HIGH SENSITIVITY STUDIES
USING A TANDEM MASS SPECTROMETER

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SCOPE AND CONTENTS:

A description of the McMaster tandem mass spectrometer is given and the usefulness of this instrument in high sensitivity applications is discussed.

The pulse characteristics of the 17 stage Allen type electron multiplier which is used on the two stage mass spectrometer were determined and possible means of achieving an improved response in counting applications are discussed.

An ion source of the crucible variety was constructed which made possible the detection of 10^{-9} grams of a tin isotope. This source was used to detect sub microgram quantities of an enriched tin sample and was also used for the qualitative analysis of a sample which contained tin extracted from a reactor irradiated fuel rod.

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TABLE OF CONTENTS

B. DESCRIPTION OF McMASTER TANDEM MASS SPECTROMETER

3. Vacuum System

4. Electronic Components and Systems

C. EXPERIMENTAL

1. Ion Source Problems

2. Anode Pulse Height Characteristics of the Electron Multiplier

LIST OF FIGURES

TABLES

A. GENERAL INTRODUCTION

The work which is reported in the experimental section of this thesis was undertaken with the hope of discovering and perfecting mass spectrometric techniques which would eventually lead to the quantitative determination of the abundances of stable and long-lived tin isotopes which are produced in neutron or spontaneous fission of heavy elements.

It is a well-known fact (Hyde, 1964) that the mass yields resulting from slow neutron fission in the symmetric fission region are very small, and are perhaps less than 0.01%. Tin with its many stable or long-lived isotopes, many of which are the end products of β^- decay chains, spans the region in which the products of symmetric fission are expected to lie.

Since tin has a large ionization potential, the mass spectrometric study of this element using a solid source mass spectrometer is very difficult. Even with an irradiation time of a few months and a thermal neutron flux of 10^{13} neutrons cm^{-2} sec^{-1} only about 10^{-9} to 10^{-8} grams of tin isotope per milligram of irradiated U^{235} would be produced.

If it is possible to extract the fission product tin from the unreacted sample with reasonable efficiency, it next becomes important to be able to ionize a large enough fraction of these tin atoms in the ion source of the mass spectrometer so that a sufficient quantity of sample ions arrives at the detector to make an accurate isotopic analysis possible. Of course the mass spectrometer must have a high transmission, and a high detection efficiency.

With the two-stage mass spectrometer, to be described later, it is possible to detect ion currents smaller than 10^{-19} amperes when the electron multiplier ion detector is operated in the pulse counting mode.

The triple filament source of Inghram and Chupka (1953) does not produce a measurable ion current when only 0.1 μ gram of tin isotope is placed onto the sample filament, nor is there any detectable improvement when the "borax bead" technique is used. (Crouch, 1960, 1962a) An ion source of the crucible variety patterned after a design described by Tyrrell, Roberts and Ridley (1965) was eventually found to be satisfactory. In this arrangement, a small ionization box is positioned onto a modified triple filament support. The centre filament holds the solid sample, and is surrounded by the ionization box. The evaporation rate of the sample atoms can be carefully controlled by adjusting the amount of current which passes through the sample or centre filament. The side filament, which is isolated electrically from both the ionization box and the centre filament is made hot enough so that electron emission occurs. The electrons so produced are accelerated towards the ionization box where, after passing through a collimating slit, they have the opportunity of ionizing the evaporated sample atoms or molecules. In this type of source the ionization efficiency for tin can be made much higher than is possible in a thermal source, since in the latter, the sample ionization potential and the work function of the ionizing surface play such a critical role, and are so unfavourable.

In the evaluation of the crucible source, known amounts of natural tin, tin enriched in isotope 116, and fission product tin extracted from an irradiated fuel rod were used. It was found that a sample size of 10^{-9} to 10^{-8} gram gave detectable ion currents, and a sample size of between 10^{-7} to 10^{-6} grams produced an ion current of the order of 10^{-17} to 10^{-16} amperes. In the former case sample decay was rapid, but with the larger sample size this decay rate was small enough to be acceptable.

Since no description of the McMaster tandem mass spectrometer has been published anywhere, I shall in the first part of this thesis describe the essential features of this machine; especially where differences from standard practice occur.

In the course of a separate investigation it was found necessary to examine the anode pulse height characteristics of the 17-stage Allen-type electron multiplier which is used as the detector-amplifier on this mass spectrometer.

The results of this work, along with a description and an evaluation of the performance of the crucible-type ion source mentioned above constitute the second portion of this thesis.

B. DESCRIPTION OF McMASTER TANDEM MASS SPECTROMETER

1. INTRODUCTION - HIGH SENSITIVITY MASS SPECTROMETRY

A mass spectrometer which is to be used for isotopic abundance determinations should have an adequate resolving power, good sensitivity, a high abundance sensitivity, and be free from background in the mass region under investigation. (Hintenberger, 1962; Wilson and Daly, 1963b)

It is important to distinguish between the concepts of resolution and abundance sensitivity. In any single-stage mass spectrometer there will not be a sharply defined image in the plane of the detector due to a line beam of ions originating in the ion source. This diffuse image is partly due to an energy spread in the ions which emerge from the source, but in general, even in a so-called double focusing system, there remains some residual image broadening. The principal cause of this diffuseness in the image has been shown to be due mainly to small angle elastic scattering of the positive ion beam by the residual gas molecules in the analyzer tube. (White and Collins, 1954b)

As far as mass measurements are concerned, an instrument is said to have a resolution of 1 part in 1000 if the smallest observable mass difference at mass M is 0.001 M. The resolution of the instrument is determined primarily by geometrical considerations. (Duckworth, 1960)

A given instrument is said to have an abundance sensitivity (A.S.) of 1000 if the smallest observable abundance of an isotope of mass $M\pm1$ at the mass M position is 0.001 times the abundance of the isotope of mass M. The abundance sensitivity is therefore a measure of the contribution which an isotope of mass M makes to its neighbours at mass $M\pm1$, and is an especially important quantity when a rare isotope is near an abundant one. The weaker isotope will then be in the tail of the more abundant. The abundance sensitivity of a mass spectrometer is not an all-inclusive figure of merit, but is a quantity whose value depends on the then present analyzing conditions, the nature of the sample, and on the residual vacuum pressure. (White, Collins, Sheffield and Roe, 1952)

In a well-designed single stage spectrometer the abundance sensitivity at mass 100 is somewhat larger than 10^4, and is limited to this value principally by the presence of small angle elastic scattering. The abundance sensitivity for a given analyzer can be increased by lowering the analyzer pressure, but there still remains some residual scattering from the surfaces of the spectrometer tube. The most satisfactory means of achieving a really large A.S. is to operate two identical magnets in series in such a way that the image of the first magnetic analyzer becomes the "source" for the second sector magnetic field. By placing an adjustable slit at the centre or "discriminator" position and by thus physically eliminating the interfering isotope, the background at the final detector due to this isotope is reduced by a factor of about 10^3 over that which is achievable when only one sector of similar dimensions is used.

Two physical arrangements of the magnets are possible and machines based on each type have been successfully constructed. In the "C" configuration the magnetic fields in the two sectors are parallel and the ions are bent in the same sense in both the magnetic fields. (White and Collins, 1954b) In the more commonly used "S" arrangement, the ions are deflected in opposite directions in the two magnetic fields. (Wilson, 1963a) The McMaster tandem mass spectrometer is of the latter type. In this arrangement the mass dispersion which is obtained at the final detector is twice that due to each field alone, but the second order image aberration $\alpha^2 R$ is also doubled. In the above machines, the abundance sensitivity is of the order of 10^7. Still higher A.S. as well as first order double focusing has been achieved by White, Rourke and Sheffield (1958). In their arrangement two 20" magnetic analyzers are placed in the "S" configuration followed by a 20" electrostatic analyzer.

In addition to a large A.S., an analytic machine should have a large resolving power, preferably larger than 1000, so that the residual hydrocarbon peaks which are often present in a mass spectrum may be adequately resolved from their isotopic neighbours. A large resolving power can be achieved by increasing the radius of curvature of the magnetic analyzer and by decreasing the source and the detector slit widths. However, since the intensity of the transmitted beam decreases rapidly as the slits are narrowed beyond a certain stage, it is preferable to use relatively wide slits in abundance determination work. This dictates the use of a large mean radius of curvature.

Of course, when small isotope currents are being produced and measured, it becomes very important to keep background contributions to a minimum. This can be achieved even when using an electron bombardment source by a careful choice of source and other materials which are in contact with the high vacuum. The present spectrometer is of an all metal construction. The hydrocarbon background is very low, and can at any rate be resolved from the desired constituents of the mass spectrum.

To achieve very high sensitivity, special attention must be given to the choice and construction of the ion source. The ions which are produced must then be transmitted with small loss, and finally detected by an efficient detection system.

Current practice in high sensitivity applications definitely favours the use of a Nier-type thick lens source. This type of source can be made to operate more efficiently than any other kind when very large accelerating voltages are used. (Dietz, 1959, 1960a) The ion source on the present mass spectrometer can be operated at voltages up to 15kV. In addition to increasing transmission through the ion source itself, the use of a high accelerating voltage has the added advantage that it also increases the transmission through the analyzer (Stevens et al., 1963) and results in a larger conversion efficiency and first stage gain in the electron multiplier. (Barnett, 1954a; Barnett, Evans and Stier, 1954b) This latter feature if of great advantage in practice. Of course an ion source must also produce ions efficiently from the sample under investigation and do this with a minimum of discrimination among the various mass components which are of importance in the sample.

A high analyzer transmission can be secured by the incorporation of a Z-focusing facility in the ion source. It has been found experimentally that the ion intensity is only attenuated by a factor of approximately 50% when the beam is made to pass through an additional magnetic stage. Compared to the overall efficiency this is not important. What is of importance, however, is that all the relevant mass components in the ion beam are attenuated equally so that the only possible sources of discrimination can be in the ion source and in the detector. Reuterswärd (1956), who has conducted extensive experiments into the possible causes of mass discrimination has found that with good design and alignment of components, mass discrimination in the analyzer section can be kept to manageable proportions.

In the early days of mass spectrometry photographic detection of the resolved ion species at the detector was used most commonly. For isotopic abundance determinations however, photographic detection has been largely superseded by electrical methods since with these, more sensitivity can be achieved and there is less ambiguity in the interpretation of the results. (Inghram and Hayden, 1954) In favourable circumstances remarkable sensitivity, can however, be obtained. White, Rourke, Sheffield and Dietz (1961b) report an isotopic ratio determination by photographic means when only 10^{-19} grams of sample were incident onto the nuclear plate.

Ion currents larger than 10^{-8} amperes can be measured electrically by catching the ions in a specially designed bucket which is made to intercept the ion beam. The current so collected is allowed to flow to ground through a large resistor (up to $10^{12}\Omega$) and the voltage thus produced is measured by a special electrometer circuit, or better yet by a vibrating capacitance electrometer (Palevsky, Swank and Grenchik, 1947), or a servo amplifier (Stacey, Russell and Kollar, 1965). Extreme sensitivity is not possible with these measuring arrangements since an integration of the ion current is involved. The systems have long time constants on the more sensitive ranges with consequent sluggish response, and there is a possibility that the input resistor may display a voltage coefficient. (Lauder, 1959)

Ion currents greater than 10^{-15} amperes can be measured in a similar way when the ion beam is first converted into an electron beam and then amplified by an electron multiplying device. This amplified current can then be integrated in the manner indicated above.

To achieve a larger detection sensitivity than is possible by an integration method, one must be able to detect and count pulses which are taken from the electron multiplier anode and are due to single ion inputs onto the multiplier cathode. Single ion detection is possible in principle when the overall multiplier gain is large enough, and when the background noise is small. (Robinson, 1962)

The electron multiplying devices commonly used in high sensitivity mass spectrometric applications are the Allen-type electron multiplier (Allen, 1950) and the photomultiplier, (Daly, 1960). Both of these devices must be operated in a magnetic field free region and are thus used as the ion detectors in sector mass spectrometers.

For possible use in the mass spectrometer fringing field an all silicon dynode strip electron multiplier can be used. (Goodrich and Wiley, 1961; White, Sheffield and Davies, 1961a) This device has virtually zero background noise and is thus much superior to its metal oxide counterpart. (Smith, 1951)

A diagram of the 17 stage Allen-type electron multiplier which is in use on the present tandem mass spectrometer is shown in Figure 1. The multiplier consists of a CuBe alloy which has been specially treated or activated so as to optimize the secondary electron emission characteristics. (Sugiura, 1962; Salser, 1966) The dynodes are mounted on four quartz rods and are separated from each other by quartz spacers. Successive dynodes are electrically connected by glass-enclosed high value (1MΩ) resistors. The whole structure is physically connected to the mass spectrometer by means of 4 positioning screws near the anode end of the device in such a way that the ion beam can strike the most sensitive portion of the conversion dynode.

In operation a highly regulated negative voltage of -5 kV. is placed on the multiplier cathode. Each dynode has a voltage approximately 300v higher than the preceding one, such that the last dynode is at approximately -300v.

An energetic ion incident onto the conversion dynode will on the average release α secondary electrons, which because of the existing electrostatic field between the first and the second dynode will be focused and accelerated to the first electron multiplying dynode. There, each of these electrons will produce β secondary electrons on the average, each of which will in turn be accelerated to the following dynode. For a total of K dynodes, the overall current gain of the multiplier can be expressed as $G = \alpha\beta^{k-1}$. In practice, α and β are

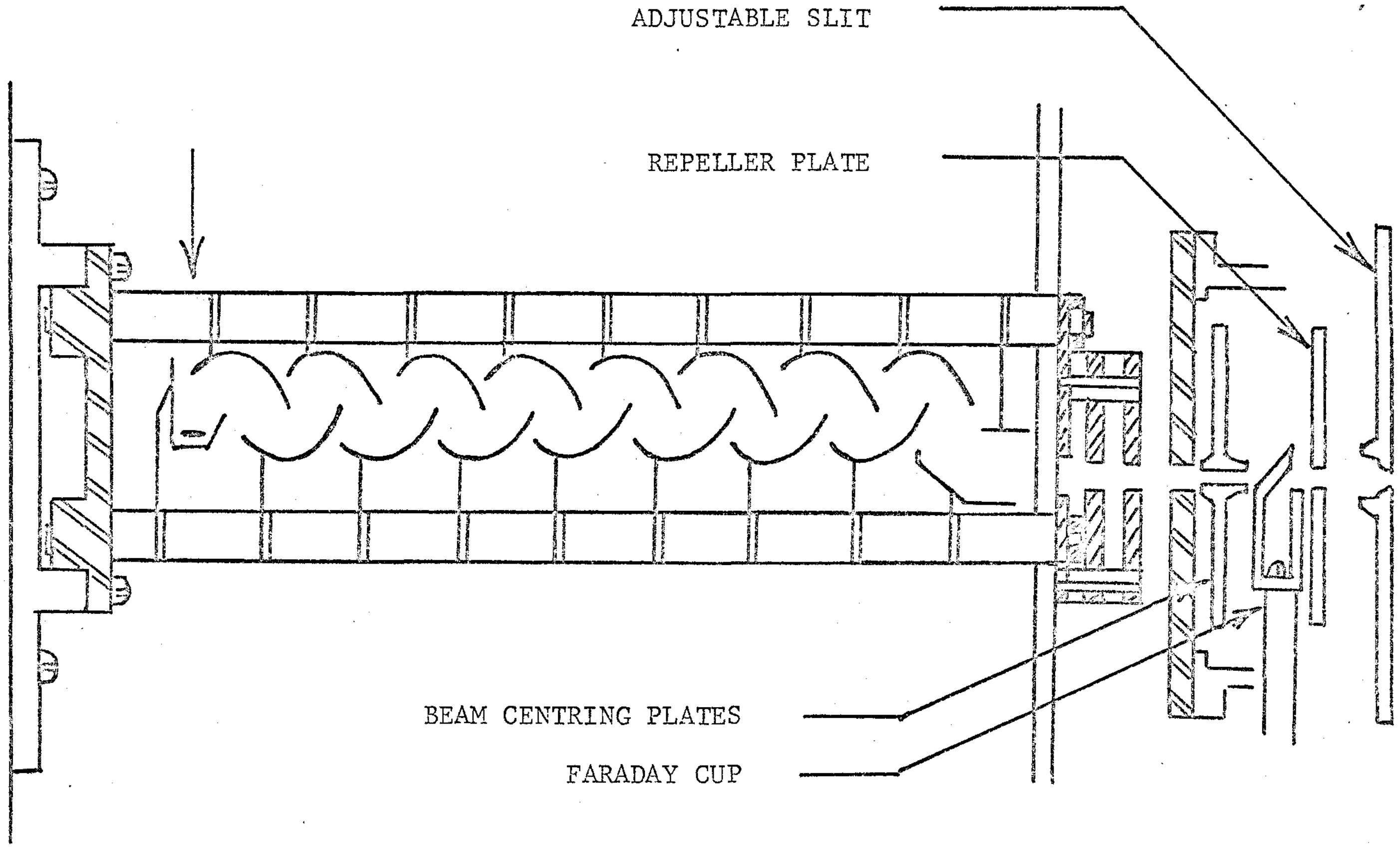


FIG.1 COLLECTOR ASSEMBLY - ELECTRON MULTIPLIER AND PLATES

greater than 2 so that for a large number of stages, the current gain can be very large.

To reduce noise due to photoelectron emission, it is necessary to use dynode materials which have a large electron work function. Satisfactory dynode materials are Cu Be and Ag Mg. (Higatsberger, Demorest, and Nier, 1954) A metal plated with Al_2O_3 (Dietz, 1965) has also been used successfully to make a conversion dynode.

The uses of electron multipliers for mass spectrometric applications have been treated by Barnett (1954a, 1954b); Inghram and Hayden (1954); Beske (1963); Seibt, Rainer and Ewald (1963); and especially by Dietz (1965).

The electron multiplier can be operated in either the direct integration (D.C.) or in the pulse counting mode. In either of these methods it is important that both α and β be large, and that the secondary electron yield at a given stage is nearly equal to the gain at that stage. A large value of α can be secured by using ions with an energy of at least 15 keV. By proper choice of dynode materials and by optimizing the inter-dynode focusing it is possible to make β reasonably large.

The electron multiplying process follows Poisson statistics and it is possible to describe the operation of the multiplier in terms of statistical generating functions. (Jorgensen, 1948; Lombard and Martin, 1961; Dietz, 1965)

In the D.C. mode of operation an isotope ratio is determined when the current due to each of the two isotopes in question has been measured and when the relative first stage gain (α) of the multiplier for each isotope under consideration is known. Since this gain is strongly dependent on the mass, energy, direction of incidence and chemical form of the sample ions (Inghram and Hayden, 1954) it is not surprising that this method of recording data is at best somewhat uncertain.

Ion currents smaller than 10^{-13} amperes can be conveniently measured by effectively using the electron multiplier as the first stage of a high gain pulse amplifying network. Single ion inputs are amplified by the multiplier and the resulting pulses are matched by means of a cathode follower to a linear amplifier and pulse-height discriminator, and from there are finally passed to a high speed counting circuit. Since the electron multiplier has a very low capacitance, large counting rates can be used when appropriate external circuitry is available. As a result, ion currents from roughly 10^{-20} to about 10^{-14} amperes can be measured by pulse counting.

When α is larger than 6 and β is more than 2.5, the detection efficiency of the electron multiplier for 15 keV positive ions is very close to unity with the result that the isotopic ratio of the ions as they arrive at the conversion dynode is very nearly equal to the ratio of the separate counting rates of the respective isotopes. In these experiments it is necessary to know the resolving time of the whole counting system in order to be able, if necessary, to apply dead time corrections to the measured counting rates. The resolving time is easily determined (White and Collins, 1954a; Dietz, Pachucki and Land, 1963) and for the present system is somewhat less than 0.6 μ second.

When an electron multiplier is used in the pulse counting mode, one must first adjust the pulse discriminator in such a way as to bias out low energy pulses which are the result of noise from the electronic circuits and those pulses which are due to spurious counts arising from the electron multiplier itself. In a well designed counting system used under good experimental conditions there is a relatively broad valley in the pulse height distribution curve between noise pulses and those pulses arising from wanted events. The pulse height distributions due to the ions whose ratio is to be determined are often rather similar and a very small error in the ratio results when the discriminator can be and has been set properly.

The anode pulse height distribution is found to be dependent on the incident ion energy, on the values of α and β, and is determined to a large extent by the characteristics of only the first few stages in the multiplier. When low energy ions (<10 keV) are used or when α is small (<4) the width of the valley in the energy spectrum narrows markedly and a consequently larger error in the ratio as determined by the counting method may result.

A detection system which is intrinsically superior to the foregoing has been developed by Daly (1960, 1963) and involves the use of a low noise photomultiplier. Here ions of 15 keV energy are deflected from their normal path at the final focus by a highly polished aluminized surface held at -40 kV. Each ion produces about 6 secondary electrons which are accelerated by this same potential (-40 kV) to strike a flat plastic scintillator such as NE 102. The resulting light pulse is amplified by a low noise photomultiplier tube which is mounted externally to the high vacuum.

The vacuum side of the scintillator is lightly coated with a metallic substance so as to prevent the buildup of charges on the phosphor. It is found possible to maintain a high vacuum in the detector region when only the scintillator separates the high vacuum from the atmosphere.

The dark current in the photomultiplier can be made very small ($<10^{-19}$ amperes) since only a modest inter-dynode voltage need be used to achieve sufficient amplification in the multiplier to drive external circuitry. This system is not as fast as the electron multiplier, but the decay time of the phosphor (<10 nanoseconds) still allows very fast counting rates to be used. With this arrangement one can be confident that very little if any bias is being introduced into an isotope ratio measurement by the detection system when ion counting is used.

The intention of the above discussion is to show that with present techniques it is possible to detect isotopic currents as small as 10^{-20} amperes. Ion transmission through a magnetic analyzer can be made resonably large. It is in the ionization process itself, and in the subsequent transmission through the ion source that by far the largest overall loss of sample material occurs. The work to be reported later was therefore undertaken with the hope that it might be possible to ionize extremely small quantities of an element such as tin more efficiently than is possible by a source which is based on the surface ionization mechanism.

2. CONSTRUCTION AND PHYSICAL LAYOUT OF THE SPECTROMETER

Two photographs of the McMaster tandem mass spectrometer are shown in Figures 2 and 3, and a schematic diagram of the high vacuum and analyzer sections of this machine appears in Figure 4. The mass spectrometer consists of two identical 90° sector magnetic fields, each of 15" mean radius of curvature constructed to operate in the "S" configuration. The machine was designed for the ion path to be parallel to the plane of the laboratory floor since this arrangement seems to be the most convenient for mounting, alignment and maintenance.

The whole spectrometer is supported by a large cast iron frame. To prevent the possible transmission of vibrations from the laboratory floor to the mass spectrometer, this frame was supported by means of 6 vibration absorbing mounting pads. Since the connections to the roughing pumps were by means of flexible rubber hoses the whole mass spectrometer is mechanically isolated from the floor.

The underside of the magnets was made of hardened steel and each magnet rests on stainless steel ball bearings. These are in turn supported by a 1/2" stainless steel plate. This means of support allows each magnet to be moved along a precise horizontal plane. Very careful final alignment is essential since the path of the ion beam has to be horizontal to within a few thousandths of an inch.

The analyzer tube consists of several sections, each made of stainless steel and fitted together with gold gasket seals. Each major section of the tube is rigidly attached to the support table by means of two massive micrometer supports which allow the tube to be properly positioned between the pole faces of the magnets.

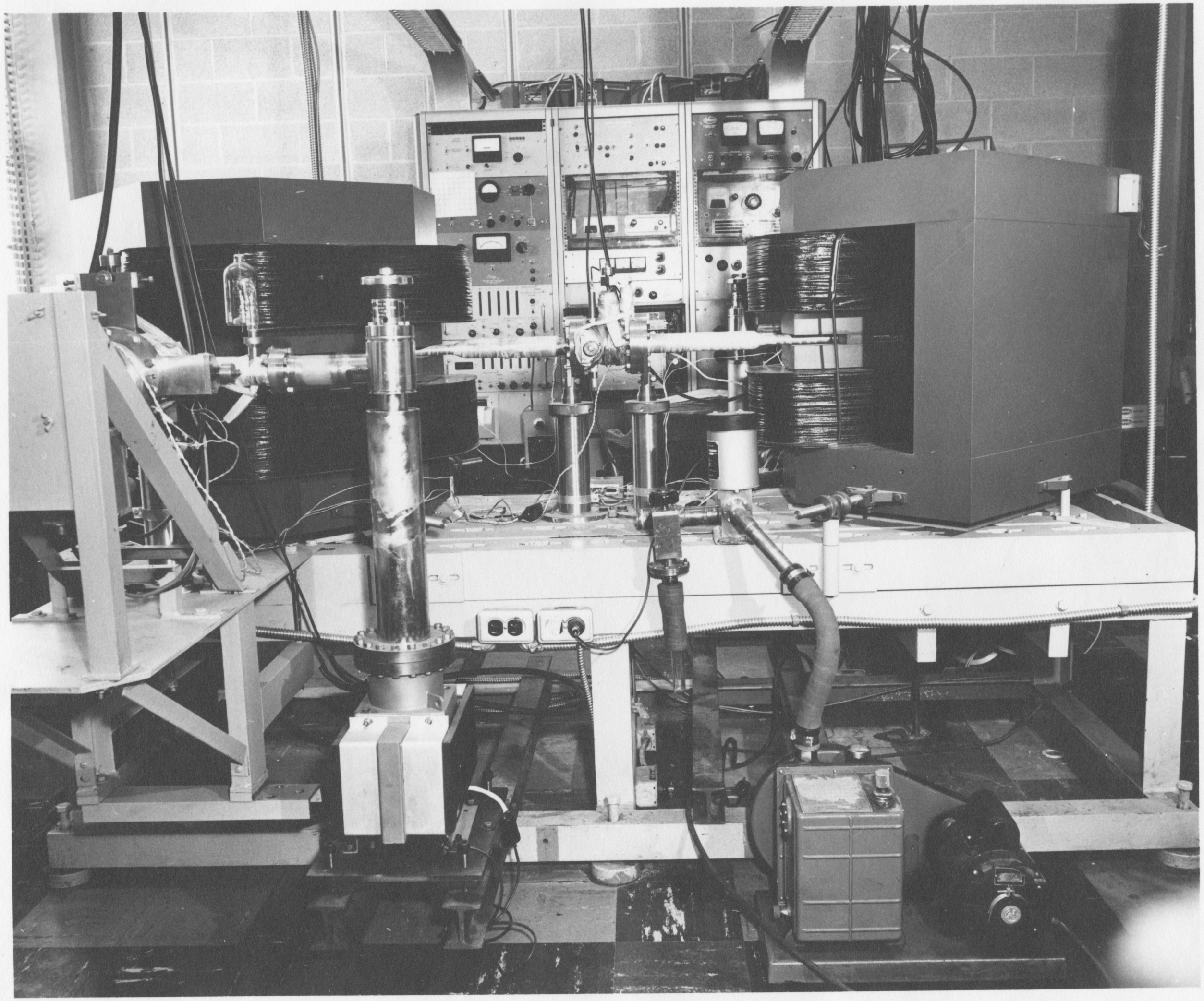


FIG. 2 PHOTOGRAPH 1 OF TANDEM MASS SPECTROMETER

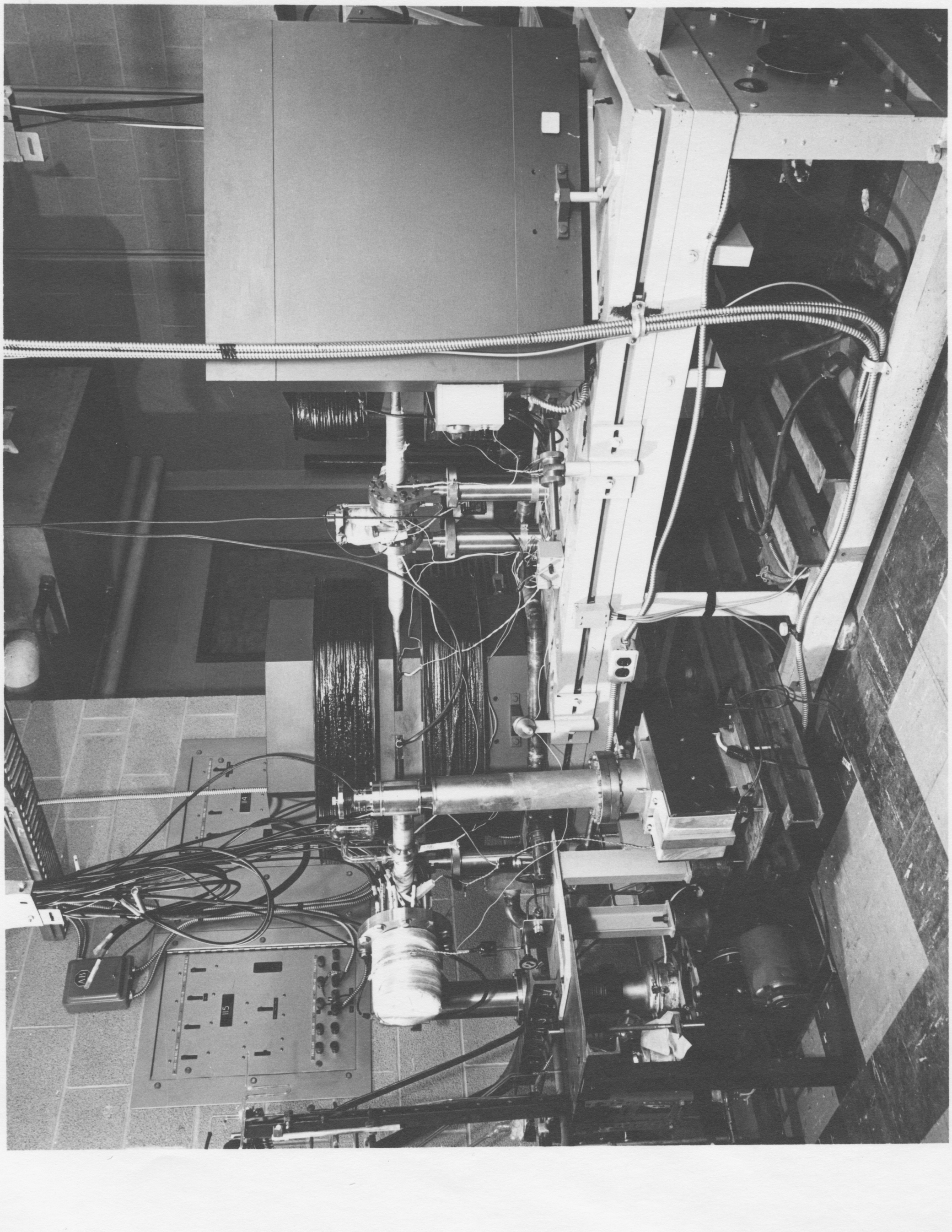


FIG. 3 PHOTOGRAPH 2 OF TANDEM MASS SPECTROMETER

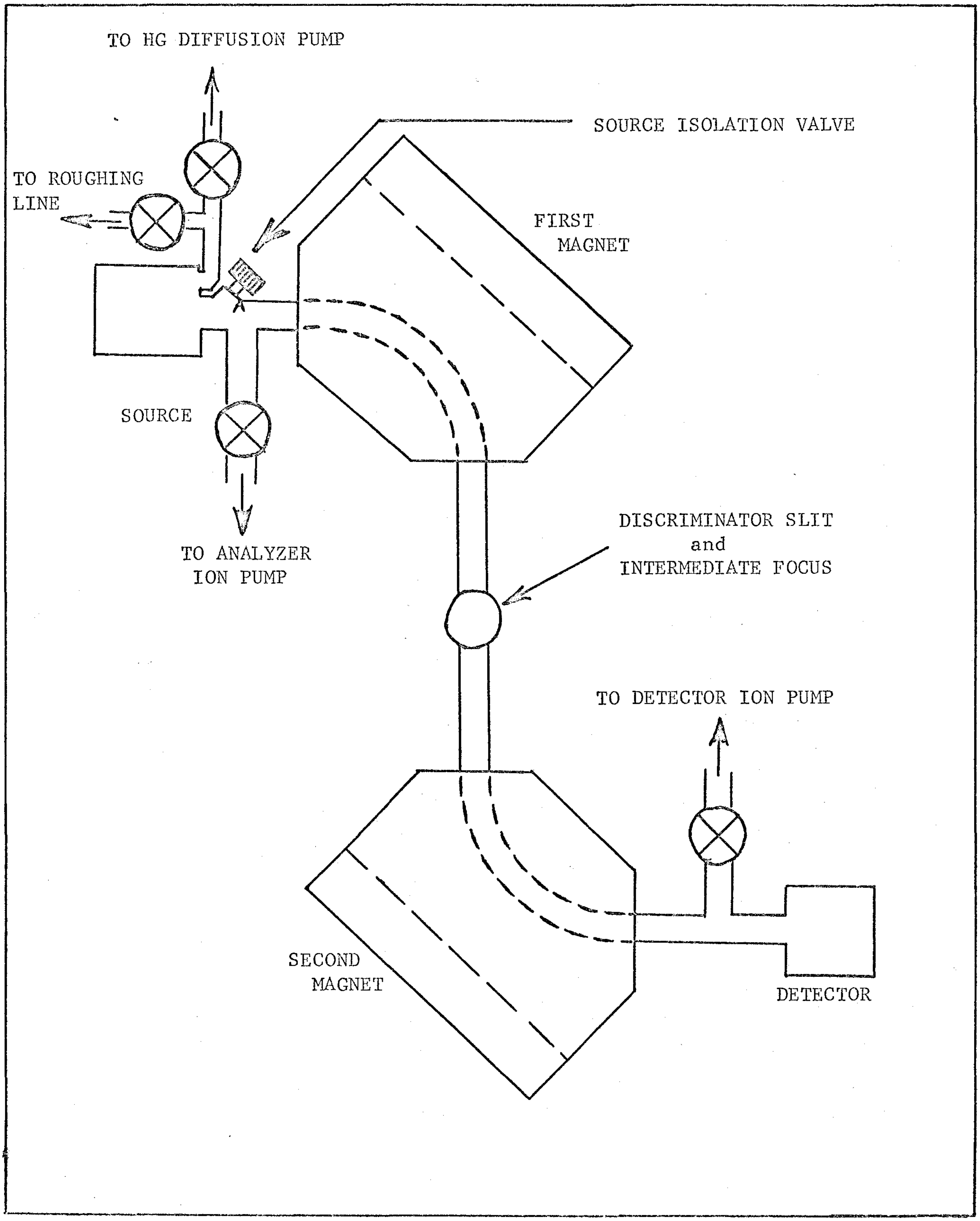


FIG. 4 PHYSICAL LAYOUT OF MASS SPECTROMETER

At each of the two focal positions there is a slit system complete with a repeller and half plates, as is shown in Figure 1, for the final collector position. The width and orientation of each slit can be adjusted independently by means of external controls. A Faraday bucket collector can be made to intercept the ion beam at the discriminator focus, thus converting the machine to a single stage mass spectrometer. This provision is useful in the establishment of the initial alignment of the magnets and in checking the ion transmission through the analyzer. The Faraday collector at the final focus can be used as a simple current collector and for checking the electron multiplier current gain.

The analyzer tube is made of 1 1/2 inch nonmagnetic stainless steel tubing which has been flattened in the region of each magnet so as to be accommodated by the 7/8 inch magnet gap. The outside of the tube is wound with resistance heating tape designed so that the whole high vacuum region can be degassed at temperatures up to 300°C for long periods of time. This feature is important when it is desired to achieve a very low operating pressure.

The magnets were designed to be identical in physical dimenions and in resulting magnetic induction. A shunt arrangement, which acts on one of the magnet coils, was provided to make possible the precise matching of the two magnetic fields. The arrangement of the magnet coils and the fine current control isshown in Figure 5.

The vibrating reed electrometer head and the pre-amplifier are mounted close to the electron multiplier at the final focal position.

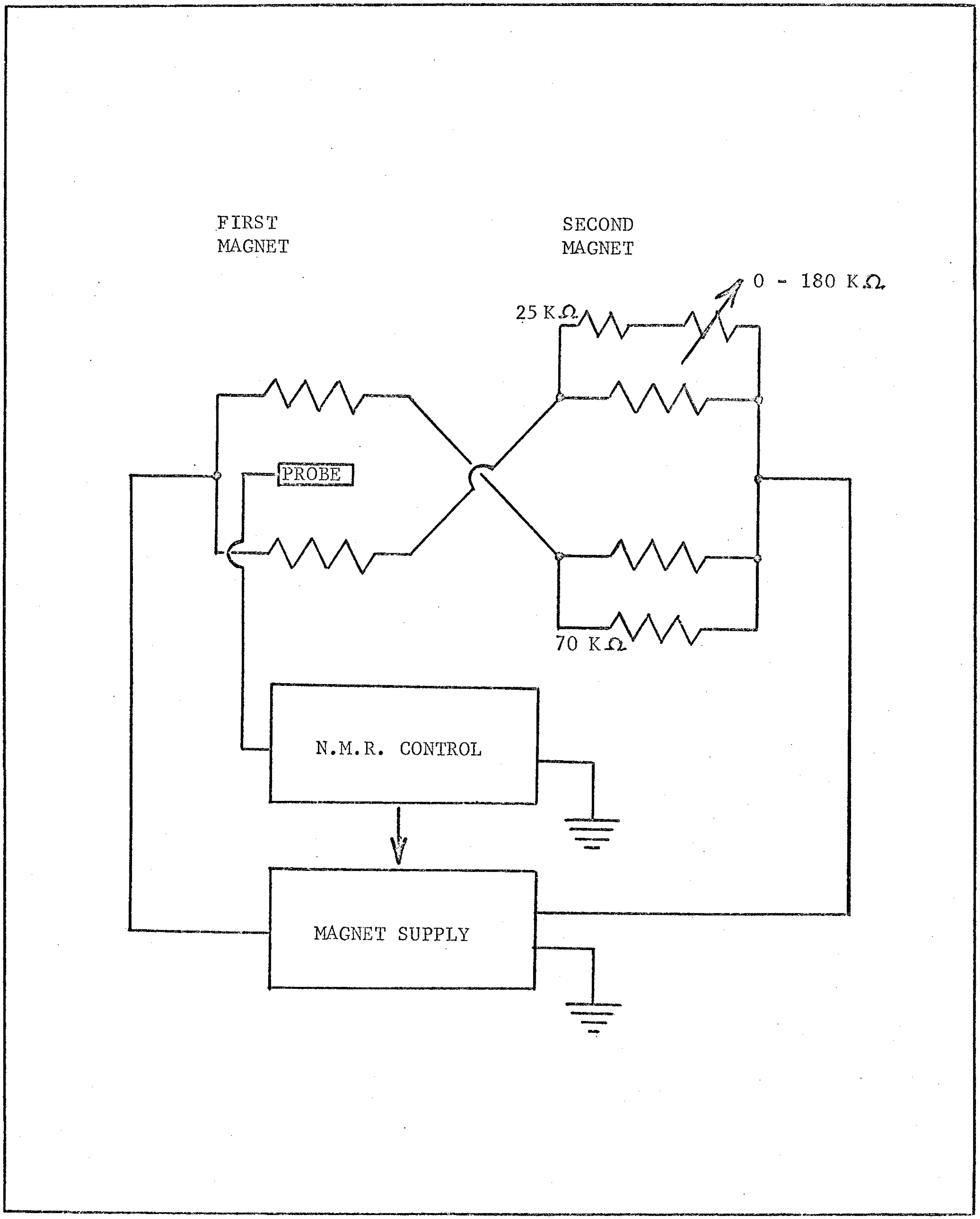


FIG.5 ELECTRICAL CONNECTIONS TO MAGNETS

All other electronic components are conveniently rack mounted and the operator's control desk is centrally located in front of the electronic units.

3. VACUUM SYSTEM

(a) General

Figure 4 gives the location of the three high vacuum pumps which serve to evacuate the analyzer tube. This figure also shows the position of the source isolation valve, which when closed allows the analyzer pressure to be kept below 5×10^{-6} torr while the source is open to the atmosphere.

As originally constructed, the high vacuum in the mass spectrometer was achieved by three large mercury pumps; one pumping on the ion source, and the other two serving to evacuate the analyzer and the detector regions. Each of these pumps was properly baffled and had a liquid nitrogen trap. These were kept filled by means of an automatic demand system which was connected to a large liquid nitrogen container. In practice this arrangement proved to be unreliable.

To make the spectrometer more useful as a research instrument, the entire vacuum system was redesigned. The source mercury pump was retained, but the source vacuum section was modified to allow for a rapid pump down of the source region following a sample change. This mercury pump can also be used to purge the entire high vacuum system of rare gases for which ion pumps show a small pumping efficiency. (Barrington, 1963)

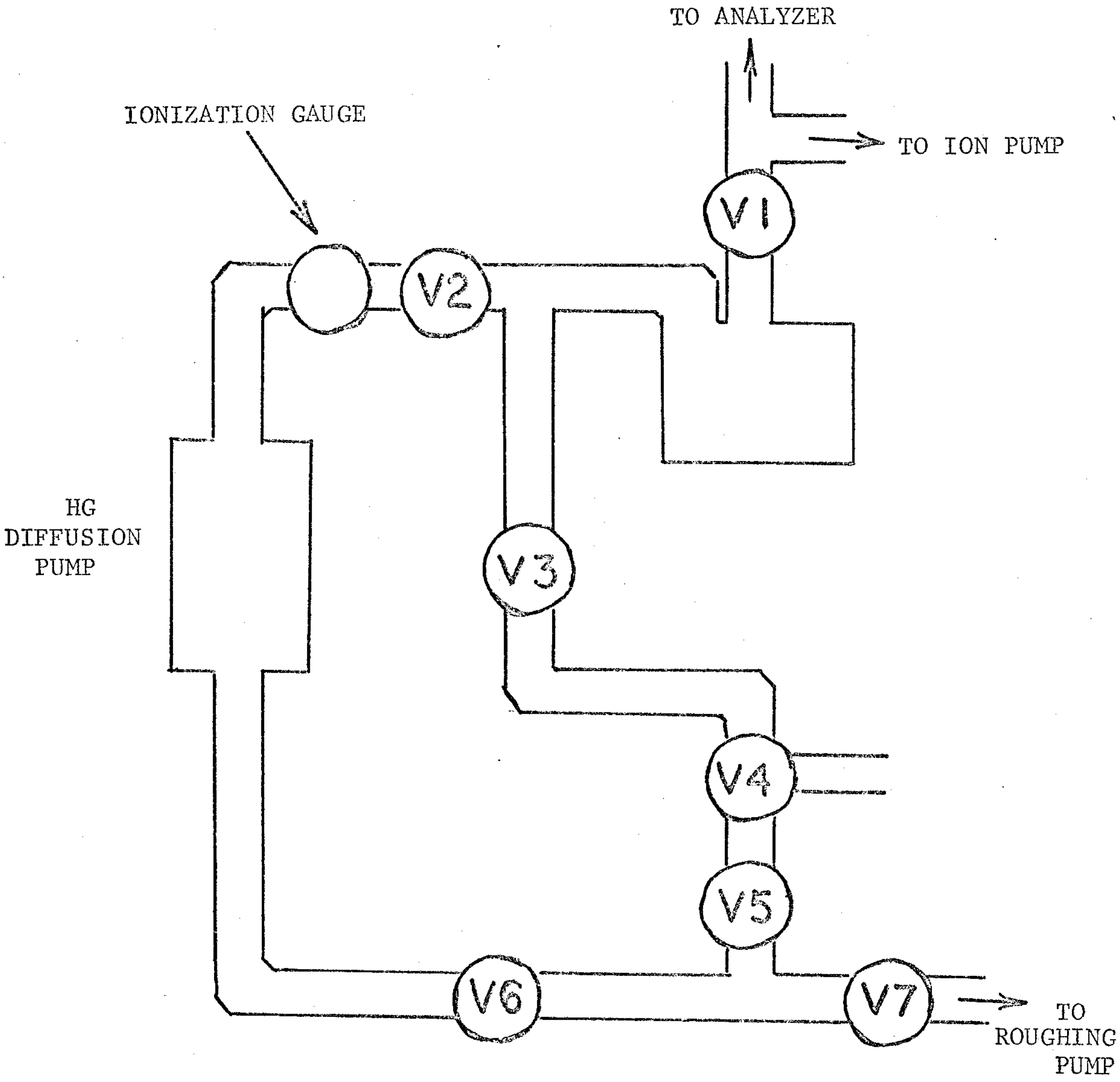
The analyzer and detector mercury pumps were each replaced by a 50 liter/second Ultek model 20-044 sputter ion pump. Both pumps are energized by the same power supply. (Ultek model 60-062L) A valuable new feature is the addition of a 2 inch right angle ultra high vacuum valve (Granville-Phillips series 205) between the analyzer tube and each ion pump, thus making it possible to use the mass spectrometer as a "static" system with a resulting increase in sample detection sensitivity. (Reynolds, 1956)

The high vacuum part of the machine, as noted earlier, is made of an all metal construction and is free from organic materials, with vacuum tight connections between the various components being made by gold gasket seals. (Tasman, Boerboom and Kistemaker, 1963)

(b) Source Pump Down System

A schematic diagram of the new source pump out system is shown in Figure 6. With the arrangement indicated, the analyzer and mercury pump pressures are better than 5×10^{-6} torr and 1×10^{-8} torr respectively when the valves V1 and V2 (Figure 6) are closed and when the source is at atmospheric pressure.

The source pump down from atmospheric pressure is achieved in two stages. In the first the source is roughed from atmospheric to backing pressure and then the mercury pump is made to evacuate the source region. When the pressure as indicated by the ionization gauge is less than 10^{-5} torr, the ion pumps are also made to pump on the source.



V1 - SOURCE ISOLATION VALVE
V2 - GRANVILLE-PHILLIPS 1" type L ULTRA HIGH VACUUM VALVE
V3 - NUPRO 1/4" HIGH VACUUM VALVE
V4 - VENTING VALVE
V5,V6 - VEECO 2" BELLOWS VACUUM VALVE
V7 - EDWARDS HIGH VACUUM MAGNETIC VALVE - Type D-11307

FIG.6 SOURCE PUMP OUT SYSTEM - SCHEMATIC

For overnight setting, and during a sample analysis, the ion pumps alone are used to achieve and maintain the analyzer high vacuum. The most important feature of this new source pumping system is that the evacuation of the source from atmospheric to operating pressure can be achieved very rapidly.

In the year that the system has been in operation, consistently good pumping has been obtained. Pressure in the analyzer region of 10^{-8} torr can be routinely obtained, even during a sample run. No interference with electron multiplier operation in either D.C. or pulse counting operation has been experienced. (Barrington, 1965)

4. Electronic Components and Systems

(a) General

A block diagram of the electronic units used on the McMaster tandem mass spectrometer is shown in Figure 7. Most of these components are of conventional design and were obtained commercially.

Several papers have appeared in the literature in which analytical machines and circuits similar to those used here have been described. (White, et al, 1952, 1954a, 1954b, 1958, 1961b, 1963; Sheffield and White, 1958; Dietz, et al, 1960b; Cathey, 1960; Chastagner, 1961; Wilson, 1961, 1963a; Young, et al, 1963; Ridley, et al, 1965a; Ionov and Karataev, 1962, 1964; Kel'man, et al, 1965)

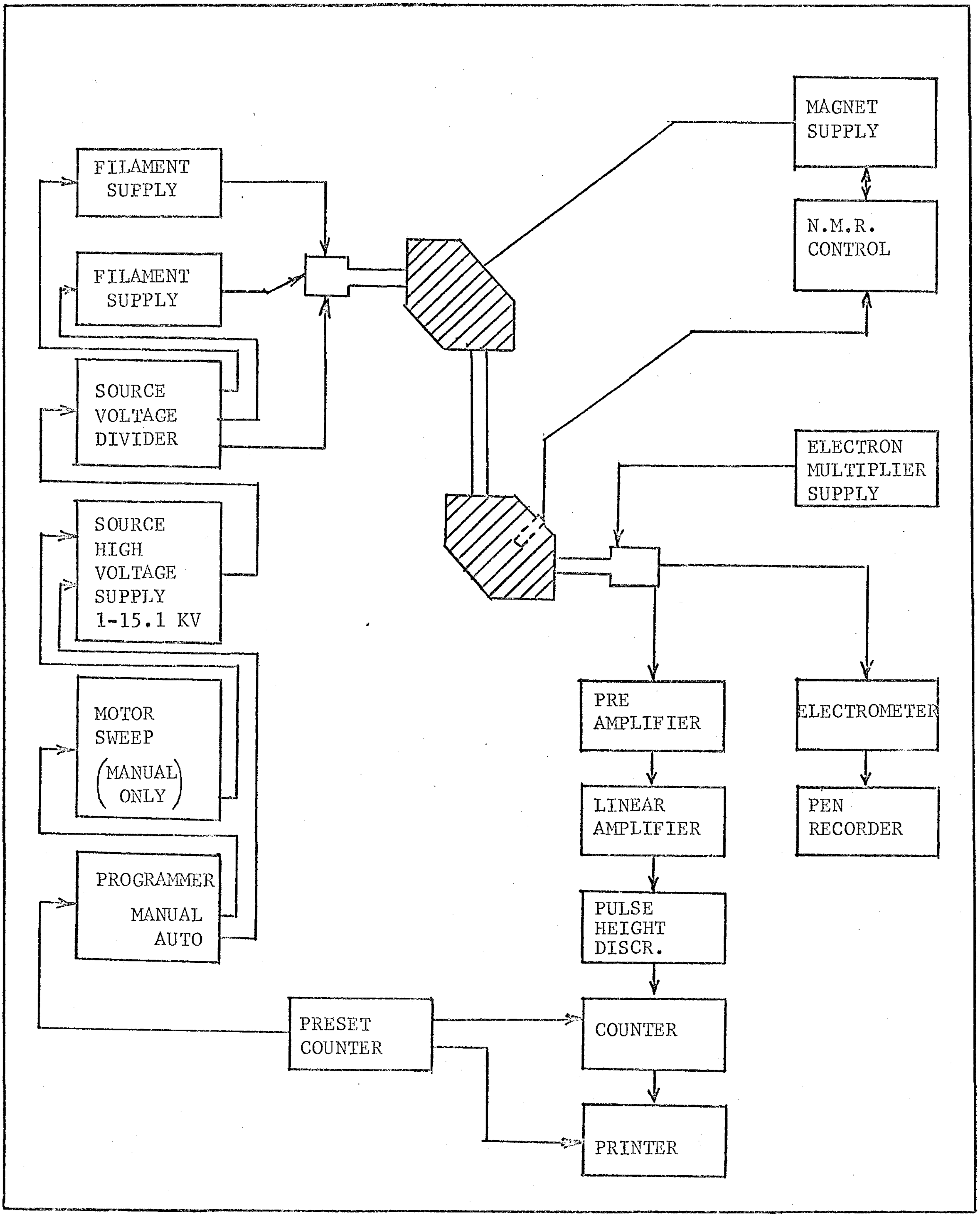


FIG.7 BLOCK DIAGRAM OF ELECTRONICS

(b) Magnets

In conventional mass spectrometers, especially in those which use an electron impact source along with small auxiliary source magnets, it is common practice to sweep the mass spectrum past the detector slit by varying the magnetic induction of the sector magnet while keeping the source voltage constant.

However, when two magnetic analyzers are used in series, and when the ions are required to have the same mean radius of curvature in each magnetic field, it is very difficult if not impossible to sweep both fields in such a way that they have the same magnitude over the path of the ion beam at each instant of time. The hysteresis effect would make rapid magnetic switching and thus ion counting very difficult. These problems can be resolved by simply keeping both magnetic fields constant, and by varying the accelerating voltage in the source in order to scan the mass spectrum.

A highly effective means of regulating the two electromagnets must be found. It is not enough to adjust the two fields to be equal and then use a current regulated magnet supply. What is needed is a method of continuously sensing and then controlling the magnetic fields.

One must have both relative and absolute stability in the magnetic fields. The former is necessary so that a given ion will experience similar conditions in each field. The latter condition must be satisfied so as to preserve a fixed relationship between the accelerating voltage and the magnitude of the magnetic fields. (B^2/V = constant, where B is the value of the magnetic induction and V is the value of the source accelerating voltage) In the ion counting mode where alternate switching from one mass peak to another occurs, it is important that the conditions for the optimum ion transmission through the machine do not change, even after a considerable time has elapsed from the time of the initial adjustment.

A schematic diagram of the electrical connections to the magnets is shown in Figure 5. Each sector has two exciting coils and the two magnets are wound in the "series-parallel" method indicated. To be able to match the two magnetic fields accurately, a shunt arrangement which was constructed of low temperature coefficent resistors was installed across the appropriate coil of the second magnet.

Both magnets are supplied by a Varian model V2200A current supply. A Varian model F-18 nuclear fluxmeter equipped for proton resonance is used to match and then maintain one of the magnetic fields at a desired value. The fluxmeter reference frequency is obtained either from a variable frequency oscillator or from an auxiliary standard crystal operated in the parallel resonance mode. In practice, the latter method of control is more reliable.

When the temperature of the laboratory is kept constant to within a few centigrade degrees and the magnets have been operating under given conditions for longer than a day, the stability of the magnetic fields is found to be excellent.

(c) Source Electronics

The ion lens system which is presently in use on the mass spectrometer is of the thick lens type, a diagram of which appears in Figure 8. The machine was originally equipped with a thermal

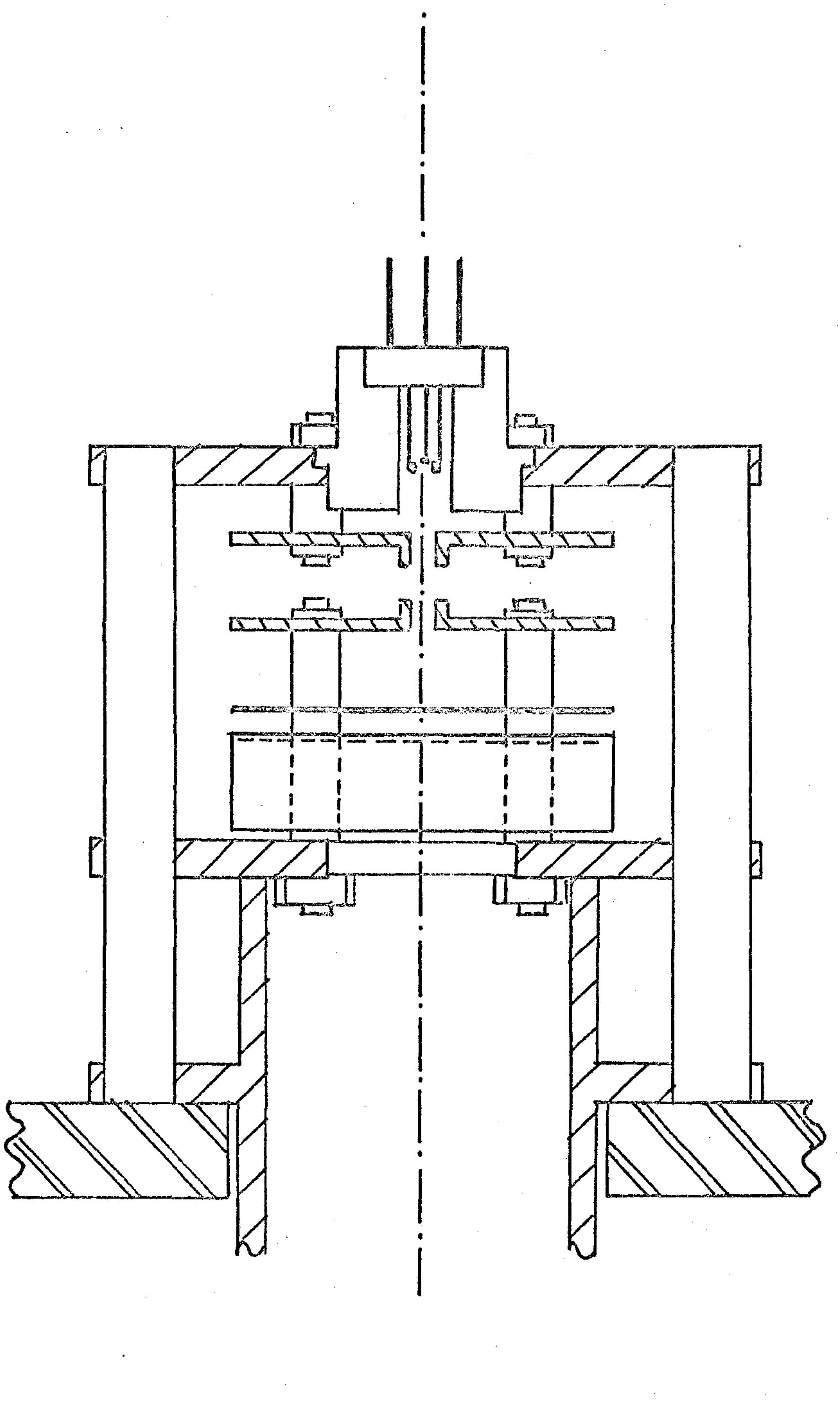


FIG. 8 THICK LENS SOURCE ASSEMBLY

ionization source of the triple filament variety. (Inghram and Chupka, 1953) The crucible type source to be described later was designed to be easily accommodated by the existing ion optical system. The construction of an alternate gas handling facility using the original source focusing plates is now under way. The spectrometer will function well with any source which can produce essentially mono-energetic ions from a localized region.

The accelerating voltage is provided by a Beva Laboratories model 315C-2P, 1-15.1 kV power supply. Since this unit has an operational amplifier in the low voltage portion of its output, a linear voltage scan can be easily introduced into the source voltage.

The potentials on each of the various source plates are derived from a specially designed voltage divider or source focusing control unit, a schematic diagram of which is shown in Figure 9. An ammeter in the low voltage portion of this divider is used to monitor possible trouble in the divider chain, since in the event of an open circuit somewhere along the bleeder no current flows through the meter.

Two identical regulated power supplies are used in the operation of the triple filament thermal ionization source. (Dressen-Barnes model 62-142) These supplies can produce 10 amperes at 35 volts, and have excellent current regulation. When the crucible or the gas source are used the emission regulated power supply shown in Figure 10 provides the required operating conditions.

The high voltage can be changed manually, or can be varied automatically at a desired rate by means of a constant speed motor

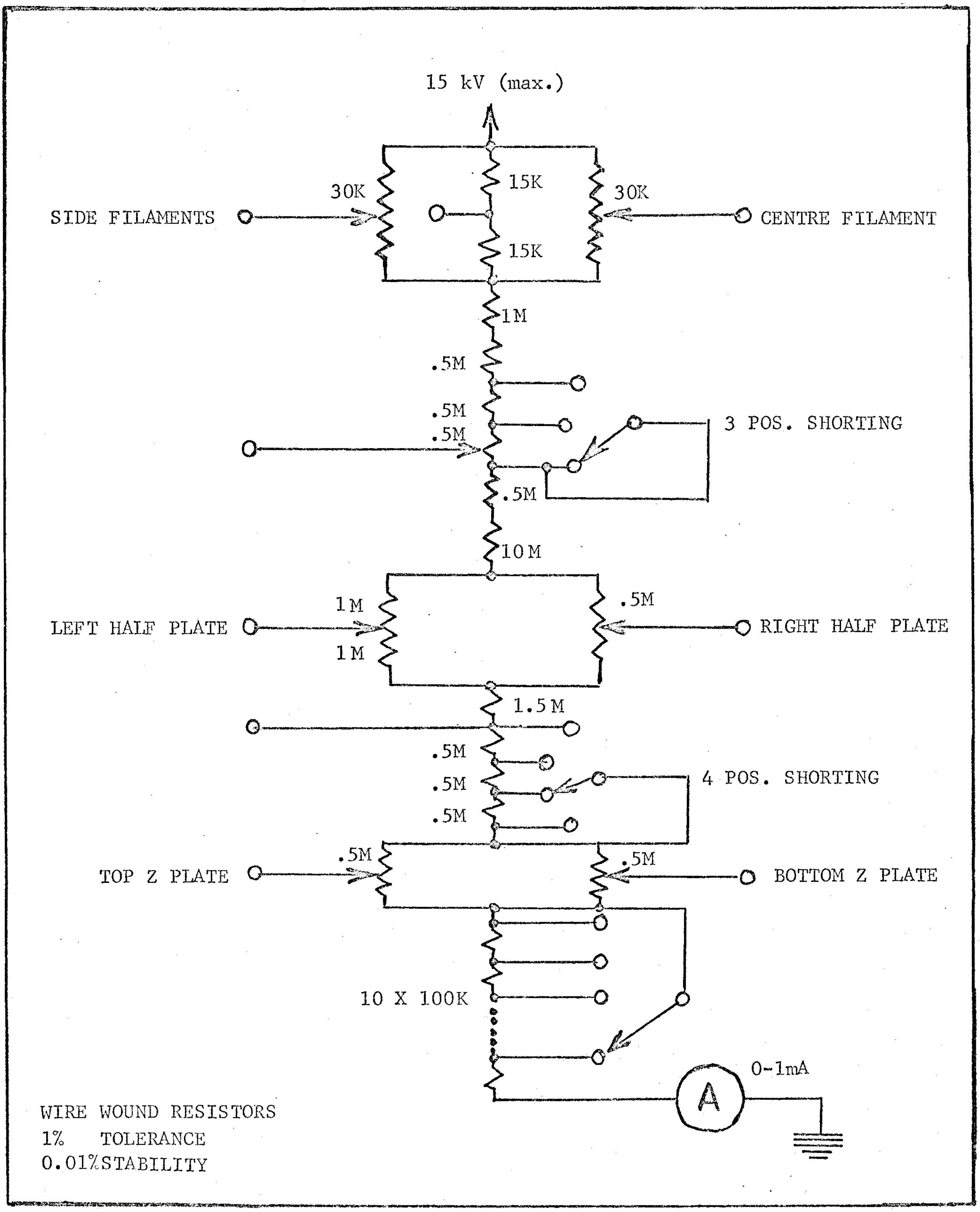


FIG. 9 SOURCE VOLTAGE DIVIDER

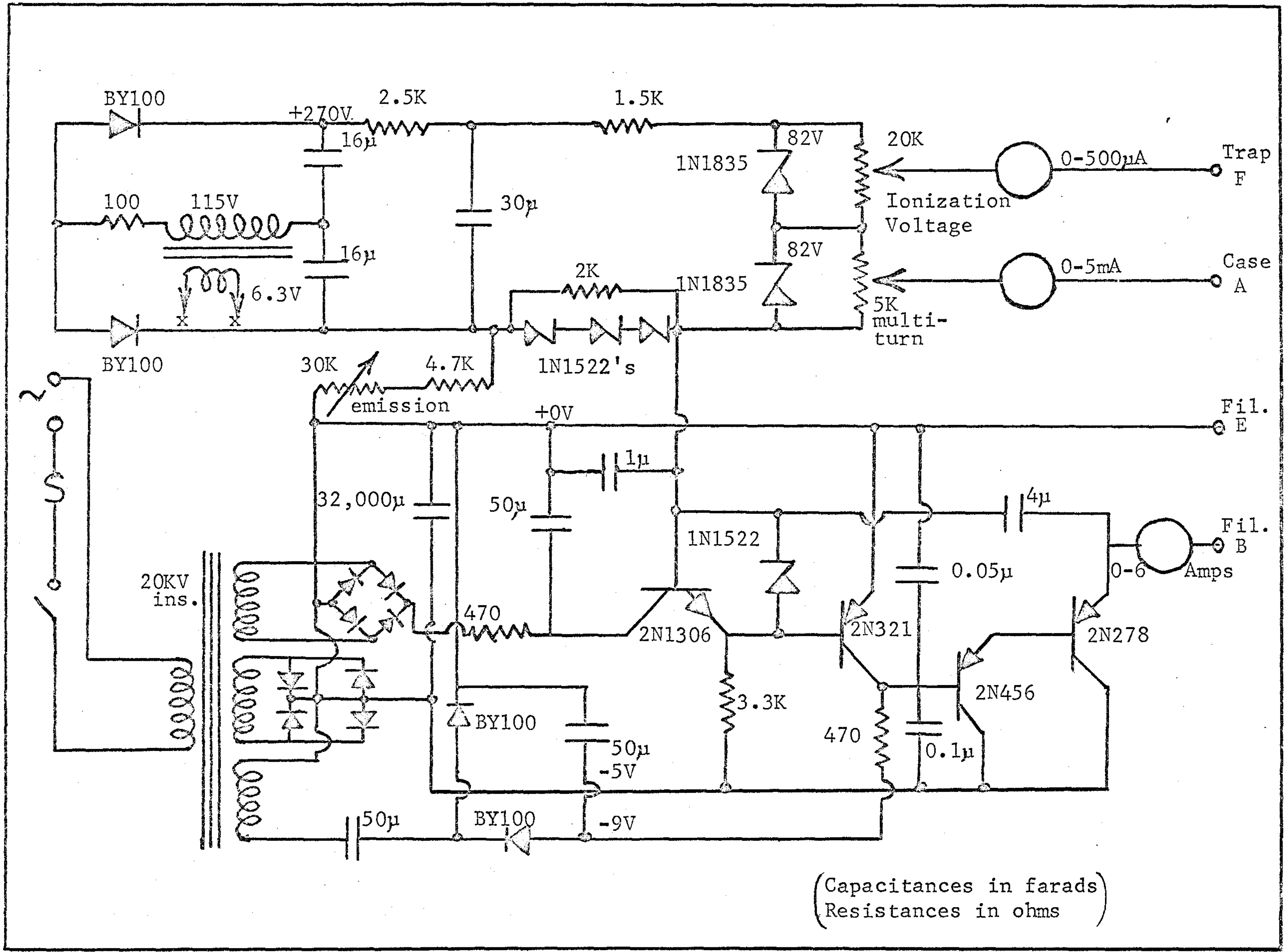


FIG. 10 EMISSION REGULATOR - SCHEMATIC

controller. (Heller model 2T-60) The maximum range of the sweep in the present system is 10% of the indicated source voltage. For ion counting applications the source voltage is alternately switched to one of two pre-selected values by means of a programmer.

(d) Detector System

Ion detection is possible by either direct collection at the discriminator, or at the second focal point; or alternately by means of an electron multiplier which is located near the final focal position. This multiplier can be operated in either the direct current integration or in the pulse counting mode.

A diagram of the final detector assembly showing the slit system and the electron multiplier is given in Figure 1. In many applications the repeller and the two beam centring plates are grounded. In operation the conversion dynode of the electron multiplier is put at -5 kV. There is a constant voltage drop from one dynode to the next, such that the anode is at approximately -300 V.

The voltage necessary to operate the electron multiplier is supplied by a Hamner model N-413 mechanical chopper stabilized power supply.

The signal taken from the collector dynode is developed across a large resistance and is amplified by a Cary model 31 vibrating reed electrometer whose output is displayed by means of a Honeywell 1/4 second recorder. (Model 153X16-V B-II-III-118)

The signal from the last dynode is A.C. coupled to the input of a Victoreen model P-30 preamplifier. Here a small signal amplification occurs and the resulting pulse is matched by the output cathode follower to a coaxial cable. The pulse is then sent to a linear amplifier (T.M.C. Model A1-4A) and must there pass a pulse-height discriminator before it can be standardized by a monostable output circuit. The standardized pulse is allowed to enter a fast counter (Beckman model 7070R) if the pre-adjusted time gate from the preset counter (Beckman model 7426AR) is open.

At the end of the particular counting interval under consideration the counts accumulated in that interval are transferred to a Beckman model 1453 printer and are typed out in digital form on paper tape.

As an alternate method of data acquisition, it is also possible to integrate the pulse counting rate by means of a ratemeter. (T.M.C. model RM-1B) In this case, the signal from the one-shot output circuit is fed into the ratemeter whose output is passed to the recorder for a physical integration of the count rate. This method of recording data was not found to be satisfactory.

A system which may prove to be more advantageous, but which has not yet been incorporated on the present mass spectrometer, is that of using an interval integrator such as is described by White, Collins, Sheffield and Roe (1952). Unlike the more conventional ratemeter, the unit there described allows the recording of low counting rates and responds rapidly to changes in these rates.

It may also be possible to increase the usefulness of the present machine by the incorporation of certain aspects of current developments in data acquisition systems (Ridley and Young, 1965b; Barton, Gibson and Tolman, 1960; McCullough and Krouse, 1965; Hagan and deLaeter, 1966) and by using more advanced operating techniques. (Dietz, Pachucki and Land, 1962, 1963; Thomason, 1963; Jaech, 1964a, 1964b; Ridley, Daly and Dean, 1965c)

A very convenient and important feature of the present detection arrangement is that while pulse counting is in progress, a simultaneous recording of the integrated multiplier output current can be made. It is thus easy to discover possible variations in an isotope ratio when this ratio is obtained in two fundamentally different ways. This arrangement also facilitates the adjustment of the source voltages.

C. EXPERIMENTAL

1. ION SOURCE PROBLEMS

(a) Introduction

When it is necessary to analyze a very small amount of sample material mass spectrometrically, it is essential that the ionization process be as efficient as possible.

In the region of symmetric fission, the important end-product nuclides of the various fission chains are Sn, Cd, Ag and Pd. When relatively large samples are available, satisfactory analyses of these elements can be performed with a thermal ionization source. (Ag: Crouch and Turnbull 1962b; Shields 1966; Sn: deLaeter and Jeffery 1965; Cd: Turnbull 1963; Pd: Turnbull 1963)

The thermal ionization mechanism has been used as a source of positive ions in mass spectrometry since 1918. (Dempster)

The effectiveness for ion production by this means has been shown by Langmuir and Kingdon (1925) to depend on the electron work function ω and the temperature T of the ionizing surface and on the ionization potential I of the sample material through the relationship

$\frac{n_+}{n_o} \approx \exp\left[\frac{e(\omega - I)}{kT}\right]$. For the elements quoted above, $I \gg \omega$ and thus the ionization efficiency for positive ion production is very small.

$\left(\text{i.e. } \frac{n_+}{n_o} \ll 1\right)$

Usually an ionizing filament made of W, Re, Ta or Pt is used, since each of these metals has a high ω and can be heated to a high temperature, thus favouring the emission of ions. It has, however, been found (Weiershausen, 1963) that for tungsten the electron work function decreases from a maximum value of 6.5 e.V. at 2000° K. to a substantially lower value as the filament temperature is increased. There thus exists an optimum temperature for the most efficient operation.

Inghram and Chupka (1953) introduced a triple filament source in which the ionization efficiency and the sample evaporation rate can be varied almost independently. Even with this improvement many elements cannot be readily ionized.

An ingenious technique has been used, the purpose of which is to raise the work function of the ionizing surface, especially when tungsten is used as the filament material. In practice one finds large quantities of alkali metal ions which originate from the tungsten filament. A large fraction of these can be removed by pre-treatment of the filaments, but the impurities which remain tend to lower the work function of the surface, thus greatly reducing the emission of the desired sample ion species.

It has been found that the addition of a small "matrix" of borax or boric acid onto the ionizing surface before or during the sample application increases the ion current which can eventually be obtained from the sample material. (Hand, 1953; Crouch, 1960, 1962a)

The factors which contribute to the enhancement of the desired ion current are not known and satisfactory analyzing conditions are not easily reproduced. The main difficulties are that the magnitude and stability of the ion currents which are eventually obtained depend very strongly and unpredictably on the length of time taken and the particular method which is used in the pre-treatment of the filament surfaces.

It is the author's belief that with present (1966) surface ionization techniques the mass spectrometric analysis of tin atoms when the sample size is smaller than 10^{-7} gram of any one isotope is impossible.

(b) Description and Construction of the Crucible Source

It was realized that a satisfactory source for the analysis of sub-microgram quantities of tin in solid form would have to be based on an electron impact mechanism. The source which is described below was patterned after a design due to Tyrrell, Roberts and Ridley (1965), and can be installed with a minimum of alteration to the existing mass spectrometer source lens system.

A diagram which shows the mounting of the new crucible source is shown in Figure 11. The ionization box with the dimensions indicated in Figure 12 is firmly positioned onto a standard triple filament support. (A.E.I. model number 273205/2, style 297156 or 254918).

In the crucible source the sample atoms in solution are pipetted onto the centre or sample filament by means of a spitzer, as ordinarily used in surface ionization work. (Spitzer and Sites, 1963; Turnbull, 1963)

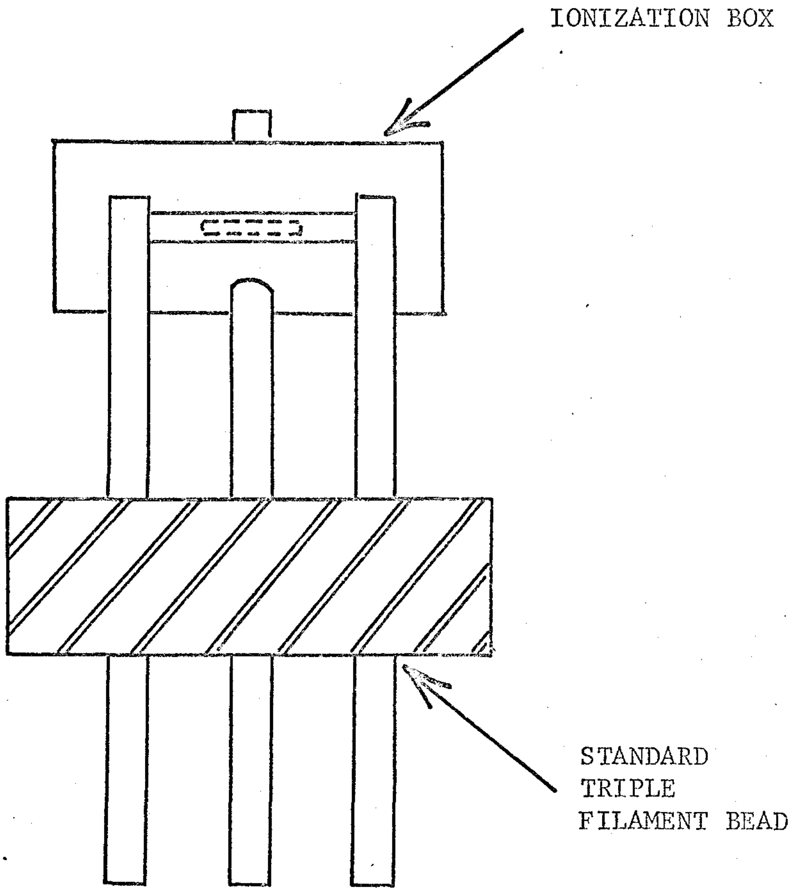
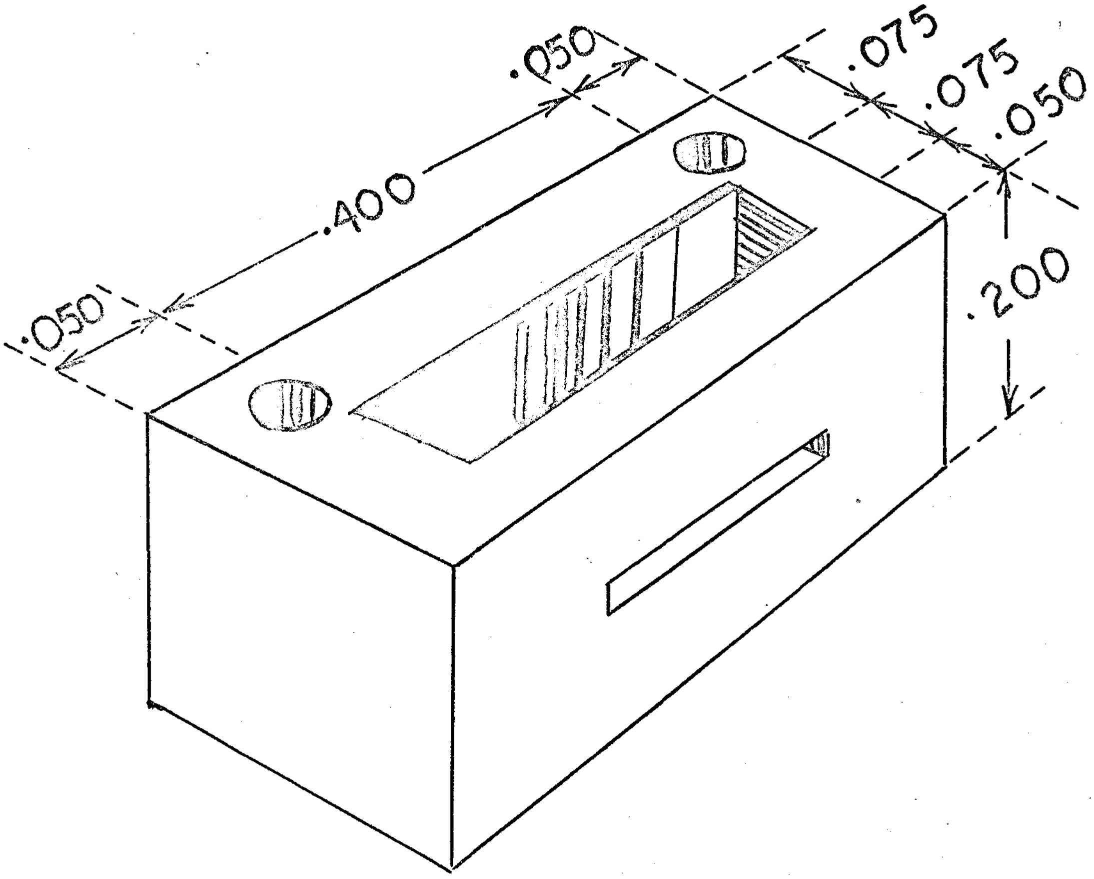


FIG. 11 CRUCIBLE SOURCE — MOUNTING



MATERIAL: ....INCONEL

DIMENSIONS OF BOX:................0.500 x 0.200 x 0.200 inch

DIMENSIONS OF COLLIMATING SLIT:...0.015 x 0.125 inch

FIG. 12 IONIZATION BOX - PERSPECTIVE VIEW

During an analysis atoms are evaporated at a desired rate by heating the sample filament electrically. The electrons which are produced by the side filament are accelerated towards the ionization box, which when properly aligned with the side filament allows a well collimated beam of electrons to enter the ionizing region. Those evaporated sample atoms which cross the path of the electrons may become ionized. The filaments are arranged so that it is impossible for an electron which is released from the side filament and which passes through the collimating slit to strike the centre filament.

The currents for the sample and side filaments are obtained from the same current regulated power supplies which are used for the surface ionization source. Figure 13 shows the electrical connections to the crucible source as used in the work which is reported below. The electron current can be controlled by the emission regulator, a circuit diagram of which is shown in Figure 10.

The ionization box was constructed of inconel with dimensions indicated in Figure 12 and was specially designed to fit onto the standard triple filament head. A description of the modifications which were made to the existing filament supports in order to accommodate the new crucible source follows.

The filaments were first removed from their Nilo-K supports and the two centre studs were each shortened by approximately 1 mm. The two pins which will hold the ionization box were then reshaped such that the sample filament supports were located centrally in the ionizing region. The two pins which are to hold the side filament were next bent so that when the box was in the operating position

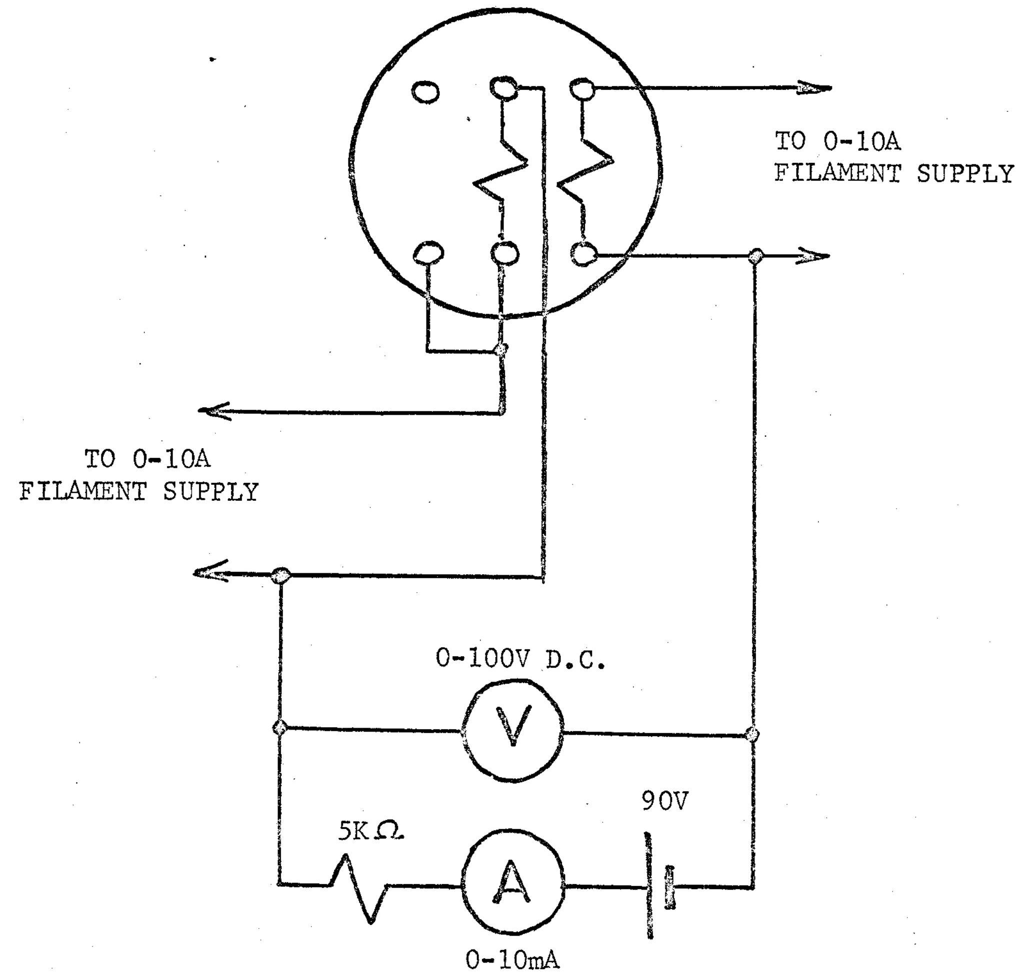


FIG.13 ELECTRICAL CONNECTIONS TO CRUCIBLE SOURCE

there was a distance of approximately 2 mm. between the box and each of the side filament supports.

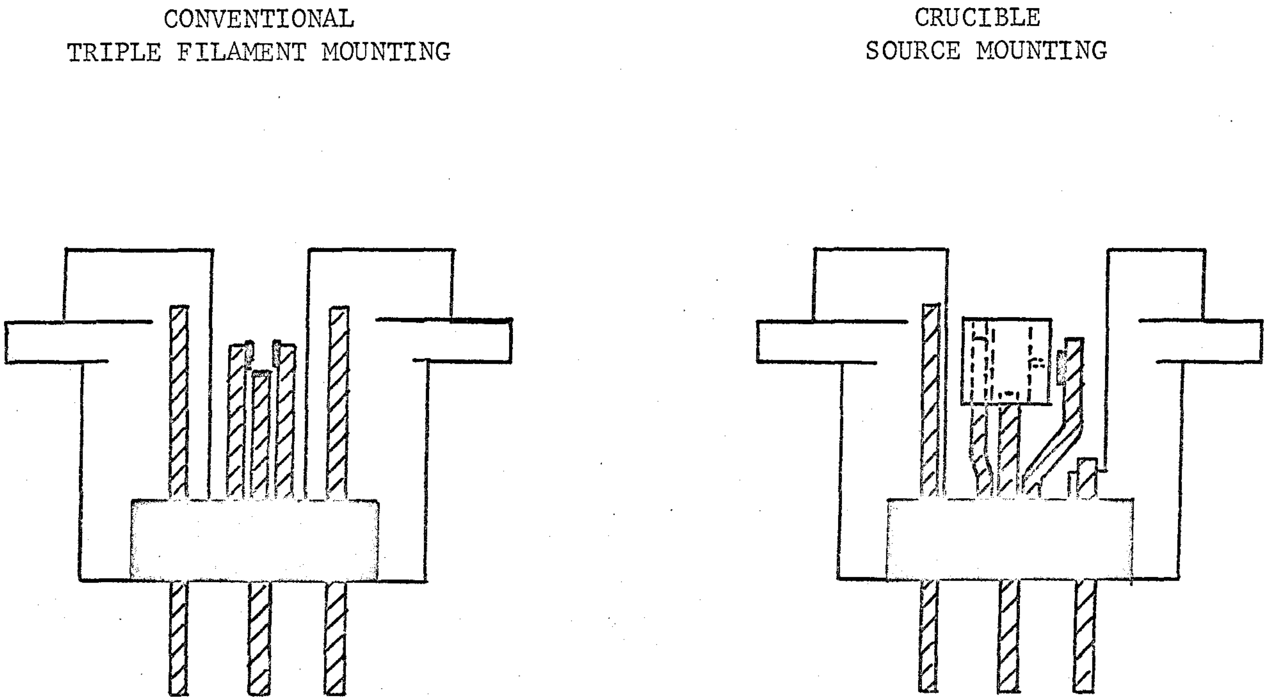
Since the new source must fit into the slightly modified source hat shown in Figure 14, both guide pins on the original triple filament bead were retained. For convenience in later alignment it was found best to shorten the guide pin which was closer to the side filament so that only about 4 mm. of this pin protruded above the glass bead. A comparison of the source hats as used with the conventional triple filament source and the electron bombardment source is shown in Figure 14.

The ionization box was removed from its mount and a 0.001 X 0.030 inch tungsten filament was spot welded to the centre supports. A filament of similar size was also welded onto the side supports so as to show a slight convex curvature towards the ionization box. It was arranged so that the smallest distance between the side filament and the ionization box was approximately 0.5 mm.

(c) Source Cleaning and Sample Introduction Procedures

For the first few filaments which were prepared very large hydrocarbon and smaller cadmium peaks were observed.

After extensive degassing of the mass spectrometer source region and the adoption of improved source handling techniques the residual hydrocarbon peaks were reduced to $< 10^{-18}$ amperes and the cadmium peaks could not be detected. Disposable sterile gloves were worn throughout the shaping of the filament supports and during the spot welding procedure.



CONVENTIONAL
TRIPLE FILAMENT MOUNTING

CRUCIBLE
SOURCE MOUNTING

FIG. 14 COMPARISON OF TRIPLE FILAMENT AND CRUCIBLE SOURCES

A satisfactory method for cleaning the two filaments, the ionization box and the filament hat will now be given.

The modified filament bead with the new filaments attached, the ionization box and the source hat were separately immersed for a few minutes in a solution of concentrated nitric acid at room temperature in order to remove traces of organic material. After a thorough rinse with ordinary tap water the three pieces were dried and thereafter handled only by clean metal pliers.

It was found early in this work that a tungsten filament electroplated with a layer of thorium oxide (ThO_2) gave the same electron emission but at a much reduced filament temperature than a similar uncoated filament. (Hanley, 1948) In the electroplating process, a current of approximately 0.4 mA was allowed to flow for about 2 minutes between a nickel anode and the side filament. The ThO_2 in suspension was kept agitated by a magnetic stirrer.

The coating on the side filament introduced no background into the recorded mass spectrum from mass 106 to 130, nor was there any detectable increase in the operating pressure, even when the side filament was hot enough to produce an electron current of 10 mA.

The final cleaning of the filaments and the inconel pieces was done by resistance and electron impact heating respectively, and was performed in a small auxiliary vacuum system.

The side and centre filaments were heated by passing 5 A.C. amperes through each filament for approximately one hour.

A facility was constructed which allowed the electrons emitted from a thoriated tungsten filament to be accelerated through a potential difference of 1 kV. The filament hat and the ionization box were thus heated to a dull red heat by the energetic electrons. Since inconel has a very low thermal conductivity, local hot spots and subsequent sputtering can occur if the heating is not done very slowly.

No "memory" effect was ever found with tin even when sample sizes as large as 10 micrograms had been analyzed immediately before a much smaller sized sample. Nevertheless, the source cleaning procedure described above was followed for each sample which was analyzed with the crucible source.

The tin in the samples was initially in the chloride form. When it was desired to work in a fluoride medium an excess quantity of HF was added to the original solution.

The sample was applied a small droplet at a time onto the horizontally positioned flat centre filament. After each application, the excess water was carefully evaporated from the sample filament, either by infrared or by electrical heating. After the sample application was complete the ionization box was carefully placed onto its supports and aligned so that the electron collimating slit was as nearly opposite the side filament as possible. A check was made to ensure that the ionization box and the filaments were electrically isolated.

The filament support with the correctly positioned ionization box in place was carefully inserted into the filament hat. The whole arrangement was then attached onto the ion lens system of the mass spectrometer source.

(d) Performance of the Crucible Source

In all the sample runs which were performed by means of the crucible source, the simple circuit arrangement shown in Figure 13 was used to provide the acceleration for the ionizing electrons. Both the sample and the side filament currents were obtained from current regulated power supplies, but no regulation of the electron emission and thus presumably of the ion current was used. In future work, the emission regulator which is shown in Figure 10 should be used.

Since this work was only intended to assess the feasibility of analyzing sub-microgram quantities of fission product tin, questions such as the possible occurrence or extent of isotopic fractionation of the sample atoms due to the evaporation and ionization mechanisms were not investigated. Work was, however, done to determine the amount and chemical forms of a sample material which was necessary to yield a given accuracy in an isotopic ratio determination, and to ensure that background isotopic peaks due to cadmium, indium and antimony did not contribute to the desired isotope spectrum.

The samples which were analyzed were of natural tin; tin enriched in isotope 116 and fission product tin which had been extracted from an irradiated fuel rod.

It was found that in both the chloride and in the fluoride forms it was possible to detect 10^{-9} grams of a tin isotope. With a sample size of 10^{-8} grams an ion beam of about 10^{-17} amperes was received at the detector, while a sample size of 10^{-6} grams produced an ion beam which was large enough so that the resulting spectrum could be usefully recorded by a conventional vibrating reed electrometer. The crucible source produces tin ions approximately 100 to 1000 times as efficiently as a surface ionization source.

Since a minimum amount of time, say at least 15 minutes is required to be able to measure an isotopic ratio with reasonable accuracy, the ion emission rate should not decrease too rapidly as a function of time.

At the same source conditions it was found that a more stable ion emission rate could be obtained from a larger rather than from a smaller sample. Thus the ion current from a tin sample of 10^{-8} grams decays to about one half its initial value in a few minutes, whereas the beam from a sample of 10^{-6} grams is stable enough to allow the useful collection of data for perhaps two hours. The ion current from a sample in a fluoride form was found to be somewhat more stable than the current from the same sized sample in a chloride medium.

When the previously described cleaning procedure is used it is possible to keep the hydrocarbon background peaks smaller than 10^{-18} amperes in the mass range from 100 to 135. Hydrocarbon interference is not a serious problem in this mass spectrometer since a sufficiently large resolving power is available to completely separate the background hydrocarbons from the isotopic peaks.

In the latter stages of this work no contamination from cadmium or from any other element in the range from mass 100 to 135 was observed when blank runs were made.

(e) Analysis of Fission Product Tin

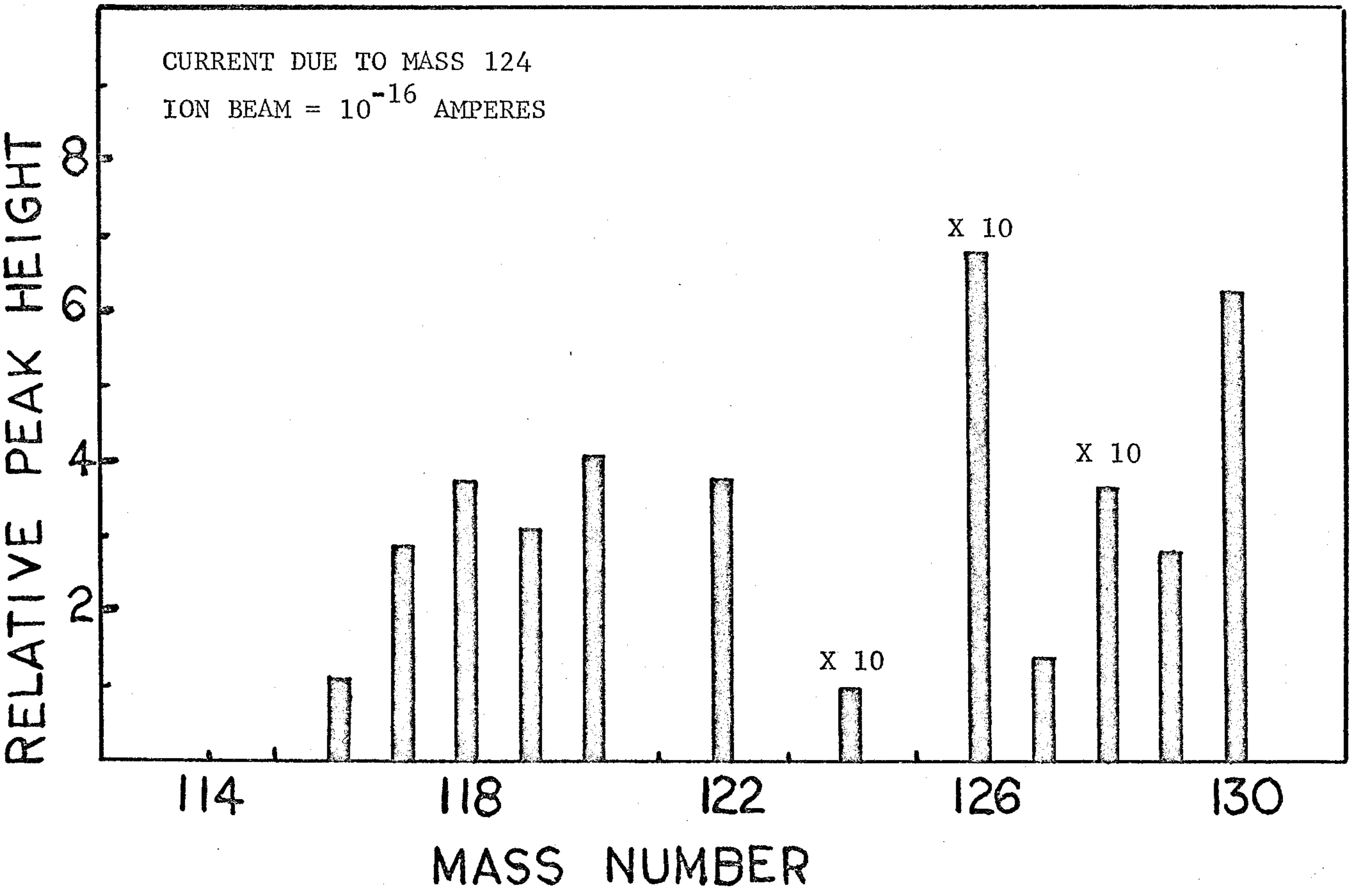
Mass spectrometric studies of the isotopes of tin resulting from neutron induced fission have not been reported in the literature.

Fission product tin was extracted from an irradiated fuel rod (Rod 76) from the Chalk River - NRX Reactor and made available for mass spectrometric analysis. This fuel rod had been exposed to a thermal neutron flux of approximately 10^{13} neutrons cm^{-2} sec^{-1} for about 5 years and it was estimated that the U^{235} burnup was in excess of 50%. Moreover, since the fuel rod was of natural uranium, the fission products formed were undoubtedly produced from the fission of U^{235}, U^{238} and Pu^{239}. From the available data on fission yields for these muclides and estimates of the fraction of U^{238} and Pu^{239} fissions in the rod it is concluded that the approximate contribution to the fission product tin from each fissile nuclide is in the ratio U^{235}: U^{238}: Pu^{239}/ 1: 1: 2.

The distillation process used to recover the tin from a solution of dissolved fuel rod was a quantitative procedure so that isotopic fractionation in the resulting tin sample was considered to be minimal. Even though work was not done to evaluate the extent of isotopic fractionation, the relative ion currents observed in this investigation are believed to be quantitatively accurate to within ± 10%.

An isotope spectrum, of which that shown in Figure 15a is representative, was obtained by scanning in stages from mass 106 to 132 while the evaporation conditions in the ion source were maintained constant. The total mass range was divided into 4 smaller ranges, which

A. RELATIVE OBSERVED PEAK HEIGHTS



B. RELATIVE CORRECTED PEAK HEIGHTS

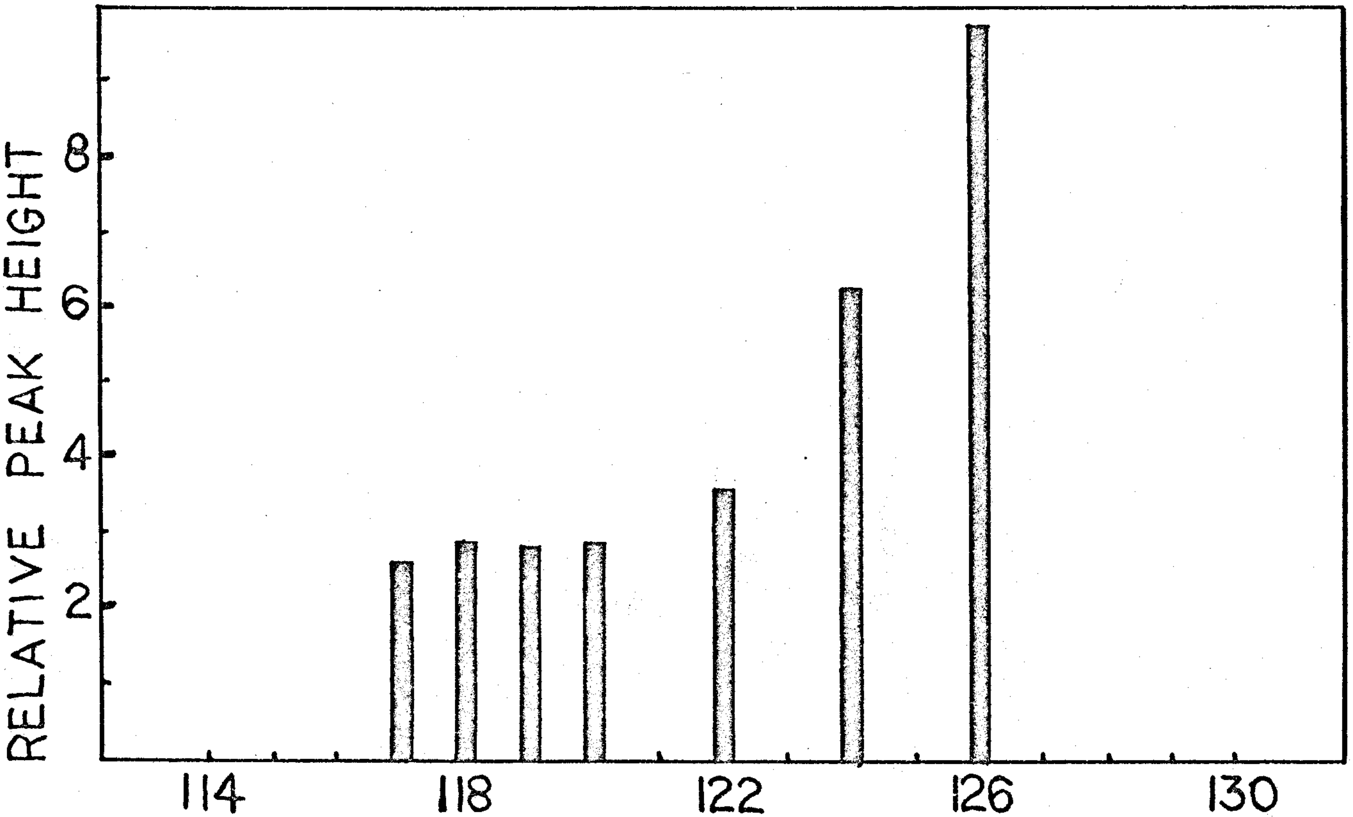


FIG.15 FISSION PRODUCT ISOTOPE SPECTRUM

extended from mass 106 to 110, 110 to 120, 119 to 130 and from mass 126 to 132. A data run was made by scanning up and down the mass range several times. The sample evaporation rate was small enough so that while data were being recorded in any one of the smaller ranges, the peak heights of a given isotope remained essentially constant. After each data run in a given range, the next higher range was scanned in a similar manner.

After the spectrum from mass 106 to 132 had been observed and the average value of each peak had been determined, the data in the range from 119 to 130 were arbitrarily normalized to the mass 124 peak. Since the peaks at masses 110, 120 and 126 are included in adjacent mass ranges, they were used to normalize all the peaks relative to the 124 mass peak.

A histogram which shows the uncorrected relative peak heights of the sample isotopes is shown in Figure 15a. The spectrum was recorded by integrating the electron multiplier current with the vibrating reed electrometer. The sample was in the fluoride form and evaporation of the sample atoms was achieved by passing 1.5 amperes through the tungsten centre filament. With an electron emission from the side filament of 5.0 mA an ion current of 10^{-16} amperes due to the ion species at mass 124 was received at the electron multiplier input. The noise level was approximately 3×10^{-18} amperes.

An inspection of the raw data, as shown in column 2 of Table 1, or as represented in Figure 15a shows that no contamination from cadmium or indium was present in the sample.

TABLE I

FISSION PRODUCT TIN DATA

Mass Number	Relative Observed Peak Height (Mass 124=10)	Peak Height Corrected for In^{115} Contribution to Mass 116 and Iron Contamination	Peak Height Corrected for Natural Tin Contamination	Relative Peak Heights of Fission Tin
106 ⟶ 109	- - -	- - -	- - -	- - -
110	1.6	1.6	1.6*	- - -
111 ⟶ 115	- - -	- - -	- - -	- - -
116	1.12	0.50	0	- - -
117	2.89	2.89	2.63	2.63
118	3.74	3.74	2.90	2.90
119	3.12	3.12	2.82	2.82
120	4.07	4.07	2.92	2.92
121	- - -	- - -	- - -	- - -
122	3.78	3.78	3.62	3.62
123	- - -	- - -	- - -	- - -
124	10.00	6.47	6.26	6.26
125	- - -	- - -	- - -	- - -
126	67.91	9.77	9.77	9.77
127	1.41	0.07	0.07	- - -
128	36.87	0	0	- - -
129	2.81	1.95	1.95*	- - -
130	6.22	0.22	0.22	- - -

* Peaks at mass 110 and 129 disappear as sample filament current is increased.

A peak at mass 116 was observed the magnitude of which remained in an approximately constant ratio to that of the peaks at masses 117 to 122 as the filament condition were varied. Large peaks are present from masses 126 to 130 which changed relative to those at masses 116 to 124 as the evaporation temperature was increased.

The origin of the large peak heights at masses 126 to 130 can be satisfactorily explained by assuming that a fraction of the 126 and 129, and the whole of the 127, 128 and the 130 peaks are due to the ion species $Fe\,Cl_2^+$. The HF and the HCl which were used, contained of the order of one part per million of iron as an impurity. Moreover, no special precautions were taken to exclude iron pick up in the sample handling. The original suspicion that natural iron was an impurity in the sample was strengthened by the fact that a yellow brown deposit was always seen on the sample filmanet after the sample had been deposited on the centre filament.

When the relative isotopic composition of $Fe\,Cl_2$ which is expected from natural iron and chlorine is calculated, and when it is assumed that the mass 128 peak is made up entirely from this source of contaminant, then the observed relative peak heights are modified to those which are shown in column 3 or Table 1. The peak at mass 130 is of the order of the background noise. The fact that the mass 129 peak does not vanish when the iron correction is made is not felt to be a serious objection to the above proposition. The mass 110 and the mass 129 peaks appear to be genetically related, since it was observed that both disappear at higher sample filament currents, well before a marked decline in adjacent peak heights was noted.

The peak at mass 116 cannot be due to Cd, since the chemical procedure used to prepare the sample effectively removed Cd to below detectable limits. Also this peak is unlikely to be due to fission produced Sn, since Sn^{116} is shielded by Cd^{116} in the 116 mass chain.

Two possibilities remain, both of which are felt to contribute to some extent to the observed peak height at mass 116. First this peak is believed to be partly due to natural tin contamination which shows up markedly at mass 116, and secondly, the Sn^{116} may be formed indirectly from the (n,γ) reaction on fission product In^{115} as outlined below. Since the fuel rod had been exposed to a large integrated flux, and since In^{115}, which is the end product of the 115 mass chain, has a large cross section for slow neutron absorption, a significant fraction of the In^{115} formed in fission would eventually be transformed to stable Sn^{116} by the following mechanism:

$$\text{fission chain} \xrightarrow{\beta^-} In^{115} \xrightarrow{(n,\gamma)} In^{116} \xrightarrow{\beta^-} Sn^{116}.$$

With a thermal neutron cross section of 200 barns, a reactor flux of 10^{13} neutrons cm^{-2} sec^{-1}, and an irradiation time of 5 years, the burnup of In^{115} is calculated to be 0.27. If it is now assumed, as appears to be true for the Sn isotopes which are formed near symmetric fission, that the fission yields are approximately the same for adjacent isotopes, it is reasonable to suggest that the yield of In^{115} is roughly equal to the yield of Sn^{117} and Sn^{118}. It is then possible to estimate the fraction of the peak height of Sn^{116} which was due to natural contamination, and the fraction which was produced from fission product indium. Taking account of the fact that the In^{115} was being produced at essentially a constant rate during the irradiation of the fuel it is estimated that 45% of the peak height at mass 116 was due to natural tin. The observed peak heights of the other stable tin isotopes were corrected on this basis, and the results are shown in column 4 of Table 1.

The data which are shown in the last column of Table 1, and which are displayed in Figure 15b are the original observations which were corrected for contamination from Sn^{116} and from $Fe\ Cl_2$. The peaks from mass 117 to 126 represent the relative abundances of the fission product tin isotopes.

It appears that the yields near symmetric fission are essentially the same at the stable mass positions from 116 to 122 and then increase at mass 124 and more sharply at mass 126. The 126 to 124 peak ratio as found here is 1.7 which is significantly smaller than the value of 5.9 which has been reported by Hyde (1964) for U^{235} fission. This indicates that U^{238} and Pu^{239} fission are contributing significantly to the yields of the tin isotopes produced in the fuel rod.

Summary

Fission product tin extracted from a natural uranium fuel rod with high burnup has been analyzed mass spectrometrically. Corrections for contamination in the mass 116 - 130 mass region have been made, and a spectrum which consists of fission product tin isotopes from mass 117 to mass 126 has been found. The relative peak heights of the fission product tin isotopes is believed to be accurate to ± 10%. In the sample which was analyzed, no significant structure in the fission yields near symmetric fission was observed and the ratio of mass 126 to mass 124 was found to be much less than that reported in the literature for fission in U^{235}.

2. ANODE PULSE HEIGHT CHARACTERISTICS OF THE ELECTRON MULTIPLIER

(a) Introduction

Much experimental and theoretical work has been done in an effort to understand the manner in which an electron pulse propagates along the dynode structure of a linear electron multiplier.

Lombard and Martin (1961) were the first to use compound Poisson statistics and the method of generating functions in an attempt to represent the electron multiplication process mathematically. These authors predicted the existence of a maximum in the anode differential pulse height distribution but in their experimental work were able to obtain only exponential-like distributions. Similar results were obtained by Baldwin and Friedman (1965) who showed that one would expect to obtain an exponential distribution when the local value of the secondary emission coefficient can have one of a range of values.

Experimental results by Tusting, Kerns and Knudsen (1962) and by Hyman, Schwarcz and Schluter (1964) clearly show the maximum in the pulse height distribution which results from single input events. Dietz (1965) has extended this work to mass spectroscopy and has obtained experimental pulse height distributions which agree well with those predicted from Poisson statistics.

When a constant intensity ion beam falls on the conversion dynode, the electron current which is collected at the multiplier anode is found to increase very rapidly as the total multiplier voltage is increased. (McCulloch, 1957) This indicates that in the D.C. mode of operation a very highly regulated voltage must be applied across the dynodes.

When the multiplier is operated in the pulse counting mode however, the observed counting rate tends to a constant value as the dynode voltage is increased. (Marchand, Paquet and Marmet, 1966) This saturation of the counting rate is a most valuable property since it allows operation on a counting plateau, where the counting rate is largely independent of the inter-dynode voltage.

When an isotope ratio is determined by pulse counting methods, the operator must be able to gauge the extent to which the presence of background noise in the multiplier and electronic circuits, and a non-zero value of discriminator setting in the linear amplifier will influence the value of the isotopic ratio which is obtained. An estimate of the bias which is thus introduced into the isotopic ratio determination can be obtained by taking the differential pulse height spectrum of each ion species under investigation, as well as the distribution of the background noise pulses.

(b) Data Recording Procedure

A study of the anode pulse height distribution from Sr^+ ions was made.

A few micrograms of Eimer and Armend (lot no. 492327) standard $SrCo_3$ mixture was loaded onto one of the side filaments of a conventional triple filament thermal ionization source. The spectrometer was adjusted to pass one of Sr^{86+} or Sr^{88+}. The source temperature was carefully adjusted so that a nearly constant ion emission rate was obtained.

Pulses from the electron multiplier which had passed through the pre and linear amplifiers were observed on a Tektronix Type 545B oscilloscope. It was found that overloading occurred in the amplifier when a gain larger than approximately 3000 was used. In all subsequent measurements the amplifier voltage gain was kept below this figure.

The pulse height distribution curves were obtained by connecting the input of a 256 channel analyzer to the output of the T.M.C. model 118 linear amplifier (J102). The analyzer output was connected to a printer which, upon command, typed out the accumulated counts per channel.

(c) Results

In abundance determinations by pulse counting several characteristics of the electron multiplier must be known. The operator must know the shape of the pulse distribution due to each ion species and the effect that a change of ion energy has on this shape. It is also important to know the energy distribution of background noise pulses, and the manner in which the measured counting rate from a constant intensity ion beam varies as the total multiplier voltage is changed.

The pulse height distributions from Sr^{86+} and Sr^{88+} were taken when the total ion energy was 12.4 keV. Both distributions were normalized and the shapes compared. In each case the total dynode voltage was held constant at 5.0 kV.

The pulse spectrum from Sr^{88+} ions is shown in Figure 16. Relatively many pulses have a very low energy. Most of these are due

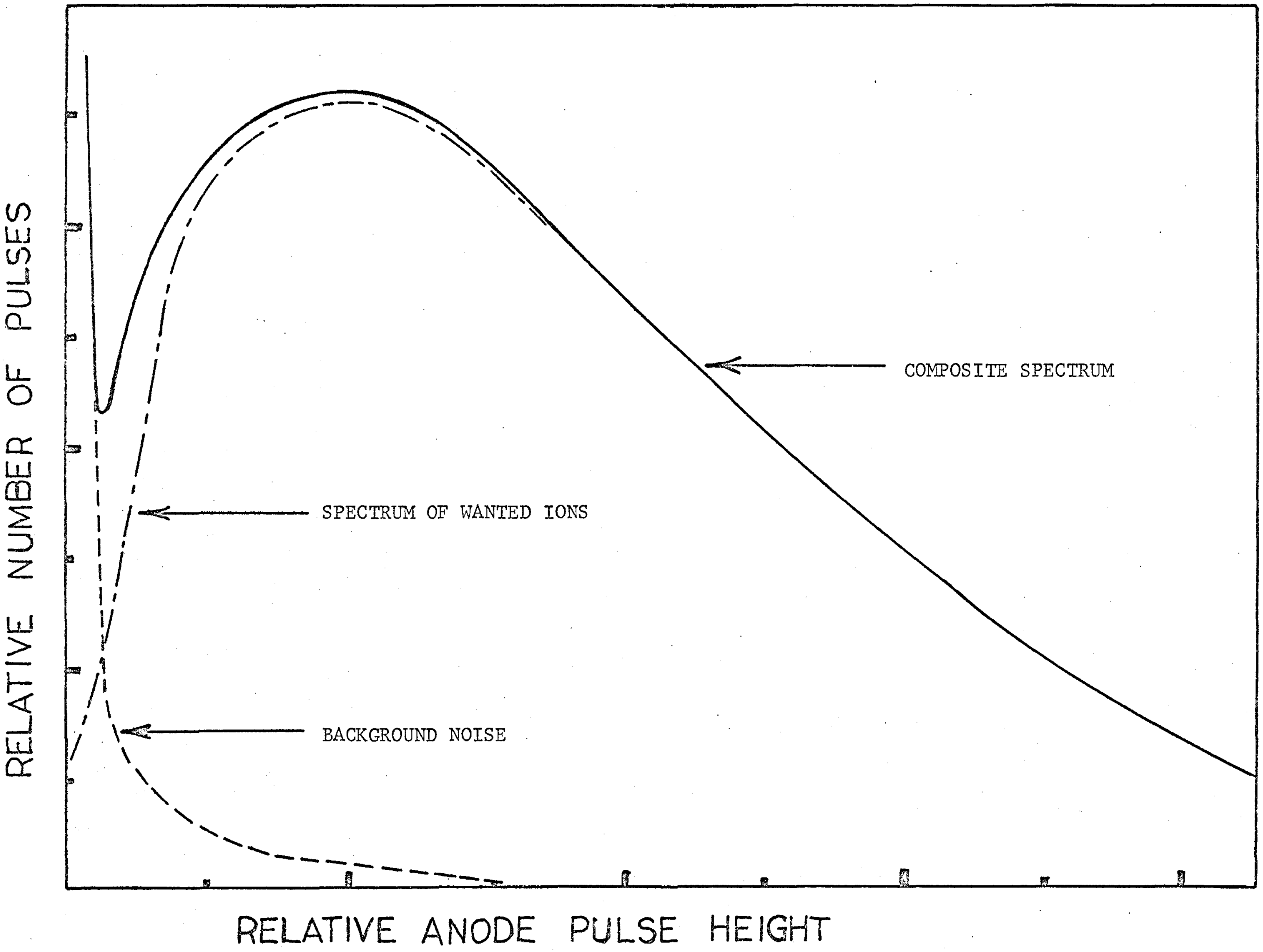


FIG. 16 ELECTRON MULTIPLIER PULSE HEIGHT DISTRIBUTION

to background noise and can be biased out by the discriminator. The spectrum of pulses from each ion species which was observed definitely showed a most probable value of anode pulse height. The distribution decreased roughly exponentially at larger pulse energies. Between the rapidly decreasing background spectrum and the maximum in the desired anode pulses there was a deep but narrow minimum.

The spectral shapes were found to be the same for both ion species, and there was no significant difference between the width and position of the minimum in the pulse energy curve. If the discriminator voltage stability is good (better than 2%) the ion counting method of measuring the Sr^{86}/Sr^{88} ratio should thus not introduce a significant error into this ratio.

The background noise spectrum was obtained by operating the multiplier with 5 kV across the whole dynode structure, but without an ion beam incident onto the conversion dynode. The spectrum which was obtained is also shown in Figure 16.

The effect of ion energy on the pulse height distribution was investigated by measuring the distribution of pulses from Sr^{88+} ions when the multiplier voltage was kept constant at 5.0 kV. and the source voltage was changed from one run to the next so that the total ion energies were 12.1 and 16.0 keV. respectively. The pulse distributions taken at the two ion energies were not found to be appreciably different from each other, and no significant change in the width or position of the pulse height valley was observed.

The relative counting efficiency of the electron multiplier for Sr^{88+} ions of different total energies was found as a function of the electron multiplier voltage. Three runs were made, in which source voltages of 4.1, 8.8 and 10.8 kV. were used. In each case the multiplier voltage was changed from 3.6 to 5.0 kV. and the counting rate due to a constant intensity Sr^{88+} ion beam was measured.

The results are shown in Figure 17. For the two larger ion energies the efficiency curves are practically identical, and at the largest multiplier voltage (5 kV.) are beginning to level off. The curve due to the lowest ion energy beam shows that the counting efficiency is smaller than was obtained for the more energetic ions.

These results indicate that the total ion energy should be as large as possible and should preferably be larger than 12 keV. Thus the multiplier gain and especially the first stage gain (α) of the present multiplier should be increased by reactivating the dynode surfaces. In that way the pulse efficiency curve should become flat well before 5 kV. has been applied across the multiplier.

When the variation of the dark count rate with discriminator and total dynode voltage is also known, the operator can choose the optimum analyzing conditions under which to operate the ion detection system in the pulse counting mode.

(d) Comments

In its present state of activation the electron multiplier is no longer suitable for use in the pulse counting mode. To be really useful in counting work the overall multiplier gain should be increased by reactivation of the dynodes. It is especially important that the

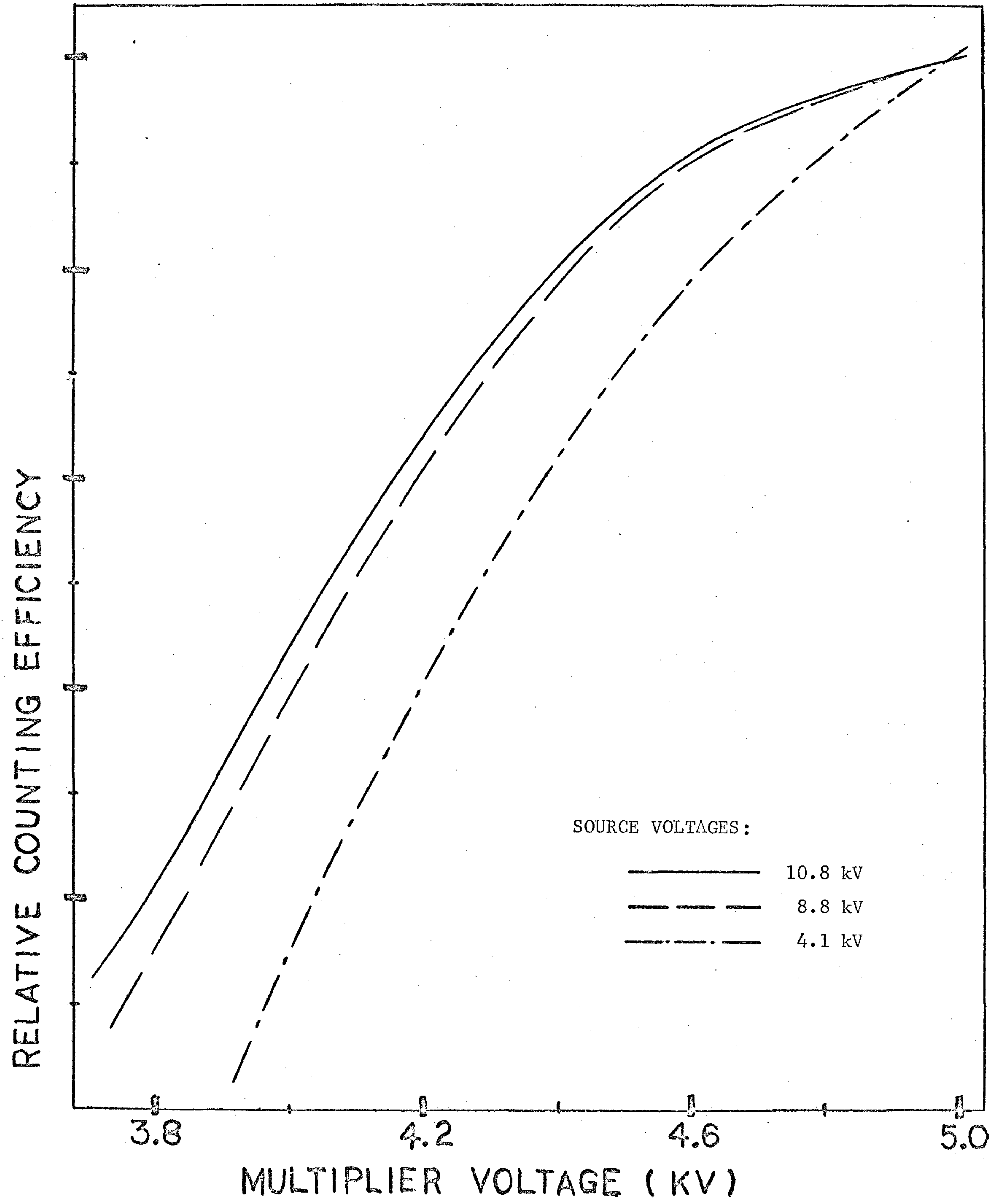


FIG. 17 COUNTING EFFICIENCY OF ELECTRON MULTIPLIER

first stage gain be made appreciably larger. Simultaneously, the dark current (6 pulses $\sec^{-1}$) must be decreased by at least one and preferably two orders of magnitude.

With a larger overall gain the count rate versus multiplier voltage curve should reach a plateau well before the maximum dynode voltage has been applied.

With a smooth newly activated Al_2O_3 conversion dynode the dark count rate should be very low and when ions of more than 12 keV. are used, the secondary emission ratio should be substantially larger than it is at present. This would have the beneficial consequence that the probability for producing zero secondary electrons per incident ion $\left(P(o) = \exp(-\alpha)\right)$ would be greatly reduced, thus resulting in an increased counting efficiency.

It might also be useful to incorporate a focusing control between the conversion and the first electron multiplying dynode. With this facility it may be possible to reduce the time spread in each electron pulse, thus directly improving the resolving time and indirectly the signal/noise of the entire detection system.

With a larger first stage gain, and a reasonably large $(>10^7)$ overall gain, as well as a focusing control across the first multiplier stage, it should be possible to increase the average energy of the anode pulses resulting from a given ion species. Thus a larger fraction of useful pulses can pass the pulse-height discriminator than was previously possible. When the noise spectrum has also been reduced it becomes possible to operate at a smaller discriminator voltage with the result that the counting efficiency is increased. Furthermore, the bias which may have been introduced into an isotope ratio because of the need to use a non-zero value of pulse discriminator voltage will be reduced, since small differences in the pulse spectra from the two ion species will likely become much less important.

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