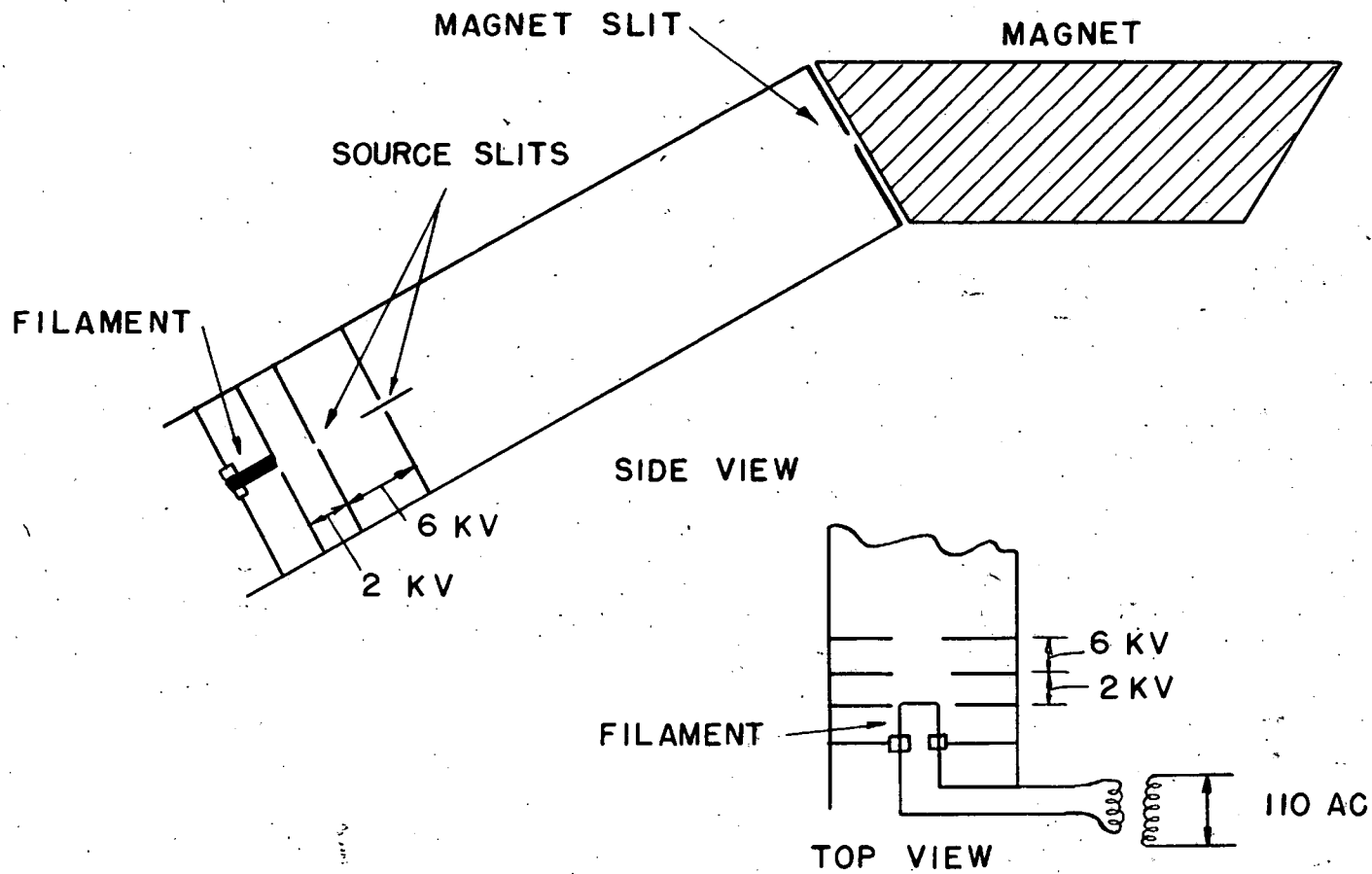
MASS SPECTROGRAPH SCHEMATIC

FIG. 1



VACUU SYSTEM SCHEMATIC

FIG. 2



SOURCE SCHEMATIC

FIG. 3