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A mass spectrometric determination of trace elements in aqueous media without preconcentration

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A MASS SPECTROMETRIC DETERMINATION OF TRACE ELEMENTS IN AQUEOUS MEDIA WITHOUT PRECONCENTRATION

Iowa State University PH.D. 1981

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A mass spectrometric determination of trace elements in aqueous media without preconcentration

by

Gordon Oluf Foss

A Dissertation Submitted to the
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1981

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

A. Description of the Problem

Recent advances in toxicology, increased environmental concerns, and the chemical industry's increasing need for high purity reagents continue to create a demand for improved analytical methods for impurities at the trace level. These modern analytical methods are of two general types. One type concerns single component or single group analyses. A single component method of analysis is the method of choice when the concentration of a component can define the status of a total system to a satisfactory degree. Single component methods are very important industrially when economical, fast, continuous, on-stream methods are required to automate an industrial plant to optimum production and minimize contamination of the final product and plant effluent. The second general type of analytical method concerns multielement or multicomponent survey analyses. Multicomponent survey methods are required to characterize industrial products, reagents, and environmental samples. Recently enacted environmental regulations have emphasized the need for survey analyses and, more specifically, the survey analysis of water. Aqueous solutions are becoming more important not only because of pollutants in lakes, rivers and potable water supplies, but also because biological systems involve aqueous solutions and these are being subjected to analyses emphasizing more and more components.

The chemical analysis of water is generally divided into two basic areas, one emphasizing the analysis of organic components and the other inorganic components. Our laboratory has continuing research projects in both areas (1,2,3). For example, one project involves a systematic determination of organic compounds in the water supplies of various cities in the United States. A sampler is sent to each of the cities and is returned with organic components from a large quantity of water sorbed on a macroreticular polystyrene-divinylbenzene resin and several milliliters of water in the sampler. The resin is extracted with diethyl ether and the organic species are determined by a gas chromatographic and mass spectrometric (GC and MS) method. The water with its inorganic contaminants is discarded. If this water could be used for a comprehensive elemental analysis, much more information regarding water quality could be obtained from such a survey.

Any method developed for a systematic analysis of aqueous samples must meet several important criteria. The method should determine all elements simultaneously, be highly sensitive, be effective over a large concentration range, be free of interferences, and if necessary use a <u>small</u> sample. In addition, the analytical method should be rapid, accurate, precise, nondestructive, and relatively inexpensive. As with any analytical technique, all of these ideals are difficult to achieve simultaneously and compromises must be made to fit a particular situation. The fundamental criterion for an analytical problem may be dictated by the small sample size and the need for a comprehensive analysis of an unknown aqueous solution. These requirements can be best filled by the determination of all the elements simultaneously. The simultaneous determination of all the elements limits the choice of techniques to the various emission techniques, i.e., the emission of ions, electrons, nuclear particles, or electromagnetic radiation from a sample. The analysis of ionic emission by mass spectrometry has the advantages of requiring conventional equipment and sample handling procedures, a relatively simple spectrum, high sensitivity, large concentration range, and small sample requirements. Ion optical systems and ion detection systems are highly developed and well documented. The primary difficulties involved in solving any analytical problem mass spectrometrically concerns introducing the sample into a suitable ion source and interpreting the large amount of data obtained from the detection system.

Introducing an aqueous solution into a mass spectrometer creates three major problems. The first problem to consider is the large volume of gas which must be pumped to maintain a normal operating pressure, $\sim 1 \times 10^{-6}$ torr (1.3×10^{-4} Pa), in the mass spectrometer ion source chamber. One milliliter of liquid water at standard temperature and pressure becomes approximately one billion liters of water vapor at 1×10^{-6} torr (1.3×10^{-4} Pa), an increase of twelve orders of magnitude in volume. Conventionally designed mass spectrometer vacuum systems have pumping speeds in the range of 10 ℓ/s to 50 ℓ/s at the ion source chamber. Modern mass spectrometer vacuum systems, in particular GC/MS systems, may have pumping systems as fast as 500 ℓ/s or faster. For a mass spectrometer vacuum system with a relatively fast pumping speed of 500 ℓ/s, water throughput is limited to 5×10^{-7} mℓ/s or 0.03 μℓ/min to maintain a pressure of $\sim 1 \times 10^{-6}$ torr (1.3×10^{-4} Pa).

The second major problem is the interference of molecular or cluster ions with elemental ions at a particular nominal mass. Water forms a number of cluster ions and any organic compounds present in the water can interfere with both molecular and fragment ions. This problem can be solved for most elements with a high resolution ion optical system.

The third problem is one of solute volatility. This always poses a problem when water is vaporized during an analytical procedure. Solute volatility effects can be minimized by using a proper ion source and can be corrected for during data reduction when any deviation from a true value is known and consistent. Problems arising from the large quantity of data available in a mass spectrum are minimized by careful analysis of the data using modern computer methods. The utilization of a mass spectrometer for the analysis of water for trace levels of elemental components is not easy. However, use of mass spectrometry presents the most straightforward solution to the analytical problem.

B. The History of the Problem

The history of the determination of water quality and of analytical chemistry dates back to the first chemical tests by the Egyptians for hydrogen sulfide in sewage water. Analytical technology for water quality determination has developed from a simple qualitative method to the sophisticated quantitative methods available today. One of the more recent instruments to be used for water quality determination is the mass spectrometer. The most important use of the mass spectrometer in water analysis today is in conjunction with the gas chromatograph to form a GC/MS system which is widely used in the determination of organic compounds present in the water.

Several investigators in the past have attempted to adapt mass spectrometric techniques to the elemental analysis of natural waters. While all report varying degrees of success, a satisfactory method for the simultaneous determination of all trace elements in water has not been demonstrated. The mass spectrometric methods that have been tried are basically adaptations of the normal spark source mass spectrometric (SSMS) techniques. The first type of water analysis done with SSMS involved evaporating the water onto a suitable electrode and analyzing the residue using standard solid sample techniques. This indirect method of analysis works reasonably well. However, it is slow and has the inherent dangers of volatile solute loss, solute segregation during the evaporation procedure, and sample contamination when the residue is mixed with a conducting medium, such as graphite. A more rapid method has been developed for water analysis with the SSMS. This involves freezing the water and using the ice pellet maintained at cryogenic temperatures as a normal SSMS sample. This direct method of analysis has been shown to be a reasonably satisfactory method (4,5); however, the detection limits demonstrated are higher than desirable and results reported to date are for only a relatively small number of elements. These deficiencies in the available methods make a study of alternative ion sources appropriate.

The most promising ion source for the simultaneous determination of trace elements in water involves a plasma. Two general types of plasmas can be considered for use as a mass spectrometer ion source. One is an atmospheric pressure plasma such as a flame or an inductively coupled plasma.

Inductively coupled plasmas have been shown to be highly efficient in the production of ions and excited atoms; however, an inductively coupled plasma requires a relatively large volume of sample, on the order of several milliliters, and involves a large pressure drop of one atmosphere (101 KPa) between the ion source and the mass analyzer of a mass spectrometer. The other general type of plasma is a reduced pressure plasma. A reduced pressure plasma is easier to design into a mass spectrometer as the pressure drop between the ion source and mass analyzer is much smaller, ∿1 torr (∿133 Pa). A source pressure of ∿1 torr is routinely used in chemical ionization mass spectrometry. The reduced pressure plasma most amenable to use in a conventional mass spectrometer is the hollow cathode discharge. Use of a hollow cathode ion source is relatively slow since the source must be disassembled for each sample. However, the hollow cathode ion source has a tremendous advantage over atmospheric pressure plasmas in that a sample size of 20 to 50 μℓ is all that is required for a complete analysis.

The hollow cathode ion source is fundamentally a glow discharge operating within the confines of the walls of a cylindrical cathode. The use of a glow discharge as an ion source dates back to J. J. Thomson's experiment on "Rays of Positive Electricity" (6) and F. W. Aston's (7,8) first mass spectrograph. Sputtering at the solid cathode, which is a primary characteristic of the hollow cathode, was first used by K. T. Bainbridge (9) for the determination of the isotope abundance of zinc. After this early use of cathodic sputtering into a glow discharge, A. J. Dempster (10,11) developed the rf spark ion source (1935), which has been the primary method for the mass spectrometric analysis of solids and thus further development of hollow cathode ion sources diminished. The hollow cathode configuration, as known today, was first used by H. Schüler and H. Gallnow (12) and A. G. Shenstone (13) as emission sources for optical spectroscopy. Until recently, little was done with the hollow cathode as a source of ions and the major development was done by optical spectroscopists.

Recently, J. W. Coburn (14) and Coburn and Kay (15,16) have described a planar diode sputtering system where ionization takes place in a glow discharge and have determined several elements. Researchers under the direction of W. W. Harrison sampled the glow discharge in a hollow cathode mass spectrometrically using several ion source configurations and determined trace elements in the cathode material at sub-ppm levels (17-22). R. N. Colby and C. A. Evans, Jr. (23) have developed a hollow cathode ion source with a water cooled support flange to control the source temperature during the analysis of the cathode material. The hollow cathode ion source has also been used as an ion implant ion source (24-31) in the semiconductor industry and for plasma reaction kinetics studies (32).

The nature of ion production from a hollow cathode by sputtering from the inner surface suggested the present work. This concerns the feasibility of obtaining ions from ice deposited within the cavity of a hollow cathode which would be characteristic of the impurities in a small water sample. The feasibility study was undertaken and included 70 elements, the development of a suitable hollow cathode ion source configuration, and the development of a suitable ion optic and detection system.

II. THE INSTRUMENT

A. General Description

The instruments described herein were designed in two stages. The first phase of the design was the development of a Cryogenic Hollow Cathode Ion Source (CHCIS) and a corresponding source housing and vacuum pumping system which could stand alone as a test station or be mounted in place of the conventional spark ion source on a Nuclide Graf 2.2 mass spectrograph. The second phase was the design of a Research Ion Optical System (RIOS) to be used in conjunction with the CHCIS, source housing, and vacuum pumping system to form a complete mass spectrometer. The CHCIS is a miniature hollow cathode lamp with a very small hole in the anode. A reagent gas pressure of approximately one torr (133 Pa) is maintained in the ion source and a potential of 1000 V is applied across the anode and the cathode resulting in a breakdown of the gas and production of a glow discharge plasma. The positive ions in the plasma are accelerated to the cathode causing atoms, electrons, and ions to be sputtered from the surface of the cathode. Any positive ions sputtered from the surface of the cathode are likely to be drawn back to the cathode by the electric field (33), but the atoms sputtered into the plasma from the cathode can be redeposited on a surface or be ionized either by electron impact or, more likely, by a secondary ionization process (15). The most likely method of secondary ionization is the Penning ionization process (34). Penning ionization involves a metastable state of the reagent gas and an atom metastable species interaction. When the ionization potential of the analyte atom (X) is less than the metastable energy of the reagent gas (R), the Penning ionization reaction as shown in equation 1 takes place.

$$R^* + X \rightarrow X^+ + R + e^- \qquad [1]$$

If the analyte atom is ionized in an area near the anode sampling hole, the resulting ion can be extracted from the plasma and accelerated by the ion source for mass analysis. The complete instrument developed in the second phase of this work is shown schematically in Figure 1. The ions extracted from the CHCIS are accelerated toward the object slit assembly along the optical path of the instrument. The object slit allows a fraction of the ions to pass along the optical path and an ion beam is formed by the angular divergence (α) limiting slit assembly and the vertical (z) limiting slit assembly. The ion beam is energy selected with a twelve inch radius, spherical electric sector and refined by an energy (β) limiting slit assembly and a second z limiting slit assembly. Twenty percent of the ion beam is then intercepted and the total ion current monitored prior to mass analysis in the magnetic sector. The mass analyzed ion beams are focussed

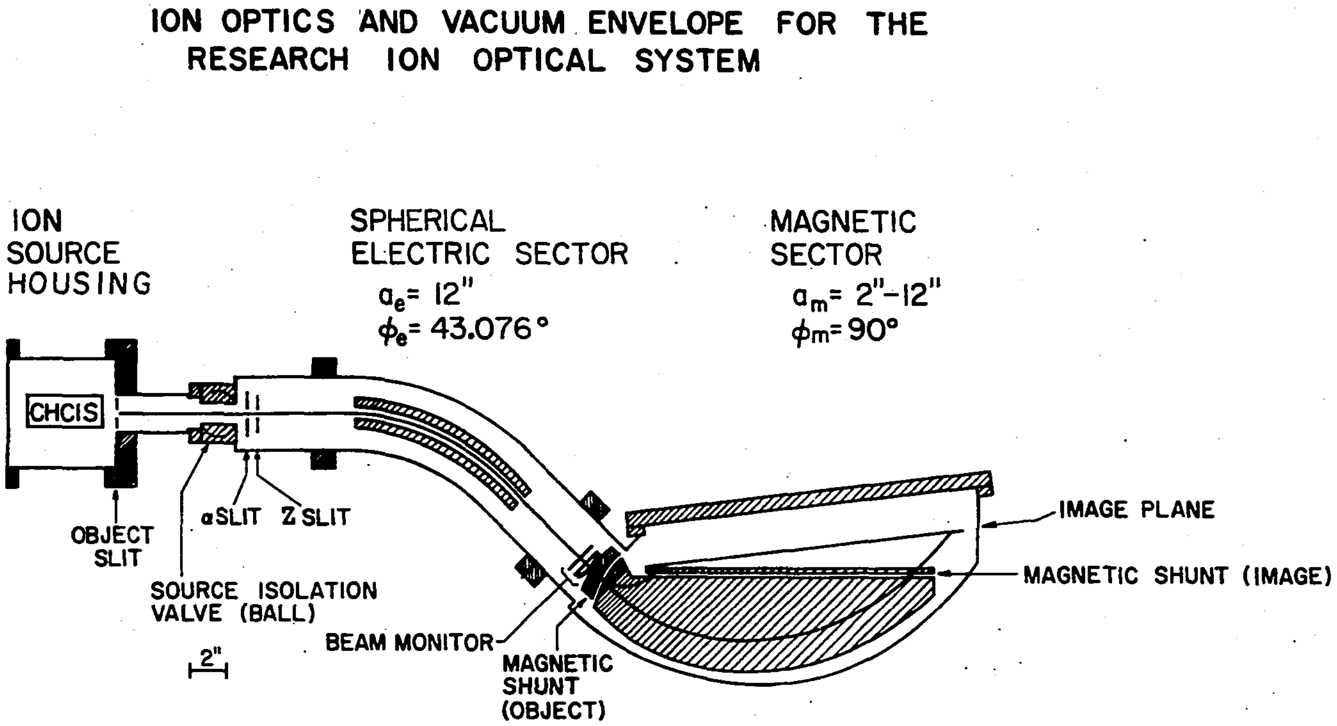


Figure 1. Schematic diagram of the Cryogenic Hollow Cathode Ion Source, source housing, and Research Ion Optical System

along an image plane. Individual mass analyzed ion beams are focussed on either of two image slits by varying the magnetic field strength and the ion currents are measured with Faraday cup detectors and vibrating reed electrometers.

This complete instrument at its present stage of development is limited to only a few analytical uses, i.e., the determination of high levels of one or two elements in a matrix simultaneously. The primary use of the RIOS until a new ion detection system is developed will be the development and testing of new ion sources. The instrument used to obtain analytical data for the determination of trace elements in water is shown schematically in Figure 2. The CHCIS, source housing, and vacuum pumping system are mounted on a Nuclide Graf 2.2 spark source mass spectrograph. The ions extracted from the CHCIS must traverse a path about fifteen inches long from the anode of the CHCIS to the object slit assembly of the spectrograph. This is done with a coaxial, cylindrical electric lens similar to that which focusses the electron beam in a television picture tube. Although the ion optics of the Nuclide Graf 2.2 are very similar to the RIOS, the design is less flexible. The primary advantage of using the Nuclide Graf 2.2 for the determination of trace elements in aqueous media is the photographic detection system of the instrument. Photographic plates are much more sensitive than Faraday cup detectors and also have the advantage of

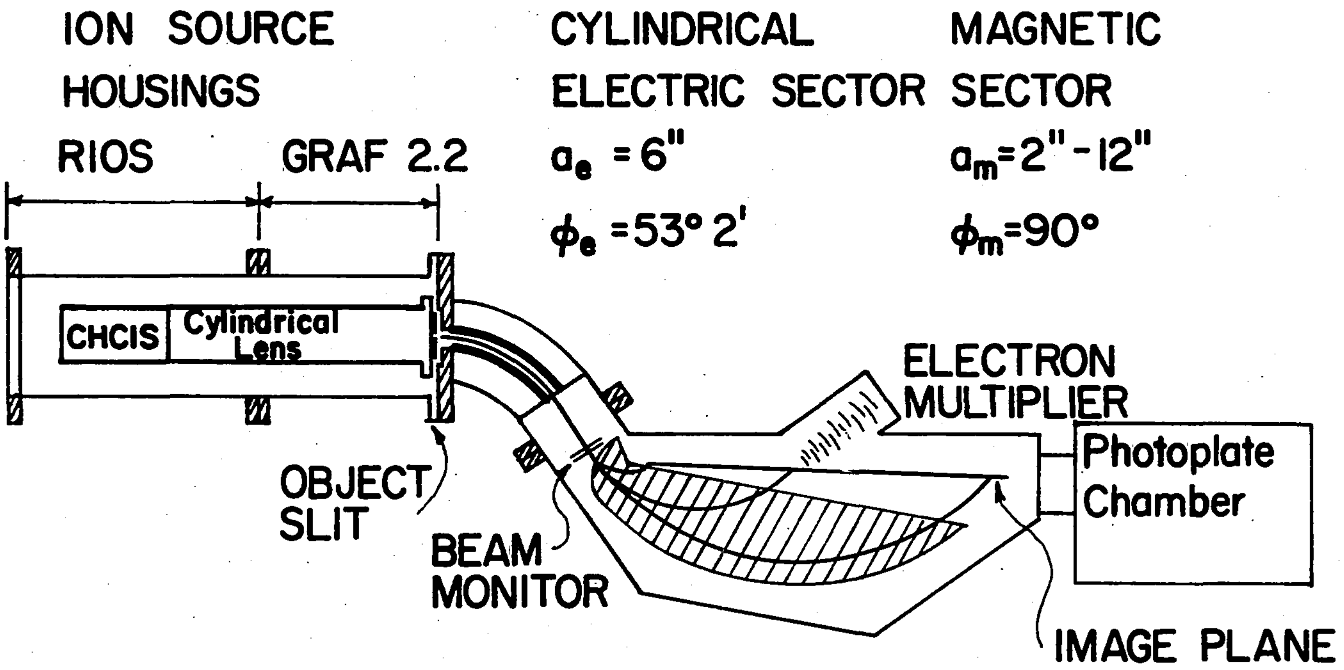


Figure 2. Schematic diagram of the Cryogenic Hollow Cathode Ion Source, source housing, lens and Graf 2.2 mass spectrograph

simultaneous detection of all ions within a selected m/z range, normally about 6 - 240 m/z. The simultaneous detection of all ions over a mass range of this magnitude is essential for a comprehensive determination of trace elements in aqueous media.

B. Physical Components

1. The cryogenic hollow cathode ion source

A cross section of the CHCIS is shown in Figure 3. The CHCIS is mounted on a stainless steel source mounting plate, which is also a clamp that presses a copper heat conducting strap against the cathode and holds the cathode in the source block. The CHCIS consists of a draw-out electrode, an anode, a cathode, a source block, and various insulators, spacers, and seals. The draw out electrode, the anode, and the source block are fastened to the source mounting plate with four 0-80 studs, flat washers, and nuts. The source mounting plate is designed to be fastened to an insulating block with three 1/8" (3.18 mm) dia. alignment pins and two 8-32 flathead screws.

The draw out electrode and the anode are one 7/16" (36.5 mm) dia. tantalum discs with four 1/8" (3.18 mm) dia. holes drilled 0.515" x 0.300" (13.1 mm x 7.62 mm) off center. The draw-out electrode is 0.015" (0.38 mm) thick with a 1/4" dia. hole in the center. A piece of 90% transparent, 90 line/inch

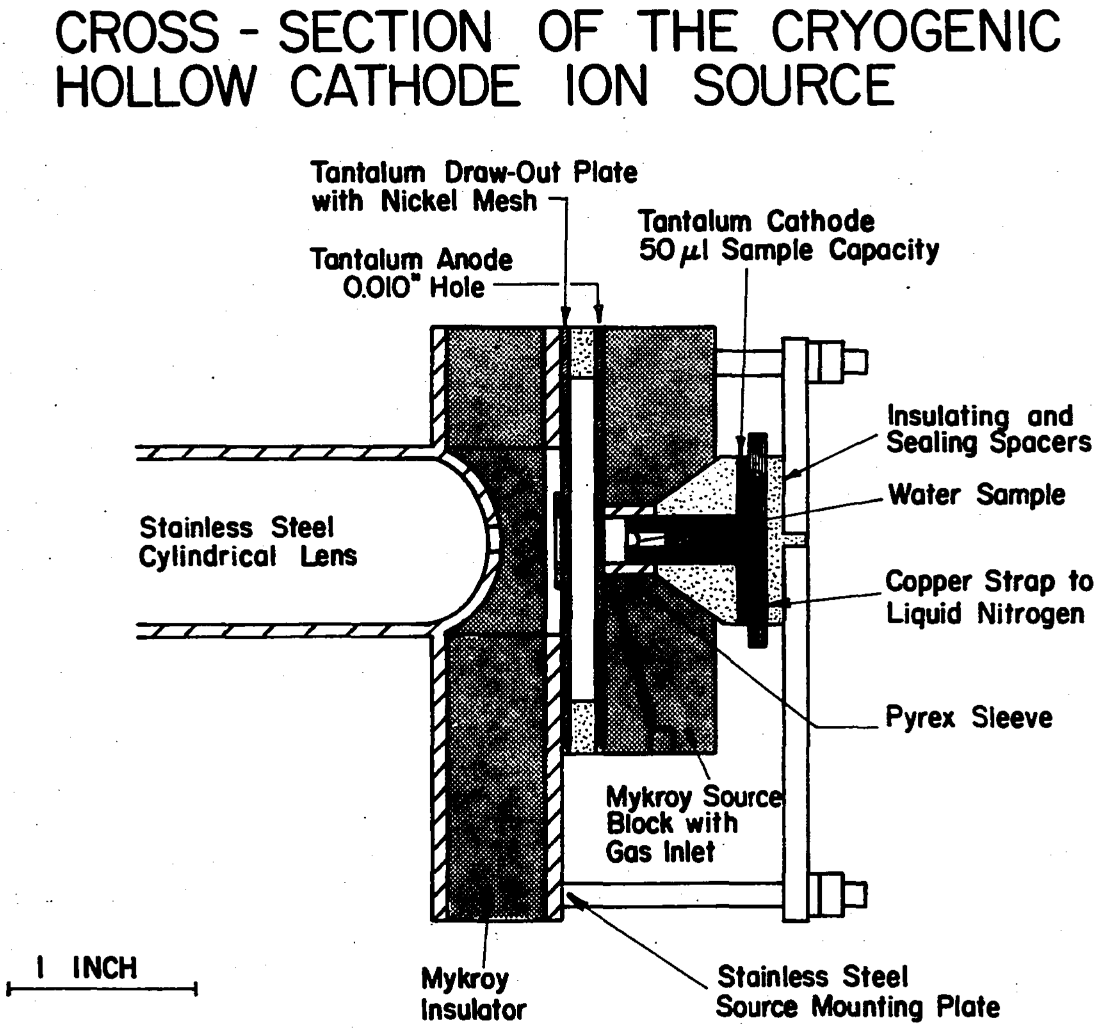


Figure 3. Cross section of Cryogenic Hollow Cathode Ion Source (CHCIS)

(35 line/cm) nickel mesh is fastened across the hole to form an electrically "continuous" surface. The anode is 0.030" (0.76 mm) thick, reduced to 0.005" (0.13 mm) at the center, with 0.010" (0.25 mm) dia. hole drilled at the center. The draw-out electrode is mounted on the source mounting plate and is at the same electric potential as the source mounting plate. Four 1/8" (3.18 mm) thick Kel-F spacers machined with alignment shoulders are used to align and separate the draw-out electrode and the anode. The source block is a 1 7/16" O.D. x 0.12" x 3/8" I.D. x 1/2" (36.5 mm x 9.5 mm x 12.7 mm) thick Mykroy ring with four 1/16" (1.6 mm) holes drilled 0.515" x 0.300" (13.1 mm x 7.62 mm) off center. The source block has an internal channel and a standard 1/4"-20 (6.35 mm-20) connector for attaching a small diameter Teflon tube leading to the reagent gas inlet. The center hole is tapered at one end to mate with a Teflon seal on the cathode and is fitted with a replaceable borosilicate glass sleeve to minimize sample contamination and memory.

The hollow cathode consists of a 1/4" (6.35 mm) O.D. tantalum rod with a 1/8" dia. x 5/16" (3.18 mm dia. x 7.78 mm) hole drilled into one end. The other end of the cathode has a 3/4" dia. x 0.030" (19 mm dia. x 0.76 mm) tantalum disc welded onto it. A Teflon seal ring is placed over the cathode to prevent reagent gas leakage between the cathode and the source block. A 1/16" x 3/4" x 8" (1.6 mm x 19 mm x 20.3 cm) copper strap is shaped to clamp around a glass liquid nitrogen cooled finger and is placed between the cathode and an insulated clamp on the source mounting plate to complete the ion source assembly.

2. The reagent gas inlet system

A reagent gas inlet system is required to maintain a pressure of approximately one torr (133.3 Pa) in the CHCIS. The pressure in the CHCIS is maintained by adding a reagent gas to the source at the same rate that it is pumped through the 0.010" (0.25 mm) hole in the anode. The reagent gas inlet used with the CHCIS is shown schematically in Figure 4. The system consists of a shut-off valve, a dual metering valve, a tee, and a battery operated vacuum gauge. Because a gas at one torr (133.3 Pa) will breakdown electrically over a distance of several feet when a potential of 24,000 volts is present, as is the case with the accelerating potential of the mass spectrograph, the reagent gas inlet system is isolated in a Plexiglass housing. Bakelite extensions on all control components provide for safe manual adjustments.

Reagent gas from a compressed gas cylinder fitted with a pressure regulator enters the reagent gas inlet system at a pressure of $\sim$5 PSI (34.5 kPa), relative pressure, through a 3" (7.62 cm) length of 1/4" (6.35 mm) diameter glass tubing which isolates the reagent gas inlet system from ground

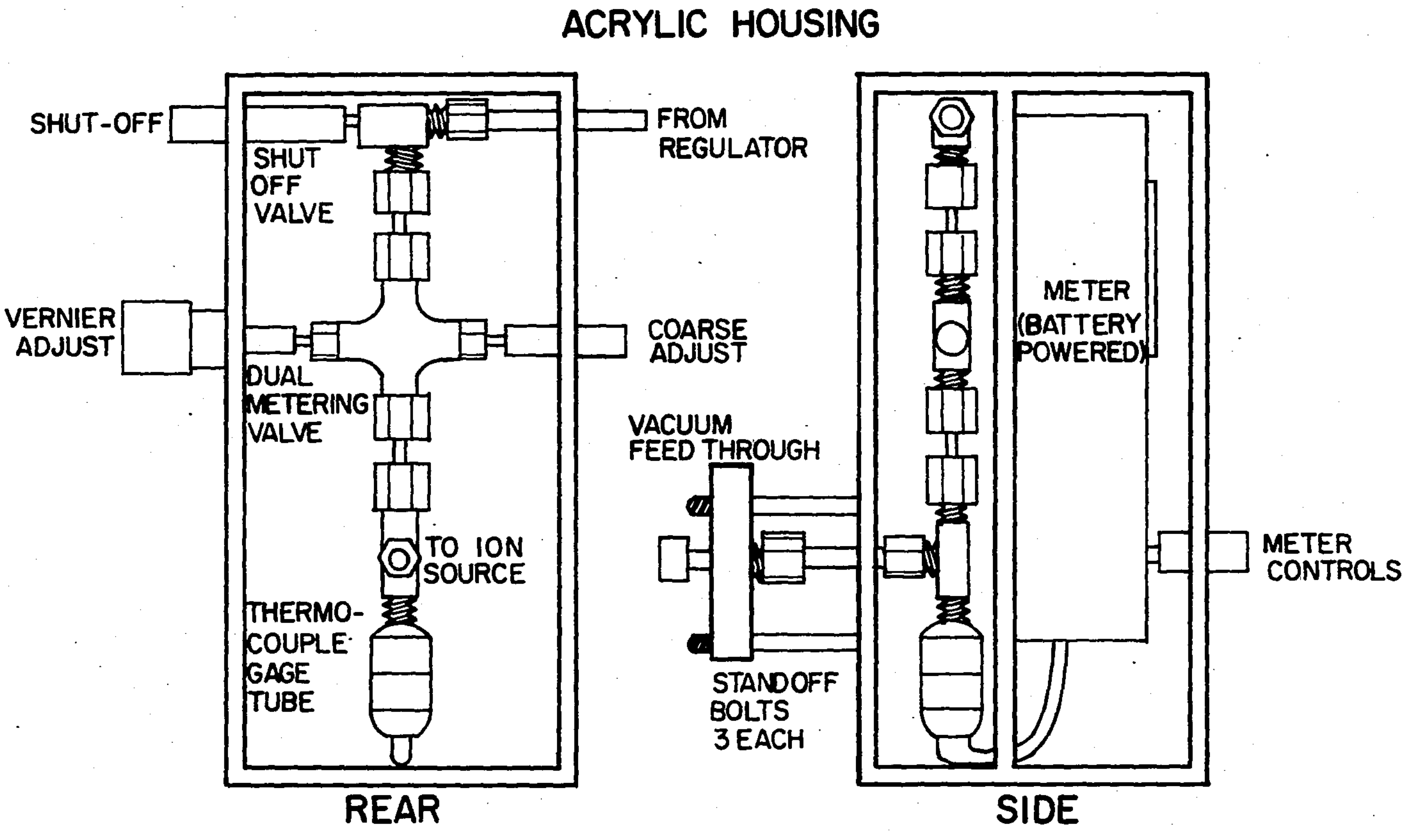


Figure 4. Reagent gas inlet system

potential. The glass tube is connected to a Nupro B-2JA shut-off valve with Swagelock connectors and Teflon ferrules. A minimum length of 1/8" (3.18 mm) copper tube connects the shut-off valve to a Nupro B-25GC double pattern metering valve. The first side of the metering valve is used to set a maximum flow limit while the second side of the valve is equipped with a vernier handle and is used to adjust the gas flow to a desired rate. The metering valve is connected to a Tee with another minimum length of 1/8" (3.18 mm) copper tubing. The Tee is connected to a 1/4" (6.35 mm) O.D. Teflon tube which carries the gas into the vacuum system through a Swagelock connector on a 1.5" (3.8 cm) Curvac flange and to a thermocouple gauge tube. Inside the vacuum system 1/16" (1.6 mm) Teflon tubing with standard 1/4"-20 threaded connectors is used to connect the reagent gas inlet system to the CHCIS source block. The vacuum gauge is a Hastings-Raydist Model TP-7A battery operated thermocouple gauge. The gauge is powered with a 1 1/2 volt dry cell battery and is calibrated over a 0-20 torr (0-2.66 kPa) range. The reagent gas inlet system is compact, electrically isolated, and maintains the pressure in the CHCIS at a measurable, selected pressure.

3. Coaxial, cylindrical electric lens

When the CHCIS is mounted on the Nuclide Graf 2.2 mass spectrograph, the anode is located approximately fifteen inches from the object slit of the mass spectrograph. A dual focal length cylindrical lens was developed in our laboratory (35) to reduce ion current loss over this distance. A cross-section of this lens is shown in Figure 5. The inner cylinder is a 1" I.D. x 5.2" (2.54 cm x 13.2 cm) stainless steel tube which is held concentric in the 2 3/8" I.D. x 14" (6 cm x 35.5 cm) outer cylinder by two Mykroy rings. These rings electrically insulate the two cylinders and allow the lens to be adjusted to the exact length desired. During operation, the outer cylinder is at electrical ground and the inner cylinder is at approximately 0.71 times the ion accelerating voltage. The lens increases ion currents more than ten-fold (see Figure 6) in tests without mass analysis. The outer cylinder of the lens has beam centering electrodes near the object slit end which are very useful for correcting source mounting aberrations. They can also be used to deflect the ion current for detector zeroing purposes.

4. Source housing and vacuum pumping system

The source housing and vacuum pumping system are designed for three modes of operation. With the source housing and vacuum pumping system mounted on a caster-wheeled stand and an

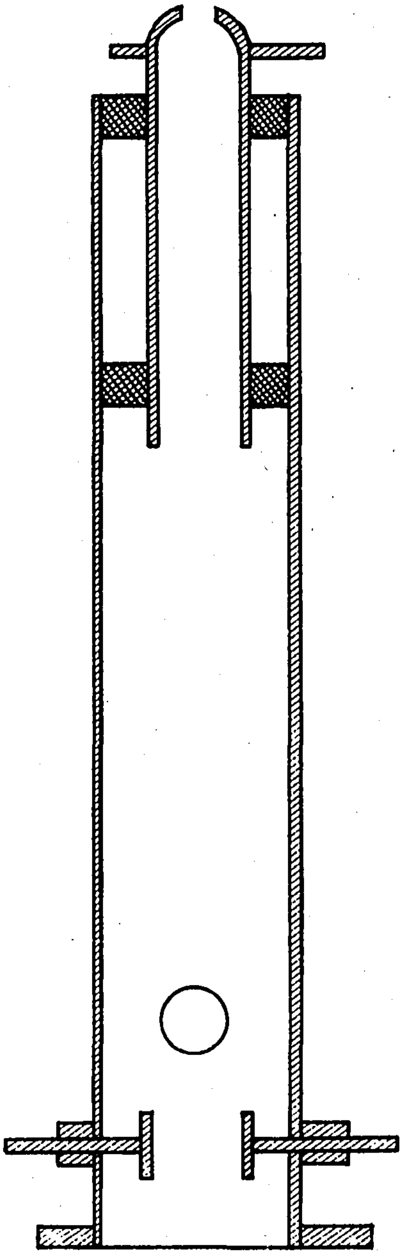


Figure 5. Coaxial cylindrical electric lens

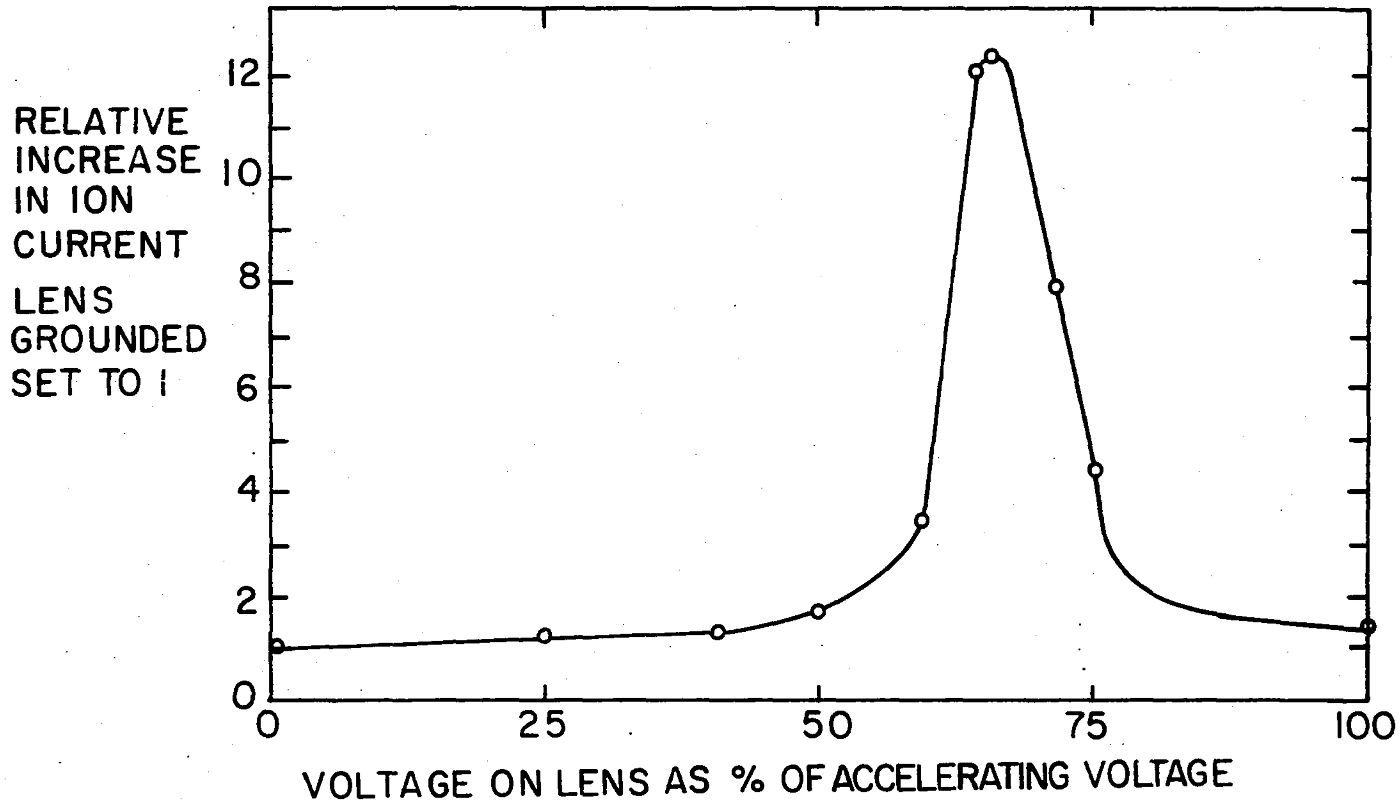


Figure 6. Graph of lens effect

enclosed tube with lens mounting holes and Faraday cup detectors attached to the instrument end of the source housing, the vacuum system is a free standing test instrument for developing lenses or ion sources without mass analysis. While mounted on the caster-wheeled stand, the source housing and vacuum pumping system can also be used with the Nuclide Graf 2.2 mass spectrograph as the flange on the source housing mates with the source flange of the mass spectrograph. The third mode of operation is in conjunction with the RIOS to form a complete mass spectrometer. When used in conjunction with the RIOS, the source housing and vacuum pumping system are mounted on a 1/2" thick (1.27 cm) aluminum plate which is placed on the granite surface plate from which all alignment measurements for the RIOS are made. The source housing and vacuum pumping system are shown assembled as they are mounted on the RIOS in Figure 7.

The source housing is a 6" (15.24 cm) nominal diameter (N.D.) stainless steel Tee with gold wire and/or o-ring sealed flanges on the straight through ends to mate with the flanges on the Nuclide Graf 2.2 mass spectrograph and a 6" (15.24 cm) N.D. CFF flange on the 90° end. The source housing has a 1.5" (3.8 cm) N.D. CFF flange centered on both sides of the Tee, another 1.5" (3.8 cm) N.D. CFF flange mounted 2 7/8" (7.3 cm) below the centered flange on both sides, two 1.5" (3.8 cm) N.D. CFF flanges mounted 45° to the

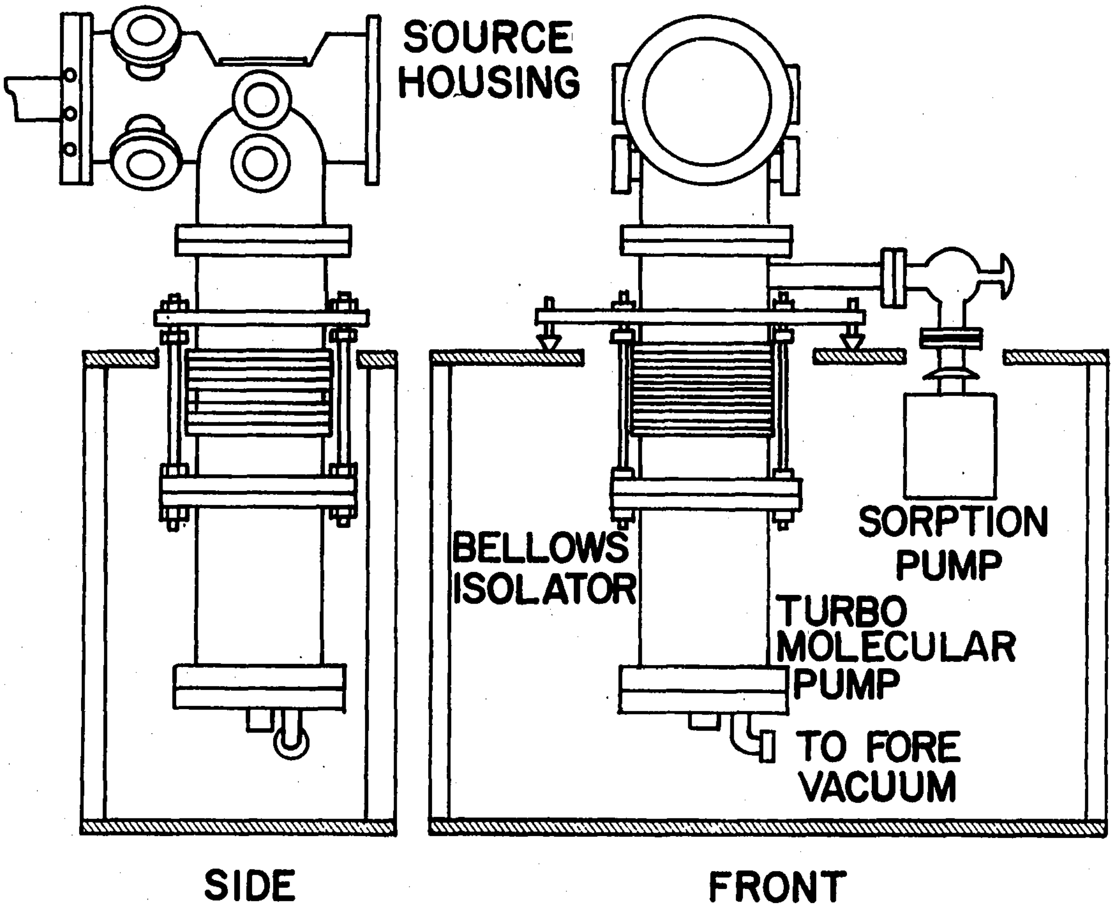


Figure 7. Source housing and pumping system

Tee on the top of the instrument end of the housing, two 2" (5 cm) N.D. CFF flanges mounted 45° to the Tee on the bottom of the instrument end of the housing, and a glass port centered above the Tee and 1 5/8 " (4.13 cm) above the center of the tube. The eight small CFF flanges provide for a large number of mechanical and electrical vacuum feed throughs which can be mounted with a high degree of flexibility. The two flanges which are centered on the Tee are especially useful for mounting mechanical adjustors for solid samples and are used with the glass port for a laser ion source also being developed in our laboratory (36). The 6" (15.24 cm) N.D. CFF flange is used to mount the source housing on the vacuum pumping system.

The vacuum pumping system is made up of several integral parts, viz., a vibration damping adjustable pump mount, a mounting plate and cabinet, a sorption pump, a turbomolecular pump, and a cooling water system for the turbomolecular pump. The vibration damping adjustable pump mount consists of a 6" (15.24 cm) N.D. CFF flange to mate with the source housing, a mounting plate with four height adjustable ball rollers, a 6" x 6" dia. (15.24 cm x 15.24 cm dia.) formed stainless steel bellows, a 6" (15.24 cm) N.D. ASA flange, and four 3/4" (19 mm) dia. threaded rods with nuts and rubber pads to limit bellows travel. The pump mount also has a 1.5" (3.8 cm) N.D. tube with a CFF flange to mount the sorption pump. The mounting plate and cabinet provide a reference surface for the adjustable rollers and a protective enclosure for the turbomolecular pump, its cooling water system, and the sorption pump. The mounting plate is a 1/2" x 11" x 30" (1.27 cm x 28 cm x 76 cm) aluminum sheet with openings cut for the pump mount and the sorption pump and holes drilled to lock the pump mount to the plate when the system is used in the free standing mode. The frame of the cabinet is 2" x 2" x 1/8" (5.1 cm x 5.1 cm x 0.32 cm) aluminum angle and the cabinet is made from expanded aluminum mesh. The mounting plate is fastened to the cabinet with six 1/4"-20 (6.35 mm-20) flat-head aluminum screws and the base of the cabinet has four 3/8" (9.5 mm) dia. holes drilled at the corners to attach it to the caster wheeled stand.

The sorption pump is a Perkin-Elmer-Ultek Model 236-1501 with a stainless steel 1.5" (3.8 cm) N.D. 90° valve and a bakeout heater. The pump consists of a container of zeolite molecular sieve which is cooled with liquid nitrogen. The sorption pump will evacuate the source housing from a pressure of 1 torr to 10^{-3} torr (133 Pa to 0.13 Pa) in less than 15 seconds and is used to expedite rough pumping of the source housing.

The turbomolecular pump is a Leybold-Heraeus Model TMP-450 with an inlet screen and 6" (15.24 cm) N.D. ASA flange. The pump maintains an oil-free vacuum without cryotrapping and has a pumping speed of 500 ℓ/s. The pump is a turbine compressor operated at 24,000 rpm. It has a compression ratio of 10^6 and is driven by a 400 Hz motor. The 400 Hz power is supplied by a solid state frequency converter. The motor has oil lubricated bearings, but the seals are arranged so the high vacuum is totally isolated from the oil. A turbomolecular pump was chosen for the instrument because of its high pumping speed, low maintenance, and because it provides an oil-free vacuum.

The cooling water system for the turbomolecular pump provides recycled distilled water cooled by tap water. A block diagram of the cooling water system is shown in Figure 8. To ensure that water cooler than 100°F (38°C) is flowing through the turbomolecular pump at all times, a thermal switch was placed on the water outlet line of the turbomolecular pump and a flow switch (Perkin-Elmer Ultek) was installed in the flow stream. These protective switches are normally closed and are connected to a protection circuit on the turbomolecular pump frequency converter to shut the pump off if cool water stops flowing. The cooling water is pumped through the system with a continuous duty seal-less magnetic drive centrifugal pump (Cole-Parmer Model 7010) and is cooled in a water cooled glass heat exchanger. The water system also has a glass reservoir so the distilled water

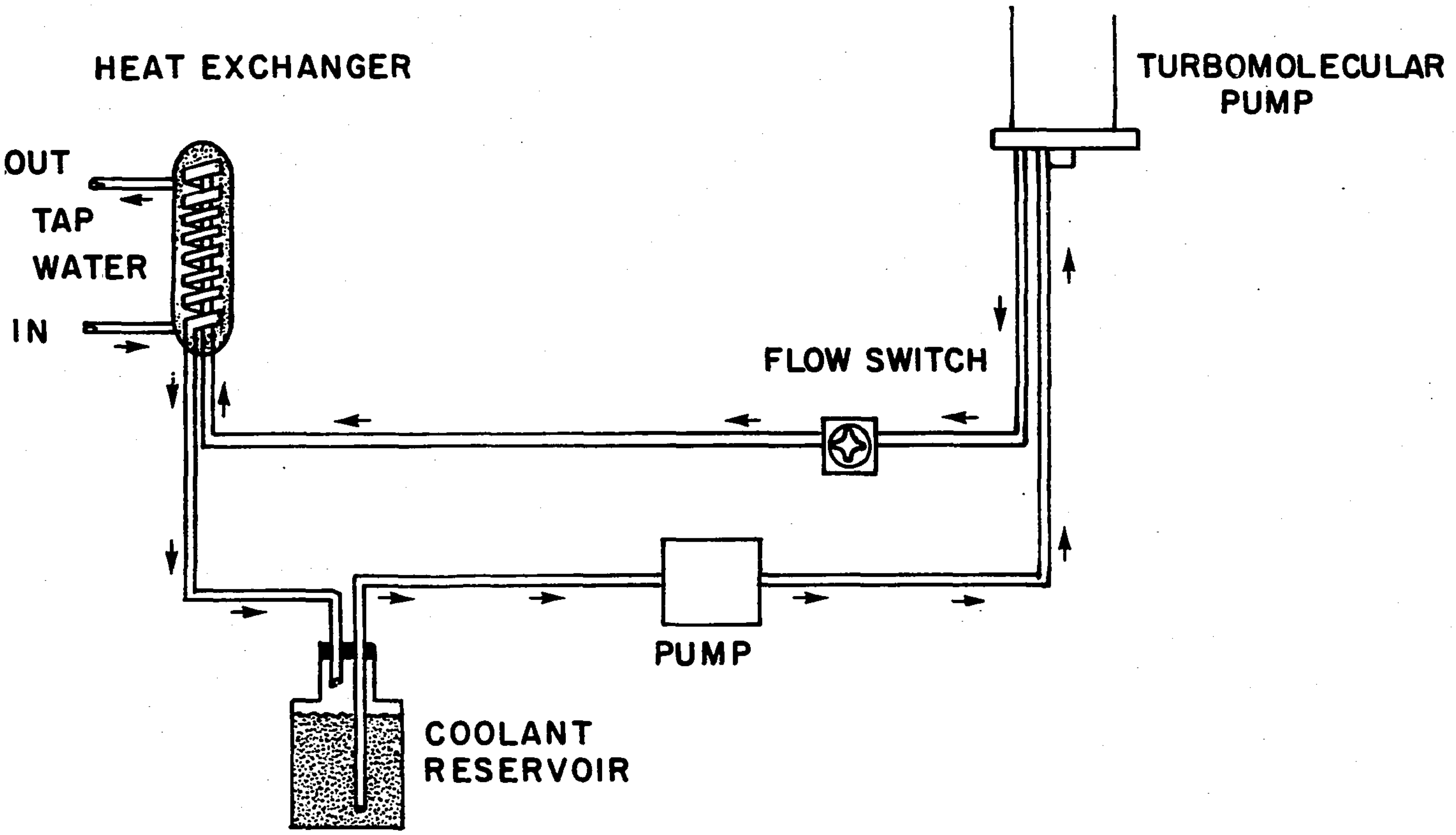


Figure 8. Cooling water system

level can be monitored and more distilled water added or changed as needed.

5. Nuclide Graf 2.2 spark source mass spectrograph

The Nuclide Graf 2.2 spark source mass spectrograph is a commercial instrument which has been extensively updated in our laboratory. The instrument has an organic free vacuum system, being pumped with three ion pumps and a cryogenically trapped mercury diffusion pump. The ion-optical arrangement was designed on the basis of the published works of H. Hintenberger and L. A. König (37). The spectrograph has fixed slits and a theoretical resolving power of 1850. The spectrograph provides the option of either a photographic plate detection system or an electrical detection system using either an electron multiplier or a Faraday cup. The major updating modifications to the instrument involve development and automation of the electrical detection system (38,39), automated spark position adjustors for the solid sample holders (40), automatic control of the illumination angle of the ion optic axis, and improved electronics in the various power supplies and control systems of the instrument.

6. The research ion optical system

a. General description The Research Ion Optical System (RIOS) is ion optically similar to the Nuclide Graf 2.2 mass spectrograph. The major differences concern the electric sectors, the ion detection systems, and the slit assemblies. The RIOS has a spherical electric sector which focuses ions in the vertical (z) direction and improved both sensitivity and theoretical resolving power when compared with a cylindrical electric sector which does not focus in the z-direction as is the case with the Nuclide Graf 2.2. The RIOS has a very flexible ion detector mounting system; however, a Faraday cup was the only detector installed during preliminary operation. The RIOS has externally adjustable slits which allow optimization of mass resolution or sensitivity for each analytical application. The ion optics for a typical mass spectrograph of the same type as the RIOS are shown in Figure 9 and ion optical parameters of both the RIOS and the Nuclide Graf 2.2 are given in Table 1.

The RIOS is assembled on a 3' x 6' x 10" (1 m x 3 m x 0.25 m) granite surface plate which forms a reference surface for alignment of the various instrument segments. A CEC 21-220 magnet was modified by removing two solenoid coils, increasing the magnet air gap to 14.5" (36.8 cm) and adding new magnetic field shaping pieces and pole shoes to achieve the magnetic field shape necessary for a spectroscope

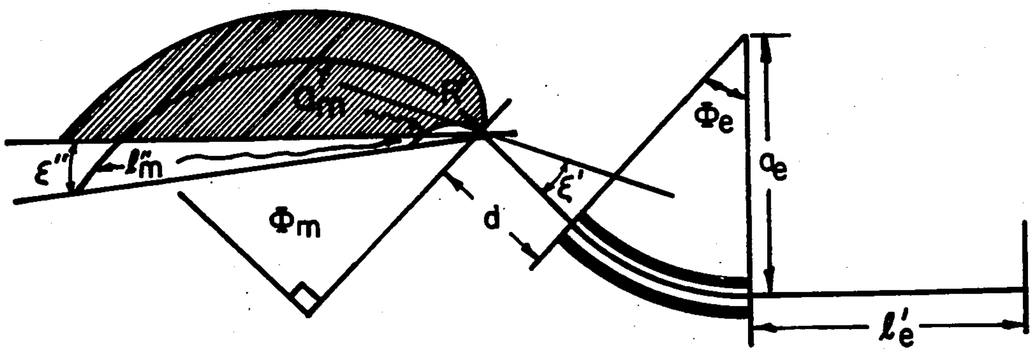


Figure 9. Ion optics of mass spectrograph

Table 1. Ion optical parameters for the Nuclide Graf 2.2 and the Research Ion Optical System

Parameter	Graf 2	RIOS
ℓ'_e	1.189'	12.834"
a_e	6.290"	12.000"
Φ_e	53°2'	43°4'48"
ε'	20°6'	20°6'
Φ_m	90°	90°
ε''	-45°	-45°
ℓ''_m/a_m	0.268	0.268
a_m	2" - 12"	2" - 12"
d	4.83"	6.000"
R'	2.62"	2.62"

The identity of the symbols may be ascertained from Figure 9.

capable of photographic detection. The magnet is mounted on a steel and granite base which centers the magnet gap at a height of 35" above the granite surface plate. The 2' x 3' x 4" (61 cm x 91 cm x 10 cm) granite base of the magnet has grooves machined around the bottom edge and an air inlet to allow the magnet to be lifted off the granite reference surface on an air cushion and positioned exactly with a minimum of effort. Although the magnet and base together weigh approximately 6000 pounds (2750 kg), it can be lifted with an air pressure of $\sim$30 PSI ($\sim$200 kPa) and positioned on the reference surface with one hand. The other adjustable segments of the RIOS are equipped with threaded adjustors on aluminum plates to adjust the various segments to the proper height.

b. The vacuum system The RIOS vacuum system consists of two separate but interconnected systems, a low or forepumping vacuum system and a high vacuum system. The low vacuum system has two forepumps and a low vacuum manifold with a dry nitrogen venting line. The RIOS is located in a low dust room and the forepumps are located in an adjacent room. A schematic diagram of the vacuum system is shown in Figure 10. The forepumps are connected to the RIOS by means of 2" dia. copper pipe and are equipped with molecular sieve traps. The vacuum lines have ball valves located near the instrument that allow the instrument to be vented without affecting the operation of the forepumps. One of the forepumps is a Welch Model 1400 which is used to pump differentially rotary feedthroughs of the externally adjustable ion beam defining slit assemblies, and is also connected to the Nuclide Graf 2.2 vacuum system. The other forepump is a Welch Model 1397 which is connected to the

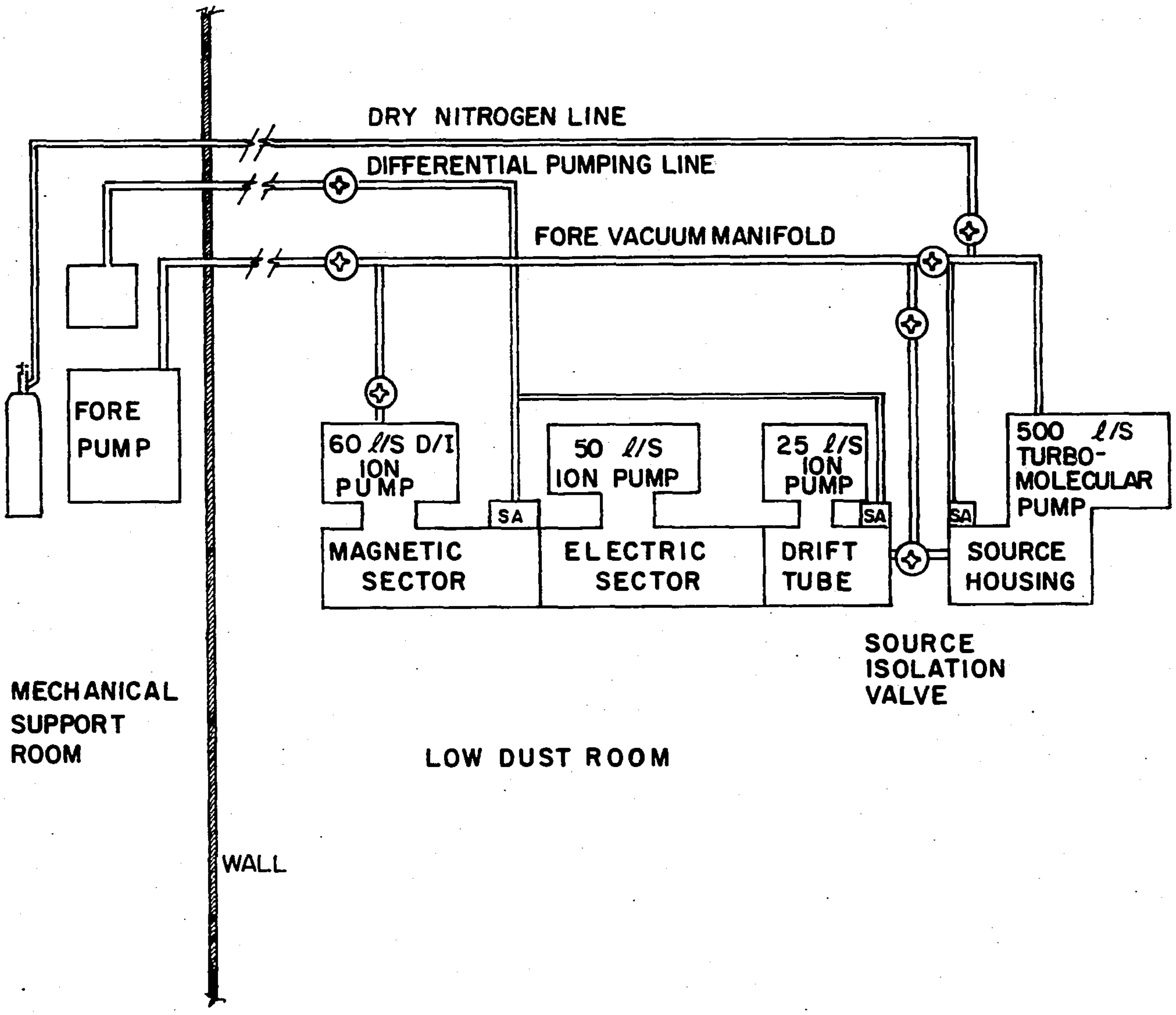


Figure 10. Schematic diagram of the Research Ion Optical System's vacuum system

low vacuum manifold and provides the forevacuum for the turbomolecular pump on the source housing and vacuum pumping system, rough pumping capability for the whole instrument, and differential pumping for the source isolation valves and rotary feedthroughs of the object slit assembly. A dry nitrogen supply line is connected to the low vacuum manifold to reduce water and dust particle contamination of the vacuum system when the source housing or the whole instrument is vented. The pressure in the differential pumping line, the low vacuum manifold, and the source isolation valve differential pumping line is monitored with 0-1000 millitorr (0-133 Pa) thermocouple gauges, Hasting-Raydist Model VU-6 meters with DV-6M tubes.

The high vacuum portion of the vacuum system can be divided into the magnetic sector with the ion current monitor and ion detection system, the electric sector, and a drift tube with the source isolation valve and ion beam defining slit assemblies. The magnetic sector housing is the largest and most complex of the three sections and is shown positioned in the magnet in Figure 11 and in the complete instrument in Figure 12. The magnetic sector is a 18" x 16" x 8" (45.7 cm x 15.24 cm x 20.32 cm) welded assembly fabricated from 1/8" nonmagnetic stainless steel sheet. A 6" x 18" (15.24 cm x 45.7 cm) o-ring/gold gasket rectangular flange provides access to the detector mounting system. A 3"

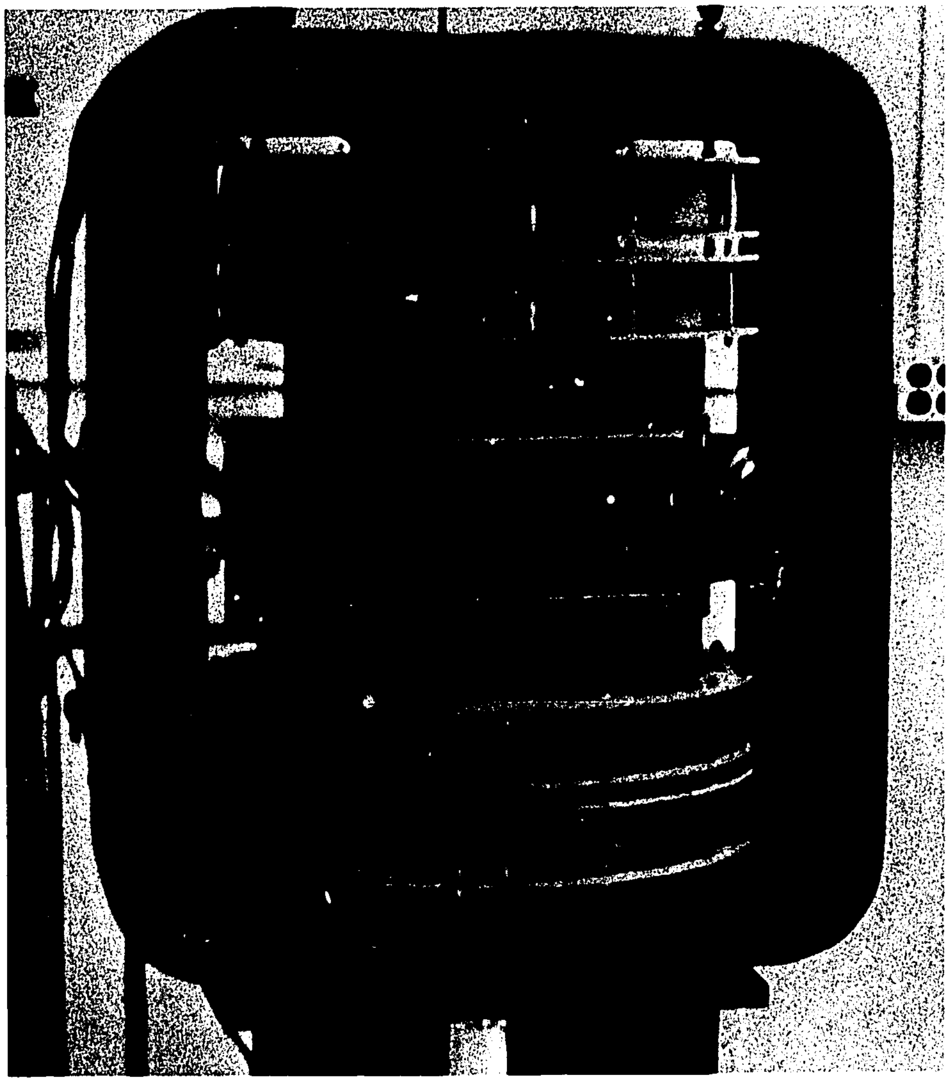


Figure 11. View of magnetic sector housing positioned in magnet

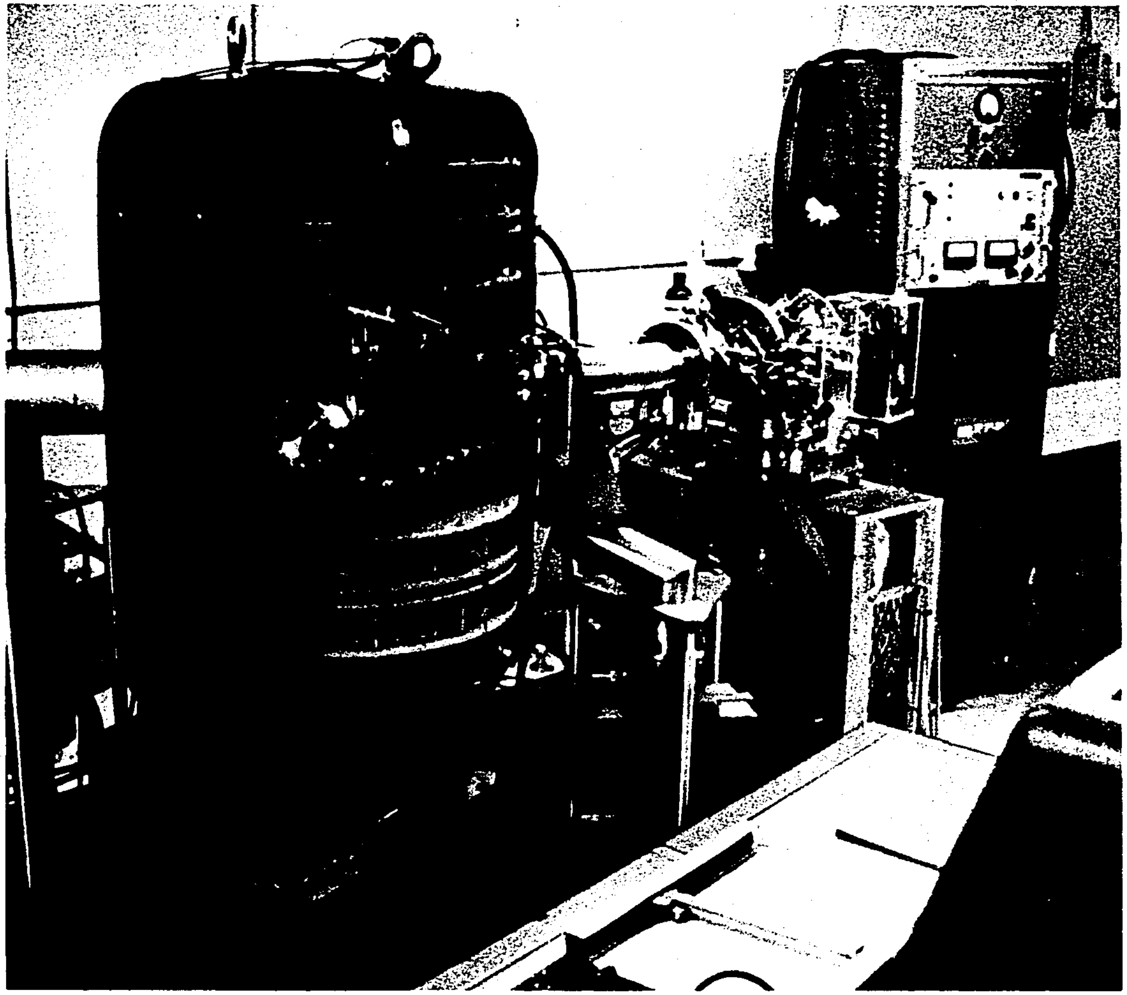


Figure 12. View of magnetic sector housing in complete instrument

(7.62 cm) N.D. Curvac flange is positioned at the high mass end of the image plane to allow a photographic plate detection system to be added at a later date. Four 1.5" (3.8 cm) N.D. CFF flanges are positioned at the top and bottom of the housing on the image plane for electrical and mechanical feedthroughs to the detection system. Four 1.5" (3.8 cm) N.D. CFF flanges are positioned along the back of the housing, two of the flanges have a 3/8" (9.5 mm) hole in the center for positioning the magnet pole pieces and two flanges have standard 1.5" (3.8 cm) N.D. holes which can be used for Hall crystal probes or other auxiliary equipment. A 6" (15.24 cm) N.D. tube is also attached to the back of the housing and has a 90° ell which has a 6" (15.24 cm) N.D. CFF flange for mating to a Perkin-Elmer Ultek 60 ℓ/s differential ion pump with titanium sublimators and a Cryo-shroud. The weight of the ion pump is supported via adjustable legs to an aluminum air-bearing-grooved surface plate. A 1.5" (3.8 cm) N.D. CFF flange is located on the 90° ell for the possible addition of a sorption pump. ARMCO iron inserts which are roughly the shape of the magnet pole shoes are welded into the top and bottom of the housing to conduct the magnetic flux to the magnet pole shoes. A 4" (10.16 cm) N.D. tube is welded at a 37° angle to the image plane on the low mass end of the housing. Four differentially pumped rotary feedthroughs, a 1" (2.54 cm) N.D. copper gasket flange, and a 4" N.D.

(10.16 cm) N.D. rotatable gold gasket flange are mounted on this tube. The 1" (2.54 cm) N.D. flange is used for a six pin glass-to-metal Kovar electrical feedthrough shown in Figure 13, which allows measurement of ion currents at various points in the ion beam monitor. The 4" (10.16 cm) N.D. rotatable flange mates with the Nuclide flange on the electric sector and has three lobes with 1/2" (12.7 mm) holes which are used with 1/2-20 (12.7 mm-20) threaded rods to align the bellows on the electric sector.

The electric sector was designed by Nuclide Corp. and consists of a series of 4" (10.16 cm) N.D. stainless steel tubes welded to form a 43° arc with a 12" (30.48 cm) radius. A 4" N.D. x 1/2" (10.16 cm x 1.27 cm) bellows and a 3" (7.62 cm) N.D. pumping port are located at the image end of the electric sector. The three open tube ends are fitted with gold gasketed flanges, object-end and pumping port male flanges and the image-end female flange. The pumping port flange is fastened to an alignment bracket/ion pump mount which is a 4" (10.16 cm) N.D. stainless steel tube fitted with a rotatable gold gasketed flange to mate with the electric sector, an alignment framework which mates with the lobes on the 4" (10.16 cm) flange of the magnetic sector housing, and an aluminum gasketed flange to mate with a 50 ℓ/s Perkin-Elmer Ultek ion pump. The weight of the ion pump is supported on an aluminum air-bearing surface plate

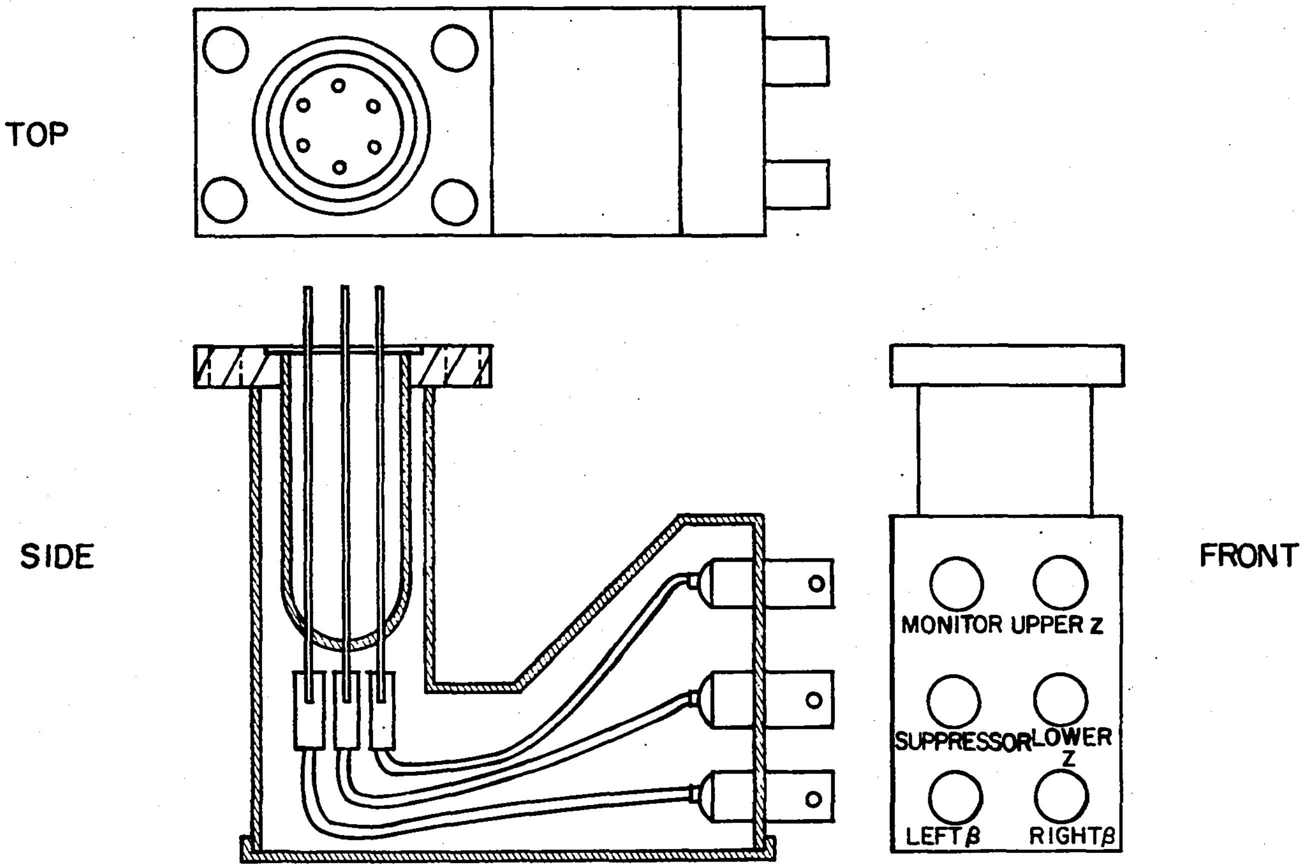


Figure 13. Ion current monitor's electrical vacuum feedthrough

with three adjustable legs for optical alignment. Two of the adjustable legs are positioned on the optical axis of the ion beam entering the magnetic sector to ease the rotational adjustment of the electric sector with respect to the magnetic sector. The alignment bracket/ion pump mount can be seen beside the magnet in Figure 12 with the ion pump attached.

The third segment of the high vacuum system is a drift tube which encloses the 12.834" (32.60 cm) object distance of the electric sector. The drift tube is a 4" (10.16 cm) N.D. stainless steel tube with a gold gasket flange to mate with the electric sector, a 2" (5.1 cm) N.D. pumping port with a 2" (5.1 cm) N.D. CFF flange, seven differentially pumped rotary feedthroughs, six Kovar glass-to-metal electrical vacuum feedthroughs, a source isolation valve, and an o-ring/gold gasket flange to mate with the source housing. A 25 ℓ/s Perkin-Elmer Ultek ion pump is mounted on the 2" (5.1 cm) N.D. CFF flange. The source isolation valve is a differentially pumped 1" (2.54 cm) I.D. ball valve which allows the source housing to be vented without affecting the vacuum in the mass analyzer. The drift tube is shown schematically in Figure 14.

c. <u>The electric sector</u> The electric sector used on the RIOS was specially designed by Nuclide Corp. in conjunction with our laboratory (41) for use with the magnetic

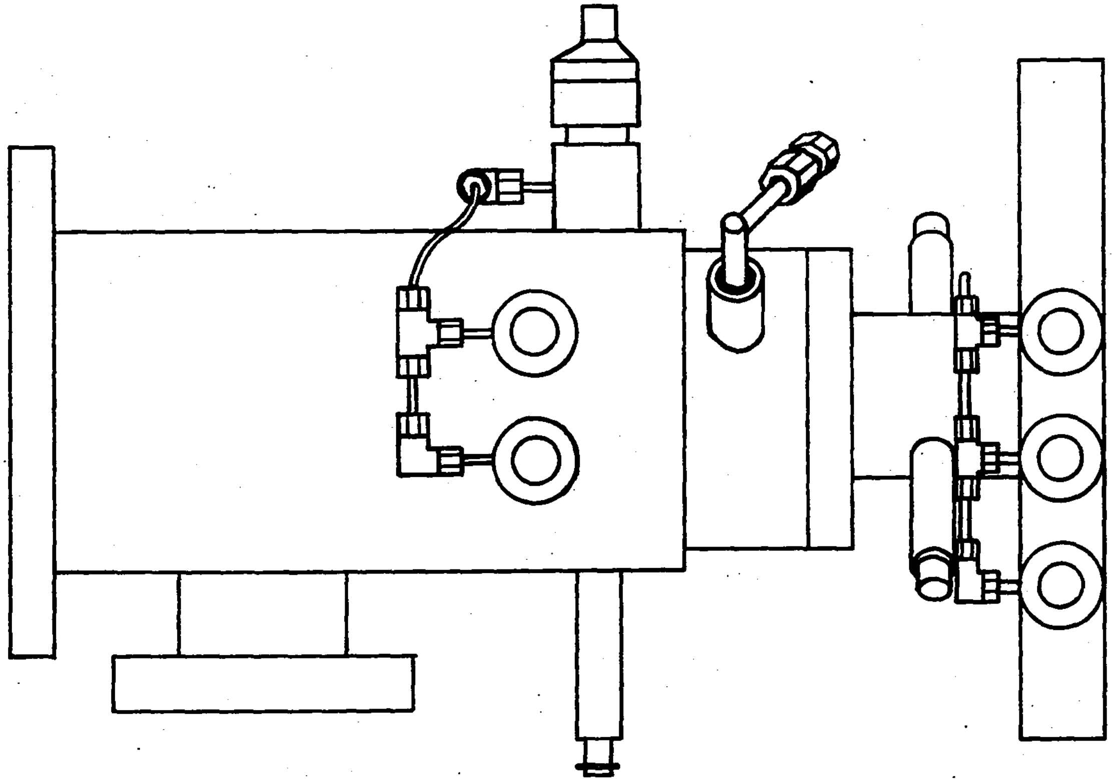


Figure 14. Drift tube

sector of the Nuclide Graf 2.2 mass spectrograph. The RIOS electric sector is a 12" (30.48 cm) radius 43°4'48" arc spherical electric sector and is made up of two specially shaped condenser plates with field termination strips at both ends. The exact dimensions and configuration of the condenser plates are proprietary information belonging to Nuclide Corp.

d. The magnetic sector   The magnetic sector of the RIOS is ion optically identical to that of the Nuclide Graf 2.2 mass spectrograph. The actual configuration of the magnetic sector of the RIOS, however, is unique. The magnet pole shoes are 2.5" (6.35 cm) thick ARMCO iron pieces machined to the exact dimensions of the theoretical optics for a 2"-12" (5 cm - 30 cm) radius spectrograph with a 1" (2.54 cm) safety distance along the back to assure a uniform magnetic field. The magnet pole shoes are held to a 0.4940" (12.55 mm) gap with aluminum spacers and stainless steel straps along the outer radius. The lower pole shoe with straps and spacers is shown in Figure 15. The pole shoes and the ARMCO inserts on the magnetic sector housing have a 2° angle machined on their mating surfaces and the pole shoe assembly is wedged into place and can be removed only by heating the arms of the magnet to release the pressure. Herzog terminators (42,43) are used at both the object and image boundaries of the magnet field to terminate the magnetic flux at the edge of the pole

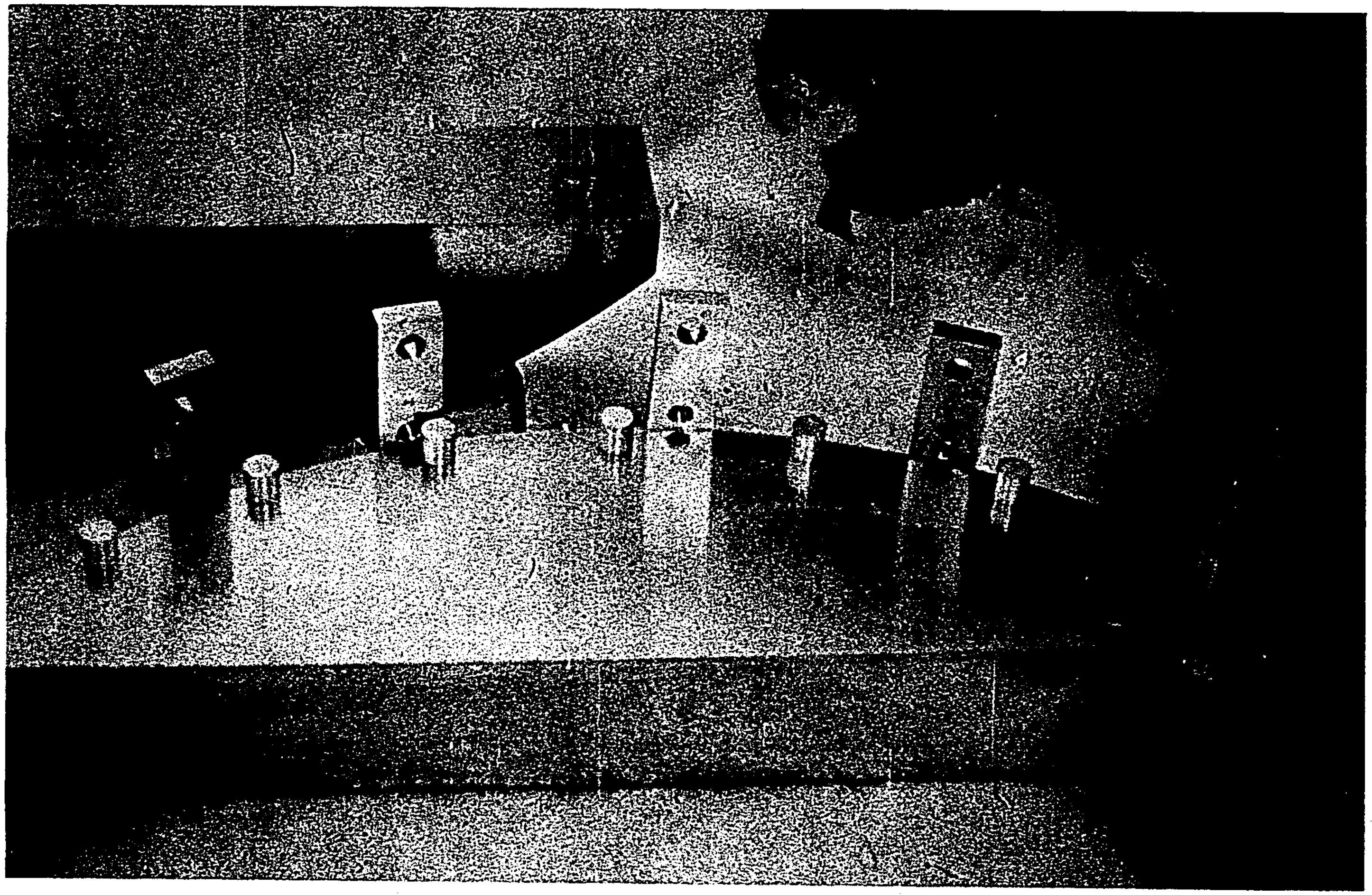


Figure 15. Lower pole shoes with straps and spacers

shoes. The terminators have a 7/16" (11.1 mm) gap and are set 1/16" (1.6 mm) from the pole piece boundary. The magnet pole shoes and the Herzog terminators are gold plated to prevent corrosion of the iron.

The ion current monitor is located inside the object Herzog terminator as shown in Figure 16. The monitor is a wire grid which intercepts 20% of the ions passing through it. The magnetic field present in the Herzog terminator prevents secondary electrons from escaping the monitor when high energy ions impact the surface of the grid and therefore prevent erroneous ion current readings.

e. Externally adjustable slit assemblies Five externally adjustable slit assemblies are used in the RIOS. Four slit assemblies are only adjustable for centering and gap width and are used in the α (angular divergence) limiting, β (energy) limiting, and two z (vertical) limiting positions. The object slit is adjustable for centering, gap width, and rotation. The slit assemblies are operated by hexagonal head control shafts with ten-turn vernier dials which can be adjusted to 1/100 turn. The control shafts are positioned in the differentially pumped rotary feedthroughs with set screws which fit into grooves machined into the control shaft as shown in Figure 17. The centering control shafts have 1/4" - 20 (6.3 mm x 20) threads on the end which fit into tapped holes on the slit assemblies. Twenty threads per inch

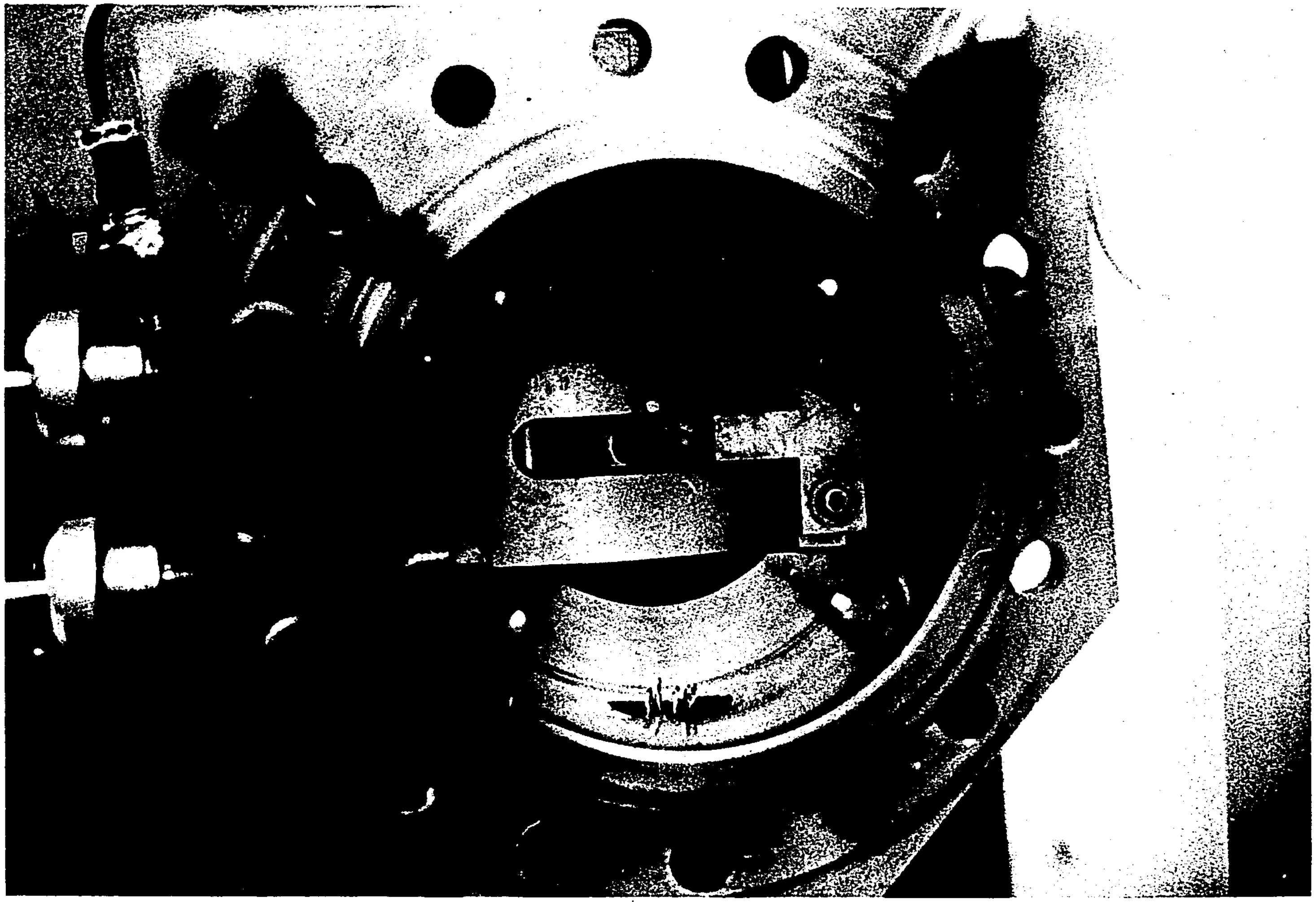


Figure 16. Ion current monitor located inside Herzog terminator

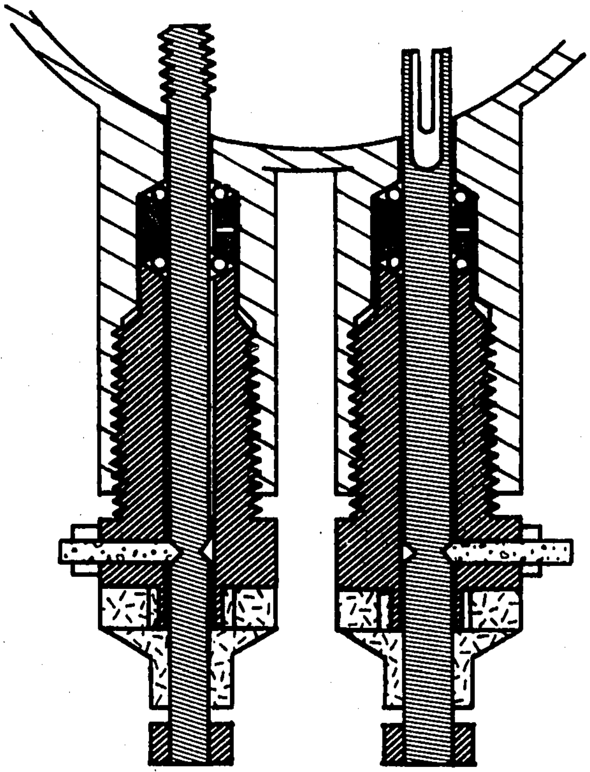


Figure 17. Control shafts positioned in differentially pumped rotary feedthroughs

(7.8 threads per cm) will move a slit assembly 0.050" (1.27 mm) in one rotation of the control shaft and with a vernier dial accuracy of 1/100 turn, the centering adjustment is accurate to 0.0005" (0.0127 mm). The gap width control shafts for the beam limiting slit assemblies have slotted 1/8" (3.18 mm) dia. holes on the end which fit over pinned shafts on the slit assemblies. These allow the slit assembly to be moved for centering and transmit rotational movement for gap width adjustment. The gap width control for the object slit assembly has an 1/8" x 1/8" dia. (3.18 mm x 3.18 mm dia.) end which is connected to a flexible joint on the object slit assembly. The object slit rotation control shaft has a 1" x 1/8" dia. (2.54 cm x 0.32 cm dia.) end with a 1/4" x 1/16" dia. (6.35 mm x 1.6 mm dia.) pin press fit in a hole 1/8" (3.2 mm) from the end which mates with a slotted hole on the object slit assembly and allows lateral movement.

The ion beam limiting slit assemblies are assembled as two mirror image pairs; however, the components are identical in all four assemblies. The α-limiting slit assembly and the first z-limiting slit assembly do not have electron suppressors. The β-limiting slit assembly and the second z-limiting slit assembly have electron suppressors. The slit assemblies are designed to allow independent ion current measurement at each slit half. The β-limiting slit assembly is shown schematically in Figure 18. Lateral motion

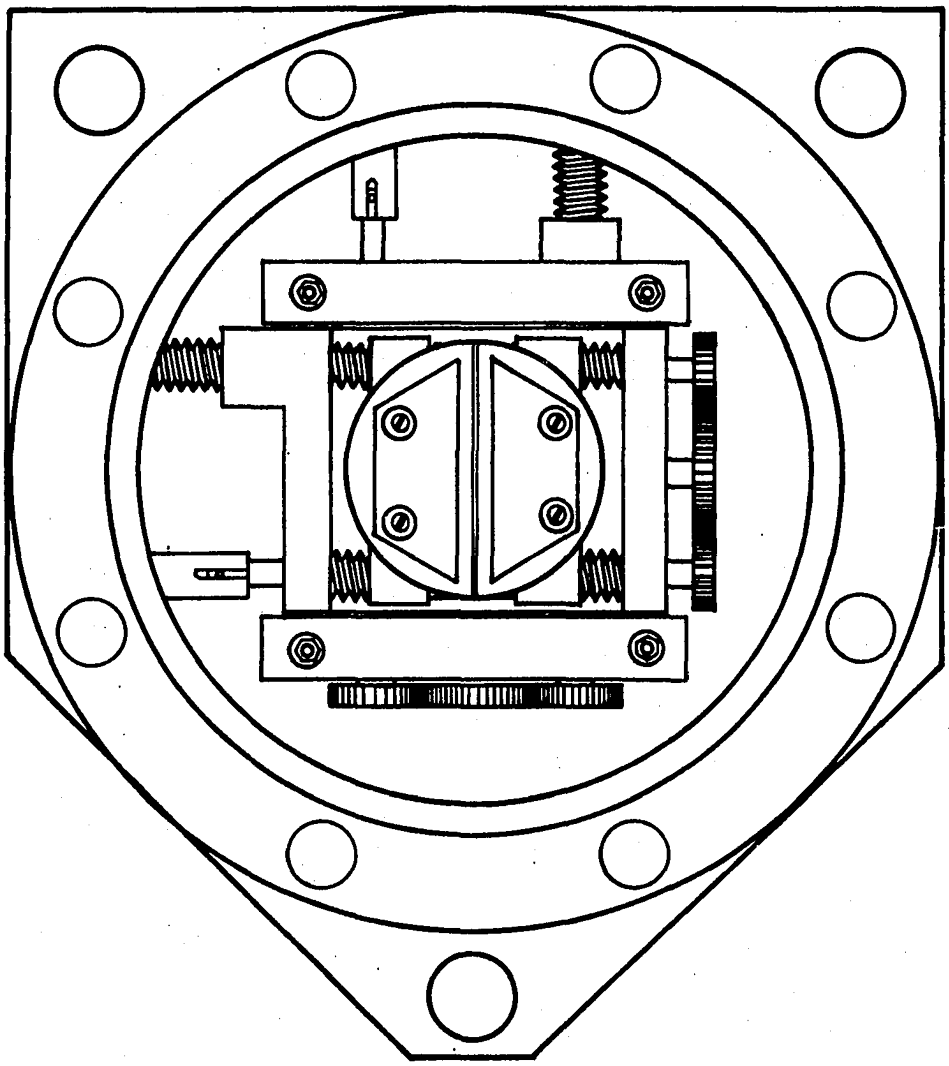


Figure 18. β-Limiting slit assembly

for centering of the beam limiting slit assemblies is permitted by 1/8" (3.2 mm) dia. Teflon rods inserted into V-grooves on the edge of the slit assembly base and mounting brackets. Gap width adjustment is done by mounting the slit halves on 3/8" x 3/8" x 1 3/4" (9.5 mm x 9.5 mm x 44.5 mm) aluminum blocks with 1/4"-40 (6.3 mm-40) threaded holes on each end. The blocks are made so half have left hand threads and half have right hand threads. These are mounted on two shafts which are threaded left hand on one half and right hand on the other. These shafts are mounted on two pillow blocks fastened to the slit assembly base and are connected mechanically with two 30 tooth gears and a 56 tooth idler gear. Forty threads per inch result in a movement of 0.025" (0.64 mm) per turn for each slit half and a gap width adjustment of 0.050" (1.27 mm) per turn. The gap width can be adjusted with an accuracy of 0.0005" (0.013 mm) with a vernier dial accuracy of 1/100 turn.

The slit halves are mounted on the aluminum blocks as shown in a cutaway view in Figure 19. The slit halves are aligned with two 1/8" threaded pins mounted in Teflon spacers and are held in place with two #2-56 screws. The electron suppressors are mounted in Kel-F insulators and attached with the same screws as the slit halves. The wires used to measure ion current on each slit half are attached to the

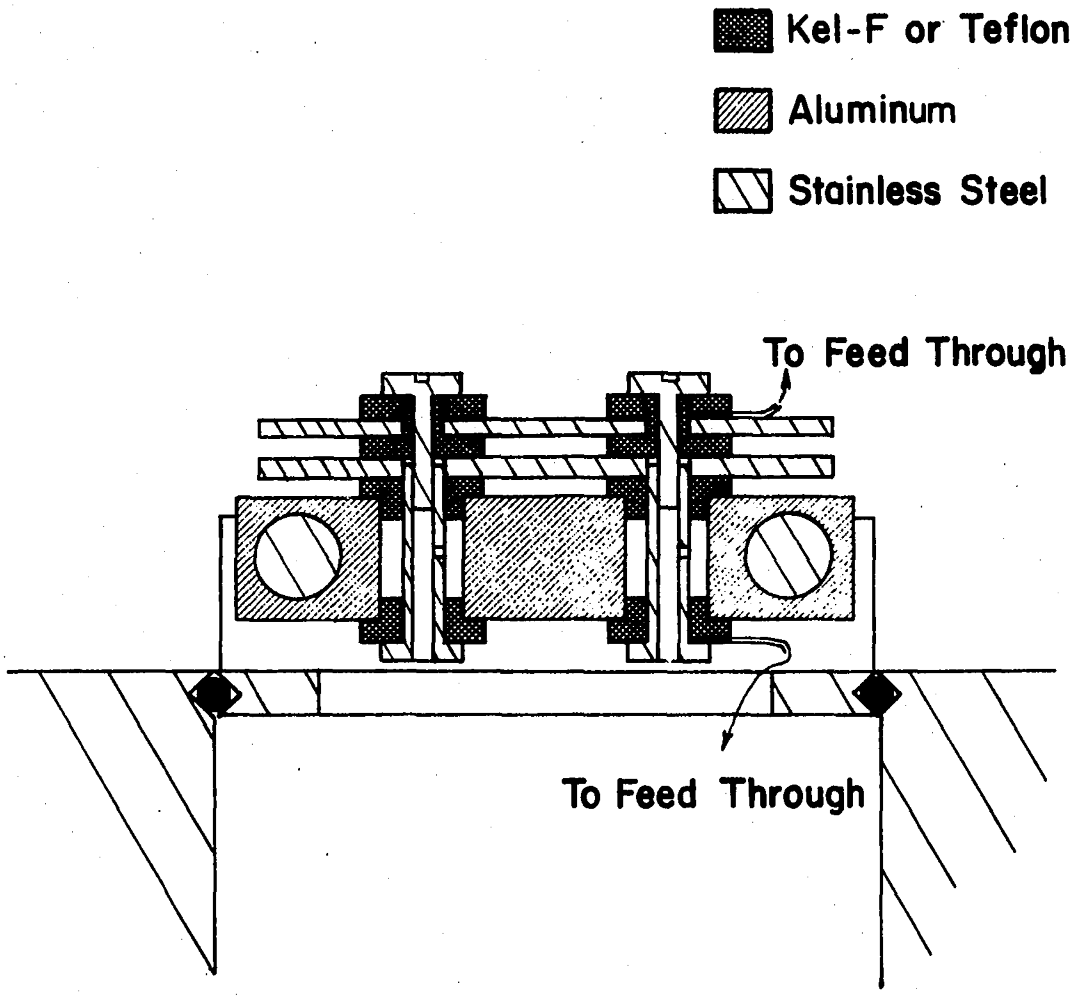


Figure 19. Slit halves mounted on aluminum blocks

threaded pin at the back of the aluminum block and are not affected when slit halves are replaced.

The object slit assembly is shown schematically in Figure 20. The slit halves are identical to those on the ion beam limiting slit assemblies. The gap width adjustment operates on the same principle as the ion beam limiting slit assemblies, but only one threaded shaft is used. The aluminum blocks are 3/8" x 5/8" x 1 3/4" (0.95 cm x 1.58 cm x 4.45 cm) with one hole tapped 1/4" - 40 (6.35 mm - 40) and another fitted with a Teflon bushing. The Teflon bushings allow the wider blocks to slide along a 1/8" (3.2 mm) dia. stainless steel rod with a minimum of binding when the control shaft is turned. Lateral motion for centering of the object slit assembly is accomplished by stainless steel balls in V-grooves of the slit assembly base and mounting brackets and an expansion mechanism with two flexible joints in the gap width control shaft. The flexible joints allow the object slit to be rotated. The rotation is done by a 1/4" - 20 (6.33 mm - 20) threaded rod on the slit assembly base which is fixed against a threaded surface on a turntable. The turntable is made in two halves with beveled inner edges which are bolted together forming a V-groove. The inner diameter of the object slit base also has a V-groove machined into it. Three stainless steel balls, held in place by 1/16" (1.6 mm) dia. pins in the turntable halves act as a ball bearing and allow the turntable

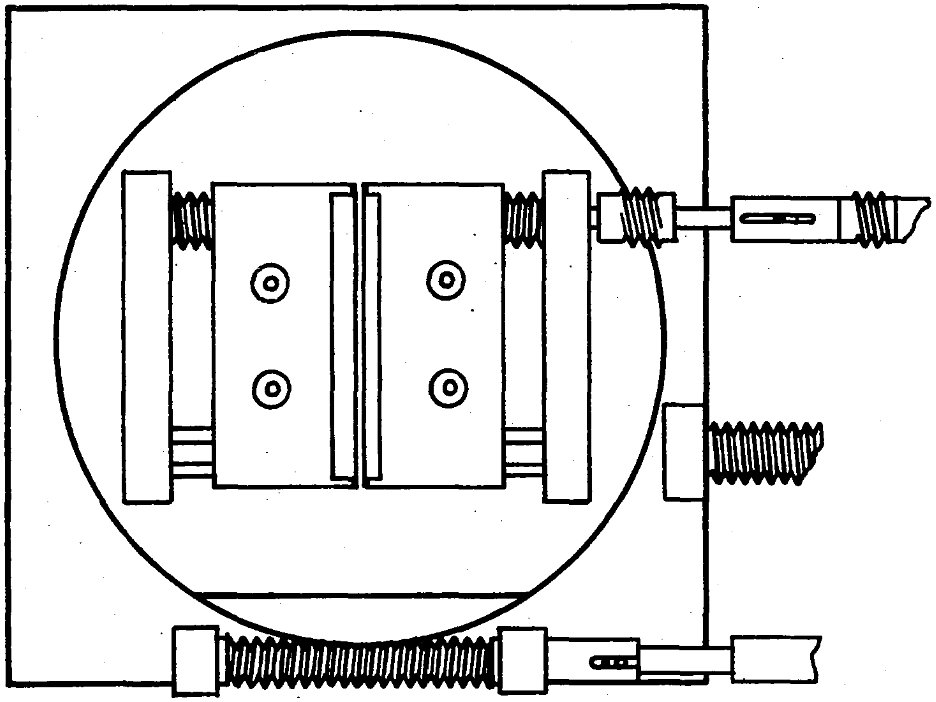


Figure 20. Schematic of object slit assembly

to rotate. The turntable diameter is 2.866" (7.28 cm) which results in a rotation of 2° per turn and an accuracy of 0.02° or 1.2' with vernier dial accuracy of 1/100 turn. All the slit assemblies have an approximate lateral motion for centering of ± ∿1/4 inch (∿6.35 mm) and a maximum gap width of ∿1/2" (∿12.7 mm). The object slit can be rotated approximately 10° either side of vertical.

f. The split Faraday cup detectors The ion current detection system for the RIOS is a Faraday cup system with two Faraday cups in a single mounting block and centered on the ion optical axis, which allows the ion beam to be adjusted accurately with respect to the z-axis. A split Faraday cup detector is shown schematically in Figure 21 and as mounted on the RIOS with shielding covers removed in Figure 22. The detector assembly consists of a mounting plate, two slit halves, an electron suppressor, two Faraday cups in a Kel-F block, and a shielding cover. The base is heavy gauge stainless steel with No. 10 slots to allow adjustment to the image plane. The base is set perpendicular to the ion beam with aluminum angle brackets. The image slit consists of two 0.010" (0.25 mm) stainless steel plates which are slotted and attached with four 0-80 studs, nuts, and washers. Image slit adjustment is done with a microscope and a thickness gauge. The electron suppressor is 0.025" (0.6 mm) stainless steel with a 1/4" (6.35 mm) inner width and is

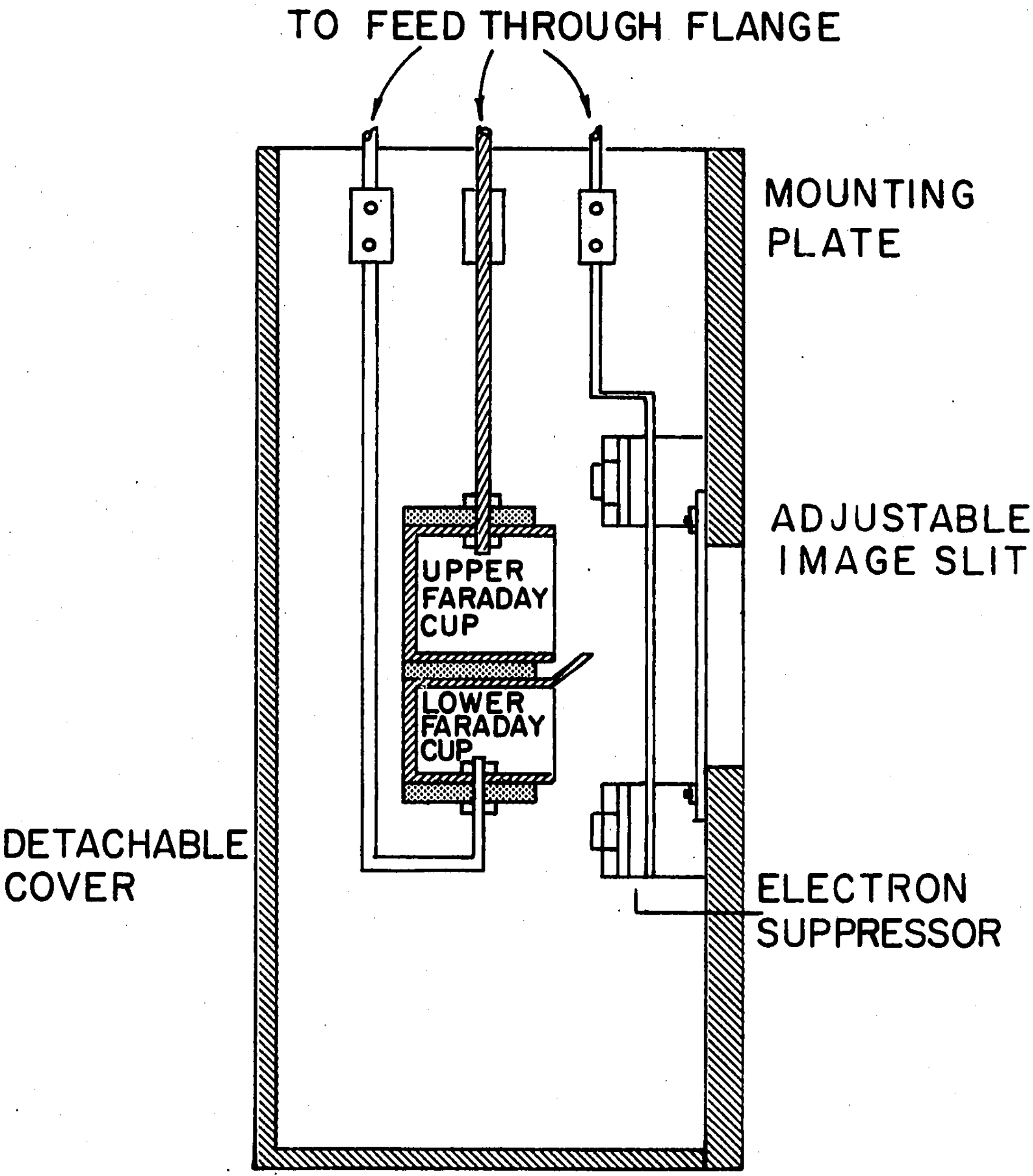


Figure 21. Split Faraday cup detector

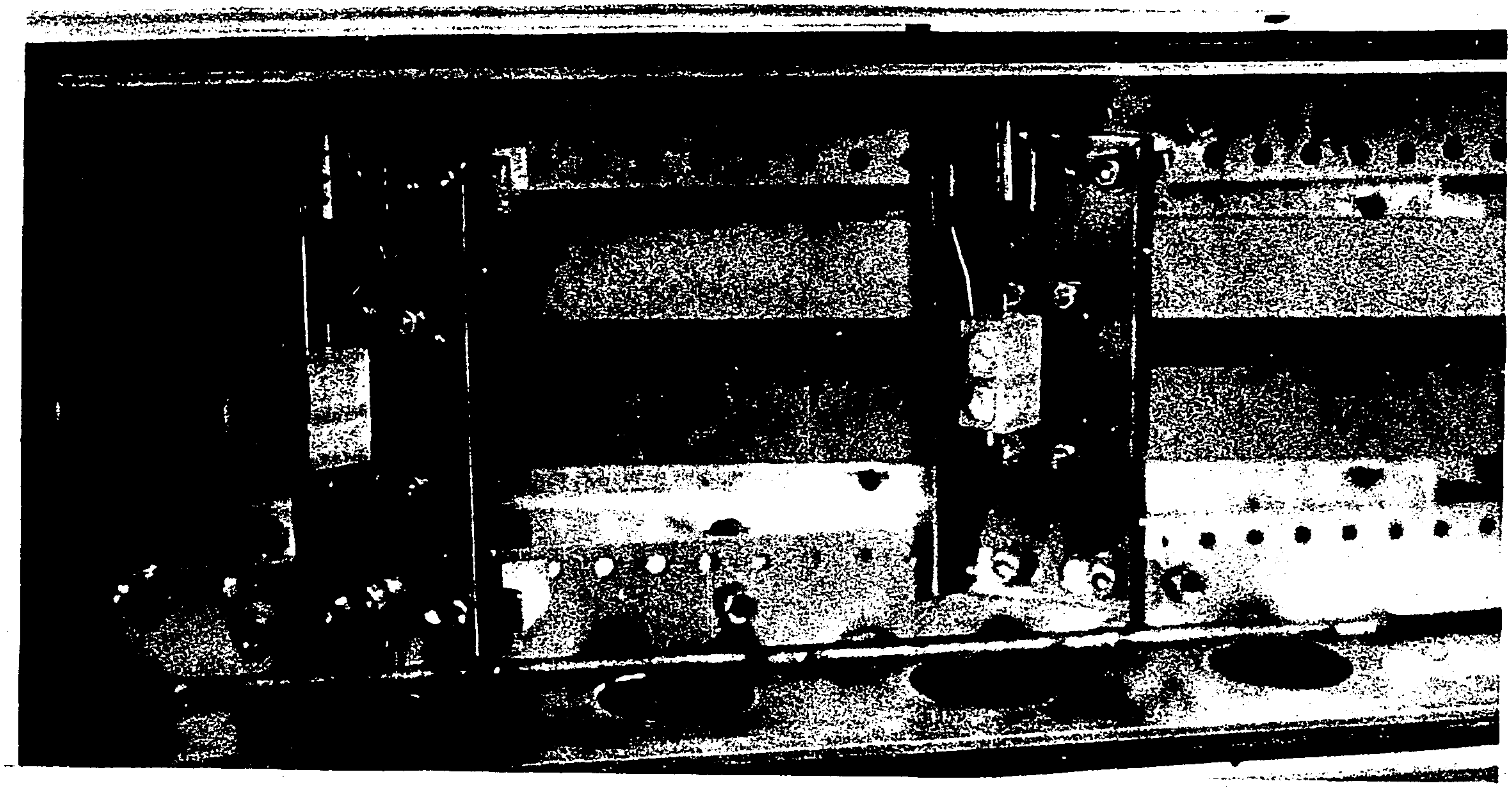


Figure 22. Split Faraday cup detector mounted on the Research Ion Optical System

mounted on the base with 1/4" (6.35 mm) Kel-F insulators and 0-80 screws and washers. Electron suppressor voltage is from a 22½ volt dry cell through a glass to metal electrical feedthrough. Two rectangular Faraday cups are mounted in a Kel-F block and are electrically isolated from each other. The lower Faraday cup has an angled lip which forms a continuous detector. The split Faraday cup detector is suspended from a triple glass-to-metal electrical feedthrough by two 1/16" (1.6 mm) dia. threaded rods which are attached to the Faraday cups with 0-80 nuts. The base is designed to accept a snap-on cover which acts as a shield for secondary electrons or ions produced when high energy ions strike surfaces inside the vacuum system.

C. Electrical Components

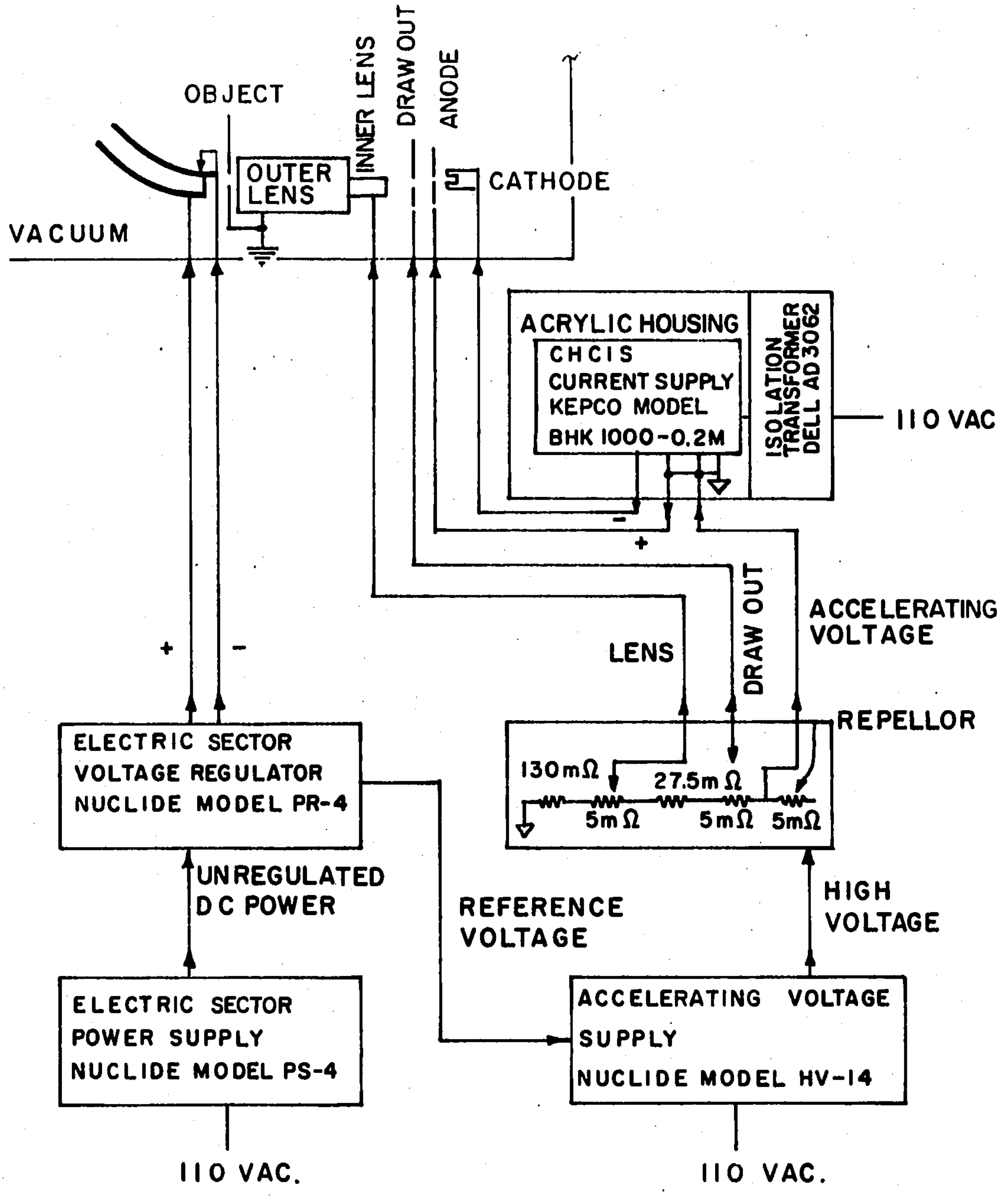
1. CHCIS source current supply

The CHCIS source current supply is a Kepco Model BHK 1000-0.2 M. This supply is capable of supplying ± 1000 volts and 200 mA and can be both voltage and current regulated. When used with the CHCIS, a metal oxide varistor, series L, model V 1000 LS160 A, is placed across the output to protect the supply from high voltage breakdowns and the positive output is tied to chassis ground. The power supply is encased in a Plexiglass cabinet with bakelite extensions on the controls and is powered via a Dell Electronics Corp., Type AD 3062, isolation transformer to allow the ion source to be floated at 24,000 volts. A block diagram of the electrical circuitry for the ion source and electric sector is shown in Figure 23.

2. Accelerating voltage supply and voltage divider

The accelerating voltage supply is a Nuclide model HV-14. This supply has an output voltage range of 0 to 35,000 volts, regulated to 0.5 volts, and has a maximum output current of 4 mA. The high voltage output is proportional to a reference input of 0 to -1100 volts obtained from the electric sector power supply system. The HV-14 has been modified with a switchable input resistor so the accelerating voltage/electric sector potential ratio would be correct for either the 6" radius electric sector on the Nuclide Graf 2.2 or the 12" radius electric sector on the RIOS. Other controls include an offset potential control, fine proportionality control, and an on-off switch. Front panel meters display both output voltage and output current.

A voltage divider is used to provide a lens voltage for the coaxial cylindrical electric lens, a draw out potential for the CHCIS, and a repeller voltage for use with other experimental ion sources. The voltage divider circuit is included in Figure 23. The voltage divider circuit is enclosed in a Plexiglass cabinet with plastic control extensions for safety.



NOTE: ALL CABLES OTHER THAN 110AC POWER AND THE UNREGULATED DC POWER ARE SHIELDED COAX CABLES.

Figure 23. Voltage divider circuit

3. The electric sector power supply system

The electric sector power supply system is a Nuclide model PR-4/PS-4. This supply is a dual regulated system which separates the DC voltage regulation and the AC power supply into two separate chassis. The output controls and meter are on the PR-4 regulator panel, and the line voltage switch, fuses, and transformers are in the PS-4 power supply unit. The output voltage is 0-3000 volts DC between the electric sector plates or 0 to 1500 volts DC and 0 to -1500 volts DC with respect to the midpoint. The output current is 8 mA maximum continuous drain and 20 mA peak for 50 milliseconds. The output voltage is regulated to ± (0.001% + 0.002 volt) between each plate and the midpoint. The output voltage can be controlled with front panel switches or by a 0 to 10 volt DC external control system.

4. The magnet current supply

The magnet current supply for the RIOS was designed by the instrumentation group of the Ames Laboratory, USDOE, in 1956. The magnet current supply is current regulated over a current range of 160 to 800 mA with a voltage maximum of approximately 1000 volts DC. The magnet current supply proved to be marginally acceptable for use with the RIOS, and it is recommended that a new solid state power supply be acquired as soon as possible.

5. The vibrating reed electrometers (VRE's)

The detection system for the RIOS uses three Cary model 31 VRE's which have been modified to use a single oscillator and prevent beat noise. The Cary model 31 VRE is capable of measuring voltages across an input resistor or capacitor of 1, 3, 10, 30, 100, and 300 millivolts full scale and 1, 3, 10, and 30 volts full scale. Two of the VRE's used for the RIOS have 1×10^{11} Ω input resistors in the preamplifier and are capable of measuring currents in the range of 10^{-15} to 10^{-16} amperes. The other VRE has a selector with three input resistors; 5×10^{10} Ω, 5×10^{8} Ω, and 1×10^{6} Ω.

6. The ion pump power supplies

Two ion pump power supplies are used for the RIOS. A Perkin-Elmer ULTEK model 224-0620 combination power unit is used to power a 60 ℓ/s differential ion pump, a 50 ℓ/s conventional ion pump, and a titanium sublimation pump. This combination power unit operates on 115 V single phase 60 Hz power and has upper limits on voltage and current of 4750 V DC and 350 mA for the ion pump supply and 8 V AC maximum with up to 500 watts of power available for the sublimation pump power supply. The sublimation pump current is metered and controlled from the front panel. The ion pump supply is also metered with 20 μA, 200 μA, 2 mA, 20 mA, 200 mA and 500 mA current ranges, a 5000 V DC range, and a 10^{-4} to 10^{-9} torr logarithmic pressure range. A Perkin-Elmer ULTEK model 222 - 0400 power supply powers a 25 ℓ/s conventional ion pump. This supply has a 4750 V DC voltage limit and a 150 mA current limit with 20 µA, 200 µA, 2 mA, 20 mA, 200 mA, 5000 V DC, and a 10^{-4} to 10^{-9} torr meter range.

7. The RIOS high vacuum gauges

The pressure in the mass analyzer of the RIOS is monitored with the ion pump power supplies. The pressure in the source housing is measured with a model 100-A cold cathode vacuum gauge manufactured by Miller Laboratories. The cold cathode gauge is useful in the 10^{-2} to 10^{-8} torr pressure range and is metered in $x10^{-7}$, $x10^{-6}$, $x10^{-5}$, $x\ 10^{-4}$, and $x10^{-3}$ torr increments.

III. EXPERIMENTAL

A. Cryogenic Hollow Cathode Ion Source Operation

The cryogenic hollow cathode ion source (CHCIS) is a single sample ion source which must be disassembled and reassembled to admit each sample to the mass spectrometer. Clean ion source parts are normally used for reassembly to eliminate potential sample memory problems. Approximately 20 minutes are required to disassemble the ion source, introduce a sample into the ion source, and reassemble the ion source in the mass spectrometer. A routine analysis using photographic detection can be done in 20 minutes although the sample will last 30-40 minutes under normal operating conditions. Although the total time required for loading and analyzing a sample results in a relatively slow sample rate of 1.5 samples per hour, operation of the CHCIS is straightforward and can be discussed as two distinct steps, loading the sample and analyzing the sample. Because this phase of the work concerns a test of the feasibility of the CHCIS for analyzing small volumes of aqueous samples, no further development was considered.

Sample loading is begun by closing the ion source chamber isolation valve on the mass spectrometer and venting the ion source chamber with dry nitrogen. The ion source is then disassembled by loosening the clamp holding the cathode in place and swinging the copper cooling strap to the side to remove the cathode. The four 0-80 nuts holding the remainder of the ion source together are then removed and the source body, borosilicate glass sleeve, anode, drawout electrode and spacers are removed. Care must be taken that electrical and reagent gas connections are not damaged during disassembly and reassembly. The ion source, less cathode, is then reassembled using a clean drawout electrode, anode, and borosilicate glass sleeve. Approximately 20-50 $\mu\ell$ of aqueous sample is placed in the hollow cathode where it is held in place by surface tension. The cathode is installed on the ion source with the cooling strap and cold finger clamp in place. The ion source chamber is closed and liquid nitrogen is poured into the cold finger. The sample freezes rapidly and the ion source chamber can be evacuated after approximately two minutes.

The sample can be analyzed after the ion source chamber has reached an operating pressure less than 1×10^{-5} torr (1×10^{-3} Pa). The various power supplies used to operate the CHCIS on a double focusing mass spectrograph are turned on and set to the proper operating voltages in a specific order to prevent damage to the ion source current supply. First, the ion source current supply AC switch is turned on and the filaments in the series tubes are allowed to warm up for 30 seconds. Then, the ion source current supply HV switch is turned on. The electric sector power supply on the mass spectrometer is then turned on and allowed to stabilize before turning the accelerating voltage supply on. The electric sector supply is then set to the predetermined operating voltage. The ion source current supply voltage limit is then set to 1000 Volts. A glow discharge is started in the CHCIS by admitting oxygen into the ion source through the reagent gas inlet system at a pressure of approximately one torr (133 Pa). After 15-20 seconds, the oxygen supply is turned off and the current limit potentiometer of the ion source current supply is adjusted to maintain a stable discharge using water vapor from the sample as the reagent gas. Data collection can begin after one to two minutes of sample pretreatment time during which the glow discharge stabilizes. The ion beam is deflected from the object slit and the ion source chamber isolation valve is opened. The ion current is turned on and off to adjust photoplates or detection system zero using an ion beam deflector to maintain a stable glow discharge. When the necessary data have been collected, the glow discharge is turned off by setting the ion source current supply voltage limit to 100 volts, which is a lower voltage than that required to maintain the glow discharge. The power supplies are then turned off in reverse order as they were turned on.

B. Research Ion Optical System Operation

1. Routine operation

The RIOS has three Cary model 31 vibrating reed electrometers (VRE) and a magnet power supply which must be turned on and allowed to stabilize prior to operation. The VRE heads must be shorted through their internal shorting switches prior to disconnecting or connecting signal cables to prevent damage to the amplifiers. They are normally left in the shorted mode when not in use. Two of the VRE's are matched with 1×10^{11} Ω input resistors and utilize an electronic shorting control panel located in the electronics cabinet. The electronic shorting control panel has a power supply which must be turned on to short the VRE heads and a selector switch which is used to select the shorting combination desired for the two VRE heads. The third VRE head has a manual switch which shorts the head and allows four resistor or capacitor values to be selected. A routine analysis will normally begin with the VRE heads shorted and the VRE amplifiers and magnet power supply turned on and stabilized.

The magnet power control panel also has a power supply for a variable speed scan motor which must be turned on when one desires to operate the instrument in a normal magnetic scan mode. This scan motor drives a forty-turn potentiometer with a vernier dial which can be correlated to a nominal mass when operated at the calibrating scan rate. A selector switch on the magnet power control panel allows one to select any of three mass setting potentiometers, a forty-turn motor driven potentiometer or two ten-turn potentiometers. The two ten-turn potentiometers can be set to predetermined masses and, when used in conjunction with the selector switch, allow magnetic peak switching to be done over a small mass range.

When the VRE's and the magnet power supply have stabilized, the sample can be introduced into the ion source and the ion source power supplies turned on in the order prescribed for a particular ion source. Normally, the ion source power supplies will be turned on at first to a standby mode prior to turning on the accelerating voltage and electric sector power supplies to prevent damage to components in the ion source supplies. The accelerating voltage supply is turned on and then the electric sector power supply is turned on and set to a predetermined operating voltage to bring the ion source and ion source power supplies gradually to the instrument operating voltages. The accelerating voltage supply and the electric sector power supply are both stable and reproducible; however, it is advisable to check periodically for ion beam centering at the ion current monitor. Ion beam centering must also be tested whenever a different accelerating voltage is used.

Ion beam centering is measured by connecting VRE's to the right and left energy resolving (β) slit halves and the total ion current monitor. The ion beam is centered by adjusting the RATIO or OFFSET potentiometers on the accelerating voltage supply until the left and right β-slit halves receive identical ion currents and the ion current at the monitor is at a maximum. Both the RATIO and OFFSET potentiometers must be adjusted to center the ion beam over an accelerating voltage range if the accelerating and electric sector voltages are to be scanned or if peak switching is desired.

2. Evacuation

The RIOS mass analyzer is evacuated by opening the roughing valve to the 60 ℓ/s Perkin Elmer/ULTEK DI ion pump. The ion source chamber roughing valve should be closed if the chamber is already evacuated. When the mass analyzer has been evacuated to a pressure of 10-20 millitorr (∿1-3 Pa), the roughing valve to the 60 ℓ/s DI ion pump is closed and the cryoshroud is filled with liquid nitrogen. The titanium sublimation pump power supply is turned on and the current set to the normal operating range (∿50 amp). After three minutes of pumping with the titanium sublimation pump, the ion pump power supplies are turned on with the protect switches set to START or UNPROTECTED. The ion pumps should start pumping within 5-10 minutes as is indicated by the voltage meter on the power supply nearing maximum output of the supplies (5 KV). The protect switch is then set to PROTECT. If the ion pumps have not started in 5-10 minutes, they will be hot to the touch and the ion pump power supplies should be turned off and the ion pumps allowed to cool for 20-30 minutes before attempting to restart them. During this start-up period, the liquid nitrogen level in the cryoshroud must be maintained and the titanium sublimation pump left on. When the ion pumps have started, the titanium sublimation pump can be turned OFF and the liquid nitrogen in the cryoshroud can be allowed to evaporate. The lifetime of the titanium sublimator filaments can be increased by opening the ion source chamber isolation valve and evacuating the RIOS to 10^{-5} or 10^{-6} torr (10^{-3} or 10^{-4} Pa) using the ion source chamber turbomolecular pump before starting the ion pump power supplies. This method allows the RIOS mass analyzer to be evacuated without using liquid nitrogen or the titanium sublimation pump; however, 30-40 minutes are added to the system pumpdown time. The titanium sublimation pump can be used in conjunction with the cryoshroud in either a timed or continuous mode to increase pumping speed and ultimate pressure if desired for a particular type of analysis. The ion source chamber is evacuated by opening the ion source chamber forevacuum valve and turning on the turbomolecular pump power supply.

3. Slit adjustment and instrument alignment

The RIOS magnetic sector is aligned accurately with the granite surface plate and mounted on an air bearing to allow easy adjustment for positioning the instrument on the surface plate. Initial alignment of the electric sector and ion source with the magnetic sector is done with an accurate machinists level set on alignment blocks on the electric sector. The level is used to align the electric sector with the magnetic sector both angularly and rotationally. Rotational and angular adjustments are made on the turbomolecular pump bellows adaptor, the electric sector ion pump support, and the electric sector/magnetic sector flange alignment bolts. These adjustments are interactive and repeated adjustments are necessary to complete initial geometric alignment.

Secondary alignment is achieved by using an ion source and the split Faraday cup detection system. The split Faraday cup detectors must be aligned and mounted carefully on the RIOS optical axis using a microscope with a graduated reticule. Vertical or z-angle adjustments are done while monitoring the upper and lower Faraday cup ion currents. The system is aligned in the z direction when the upper and lower Faraday cup currents are equal. Secondary rotational and magnetic sector entrance angle adjustment is done while monitoring peak shapes and resolution of the RIOS. Secondary alignment is complete when peak shape and resolution are optimized without adjusting the slit assemblies.

Final adjustment and alignment of the system involves setting the externally adjustable slit assemblies. During system assembly, the vernier dials were set to 0.00 with the slits closed and 5.00 with the slit assemblies centered using a microscope with a graduated reticule. The secondary alignment adjustments are made with the slit assemblies centered and open to a relatively wide gap. The slit assemblies are adjusted during final alignment to give the desired resolution and further optimize peak shape. The major difference in secondary and final alignment involves the image slits on the split Faraday cup detectors. Secondary adjustments are done with the image slits set wide for optimum sensitivity. Final adjustments are done with the image slits set to a normal operating gap of .001" - .010" (.03 mm - .3 mm).

C. Instrument Operating Conditions

Normal system operating conditions used in the study are shown in Table 2. Reproducibility of instrument operating conditions is very important as small changes in source pressure, current, or temperature can have a dramatic effect on sensitivity of the CHCIS.

Table 2. Cryogenic hollow cathode

Operating Conditions	
Sample Volume	20 - 50 µl
Discharge Gas	O_2 (only to start discharge)
Exposure Time	to 30 V (10^{-8} farads) (8-10 min.)
Typical Ion Currents	10^{-10} A at monitor Graf 2.2
	10^{-9} A at monitor RIGS
Pressures	
At Hollow Cathode	∿1 torr (∿130 Pa)
Source Housing	10^{-5} torr (10^{-3} Pa)
Analyzer	10^{-7} to 10^{-8} torr (10^{-5} - 10^{-6} Pa)
Voltages	
Breakdown	up to 1000 V available
Running	∿250 V (3 to 5 mA source current)
Ion Acceleration	25000 V
Mass Range	
7 - 240 u on 38 cm photoplate	Graf 2.2

D. Chemical Analysis

Nine different standard solution concentrates containing a total of seventy elements were prepared according to the conditions indicated in Table 3. Each of these concentrates was diluted prior to analysis to form six standard solutions over a 10^6-fold concentration range and mixed with an internal standard at 100 ppmA. These solutions were analyzed using the CHCIS with the Nuclide Graf 2.2 mass spectrograph in the photographic detection mode. The transmittances of the mass spectral lines on the photographic plates were measured using an automated microphotometer system (44). These data were partially reduced by a computer program developed for spark source mass spectral data reduction (45) to ease exact mass determination and conversion of transmittance data to concentration values. The concentration values used in further data analysis were not modified by the spark source sensitivity factors used in the final stages of the computor program. The concentration values for each of the elements in the set of standard solutions were further reduced by linear regression analysis and sensitivity factors, detection limits, and correlation coefficients for linear regression were calculated for each element. The linear regression constants were then used to calculate the concentration of trace elements in an USEPA prepared unknown

Table 3. Standard solutions

Solution Internal Standard	Element	Concentration ppmA	Form Weighed
GOF-I	Li	102.4	LiCl
Cd	Mg	105.2	$MgCl_2 \cdot 6H_2O$
100 ppmA	Ca	105.8	$CaCl_2$
	Ba	101.9	$BaCl_2 \cdot 2H_2O$
	Cl	728.2	Above
	Na	101.9	NaBr
	Rb	98.8	RbBr
	Cs	101.3	CsBr
	Br	302.0	Above
	K	99.2	KI
	Sr	98.2	SrI_2
	I	295.7	Above
	Be[a]	100.0	$Be(NO_3)_2$
GOF-II	P	164.3	$Na_2HPO_4 \cdot 7H_2O$
	As	500.3	$Na_2HAsO_4 \cdot 7H_2O$
Br			
	Sb	501.2	$NaSb(OH)_6$
100 ppmA			
	S	623.9	Na_2SO_4
	Se	479.9	Na_2SeO_4
	Te	513.8	$Na_2H_4TeO_6$
GOF-III	Ru	99.3	$RuCl_3 \cdot 2H_2O$
Br	Rh	100.3	$RhCl_3 \cdot 2H_2O$
100 ppmA	Pd	100.9	$PdCl_2$
	Os	107.8	$OsCl_3$
	In	93.7	$InCl_4$
	Pt	93.9	$PtCl_4$
	Au	99.1	$HAuCl_4 \cdot 3H_2O$
GOF-IV	Zr	997.2	$Zr(NO_3)_4 \cdot 5H_2O$
Cd	Ag	999.6	$AgNO_3$
100 ppmA	Hg	998.7	$Hg(NO_3)_2 \cdot H_2O$
	Tl	999.4	$TlNO_3$
	Pb	1000.9	$Pb(NO_3)_2$
	Bi	961.8	$Bi(NO_3)_3 \cdot 5H_2O$

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[a] Be metal dissolved in HNO_3.

Table 3. (Continued)

Solution Internal Standard	Element	Concentration ppmA	Form Weighed	Solution Internal Standard	Element	Concentration ppmA	Form Weighed
	Th	998.6	$Th(NO_3)_4$	GOF-VII	Sc	999.7	Sc_2O_3
	U	998.7	$UO_2(NO_3)_2 \cdot 6H_2O$	Br	Cr	1002.7	$CrCl_3 \cdot 6H_2O$
	Al	996.8	$Al(NO_3)_3 \cdot 9H_2O$	100 ppmA	Mn	999.8	$MnCl_2 \cdot 4H_2O$
GOF-V	B	990.9	H_3BO_3		Ni	999.3	$NiCl_2 \cdot 6H_2O$
Br	Mo	1001.8	$MoO_3 \cdot 2H_2O$		Cu	1000.0	$CuCl_2 \cdot 2H_2O$
100 ppmA	Si	100.4	$H_4[Si(W_3O_{10})_4] \cdot 26H_2O$		Ga	494.9	$GaCl_3$
	W	1204.9			Cd	1006.2	$CdCl_2$
GOF-VI	V	1000.4	VCl_3		Ge	100.0	GeF_6[c]
Br	Fe	1070.2	$FeCl_3 \cdot 6H_2O$		F	600.0	Above
100 ppmA	Co	1017.8	$CoCl_2 \cdot 6H_2O$	GOF-VIII	La	998.4	La_2O_3
	Zn	1026.1	$ZnCl_2$	Ag	Pr	1007.4	Pr_6O_{11}
	Sn	999.6	$SnCl_3 \cdot 2H_2O$	100 ppmA	Nd	997.6	Nd_2O_3
	In	992.4	$InCl_3$		Eu	1007.2	Eu_2O_3
	Mo	972.9	$MoCl_5$		Gd	1005.7	Gd_2O_3
	Ti[b]	1004.4	$TiCl_3$		Tb	1007.2	Tb_4O_7

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[b] From 20% solution $TiCl_3$.

[c] GeF^6 added to first dilution where elements were at 100 ppmA.

Table 3. (Continued)

Solution Internal Standard	Element	Concentration ppmA	Form Weighed	Solution Internal Standard	Element	Concentration ppmA	Form Weighed
	Er	1009.6	Er_2O_3				
	Lu	1011.0	Lu_2O_3		Ho	1009.2	Ho_2O_3
GOF-IX	Ce	1014.9	CeO_2		Yb	1007.6	Yb_2O_3
Ag	Sm	1006.0	Sm_2O_3		Tm	1005.8	Tm_2O_3
100 ppmA	Dy	1006.0	Dy_2O_3		Y	1040.7	Y_2O_3

solution TM 575. A sample of natural water from Lake Laverne on the Iowa State University campus was analyzed to determine the interference effects of organic constituents with the CHCIS and two tap water samples were analyzed to further test the feasibility of using the CHCIS for chemical analysis. The unknown or test samples were not filtered or processed in any way. The samples were merely introduced into the CHCIS as described previously.

IV. RESULTS AND DISCUSSION

A. The Cryogenic Hollow Cathode Ion Source

The cryogenic hollow cathode ion source was developed to determine the feasibility of using a glow discharge ion source on a mass spectrometer to determine trace elements in small volumes of aqueous media without sample preconcentration or evaporation to dryness. The photographic detection techniques used in this study are the same as those used in semiquantitative survey methods via spark source mass spectrography and the results can be expected to vary as much as a factor of 2 or 3 from the expected results. A summary of the data gathered from the set of standard solutions containing seventy elements is shown in Table 4. The data were gathered using internal standards (See Table 3, Column 1) to correct for variations in ion intensities from exposure to exposure and from sample to sample. The correlation coefficients are for a linear regression analysis of a log-log plot of the results to increase the spread in the data points. The relative sensitivity for the elements was determined from the antilog of the intercept of the linear regression analysis, which is the apparent sensitivity at 1 ppmA, and is corrected to $Fe = 1$. The estimated detection limit was determined by observing the concentration of standard solution at which an element was first detected and

Table 4. Correlation coefficients, relative sensitivity, and estimated detection limits for the elements in the standard solutions

Element	Correlation Coefficient	Relative Sensitivity Fe = 1	Estimated Detection Limit (ppmA)	Element	Correlation Coefficient	Relative Sensitivity Fe = 1	Estimated Detection Limit (ppmA)
Li	0.9136	0.27	1.0	Cr	---	0.4	0.05
Be	0.9415	0.13	1.0	Ni	Interference by Ni Grid		
B	---	---	10.0	Cu	0.413	1.38	0.1
F	H_3O Interference at M/z 19			Zn	0.9834	2.87	0.2
Na	0.2360	19.7	0.01	Ga	0.9560	0.74	0.4
Mg	---	---	>100	Ge	0.8848	4.71	0.1
Al	0.9339	10.6	0.01	As	---	---	4.0
Si	---	---	>100	Sc	0.9960	1.48	1.0
P	Interference at M/z 31			Br	0.9301	40.0	0.001
S	O_2 Interference at M/z 32			Rb	0.9245	5.7	0.001
Cl	0.9451	2.46	0.01	Sr	---	---	20.0
K	0.0400	42.24	0.01	Y	0.9930	0.53	1.0
Ca	---	---	>100	Zr	0.9798	0.01	10.0
Sc	Interference at M/z 45			Mo	---	2.92	0.2
Ti	---	---	80	Ru	0.9875	0.38	1.0
V	0.9695	49.8	0.05	Rh	0.9562	0.13	1.0
Cr	0.9383	3.06	0.01	Pd	---	---	10.0
Mn	Interference at M/z 55			Ag	0.9959	0.43	3.0
Fe	0.9691	1.0	0.1	Cd	0.9424	2.57	0.1

Table 4. (Continued)

Element	Correlation Coefficient	Relative Sensitivity Fe = 1	Estimated Detection Limit (ppmA)
In	---	---	1.0
Sn	---	---	2.0
Sb	0.9759	0.21	5.0
Ta	0.9525	0.23	3.0
I	0.9655	81.9	0.001
Cs	0.9415	10.8	0.001
Ba	---	---	50.0
La	---	---	50.0
Ce	---	0.003	10.0
Pr	---	---	50.0
Nd	---	---	>1000
Sm	---	0.097	3.0
Eu	---	---	>1000
Gd	---	---	>1000
Tb	---	---	200.0
Dy	0.9711	0.48	1.0
Ho	0.9999	0.11	3.0
Er	---	---	>1000
Tm	0.9917	0.13	2.0
Yb	0.8805	2.77	0.5
Lu	---	---	100.0
W	---	---	>1000
Os	---	0.22	3.0
Ir	---	---	40.0
Pt	---	---	5.0
Au	TaO Interference at M/z 197		
Hg	0.9760	157.5	0.0003
Tl	0.9913	1.0	0.4
Pb	0.9939	1.99	0.3
Bi	0.8107	2.58	1.0
Th	0.8737	2.26	1.0
U	0.9116	0.43	2.0

extrapolating over the lower factor of 10 dilution. Due to the poor sensitivity of some elements, correlation coefficient and/or relative sensitivity results are not available. Possible reasons for the poor sensitivities of these elements are listed in Table 4. Detection limits are given in ppmA (parts-per-million atomic), which in this case is the number of atoms or ions of trace elements per million atoms of oxygen as molecules of water.

Many elements in the standard solutions were detected only as singly charged atomic ions; however, certain classes of elements reacted with the water in the discharge to form oxides or hydroxides. Halides (X) were detected as X^+, X^{+2}, X^{+3}, XO^+, HX^+, HXO^+, $HXO_2{}^+$, $XO_2{}^+$, $HXO_3{}^+$, $XO_3{}^+$, $HXO_4{}^+$, $XO_4{}^+$, $X_2{}^+$, and $HX_2{}^+$. The form of phosphorus, arsenic, and antimony and sulfur, selenium, and tellurium was dependent upon the pH of the solution and the form of the ion dissolved. When these elements were dissolved as oxides in hydrochloric acid, the ions detected were the single charged atomic ions (A^+) and simple oxide ions (AO^+). When the sodium oxygeno salts were dissolved directly, oxide ions of the type dissolved ($AO_4{}^+$) were also observed. Some other elements were detected as a simple oxide ion in addition to a singly charged atomic ion with the intensity of the oxide ion very low with respect to the atomic ion.

Interference or background lines were observed at several masses. A nickel grid on the draw out electrode produced nickel ions on all blank and sample plates. Tantalum and tantalum oxide ions were also observed on every photoplate. Lines at M/z 8, 8.5, 9, 16, 17, 18, 19, 20, 21, 32, 33, 34, 35, 36, 37, 39, 40, and 55 were present on every photoplate and were caused by water clusters. Water cluster ions were observed at M/z's corresponding to $(H_2O)_nH^+$ dependent on operating conditions to $n = 7$ or M/z 127. Metastable ions for these water cluster ions losing a molecule of water were observed throughout the mass range ∿6 to 234 μ at expected M/z locations when the appropriate parent ion was detected. Ions due to nitrogen, carbon dioxide and other normal air constituents in the water were also observed as no attempt was made to purge the water of dissolved air. Nitrogen also reacted with hydrogen and oxygen in the glow discharge forming oxides and hydrogenated oxides at M/z's 14, 15, 28, 30, and 44. These interference or background lines caused a minimum of problems due to the high resolution mass spectrograph used in the experiments. However, their presence predicates a need for high resolution mass analysis when using the CHCIS for determining some elements.

The data from EPA standard TM575-3 are shown in Table 5. The results are reasonably good considering the low concentration of trace elements, the semiquantitative survey method

Table 5. EPA standard TM575-3, Br internal standard

Element	Determined Concentration ppmA	ppm	True Value ppm
Al	0.176	0.264	0.904
As	0.3	1.25	0.154
Be	<1.0	<0.5	0.398
Cd	<0.1	<0.6	0.073
Co	0.07	0.229	0.396
Cr	0.03	0.086	0.209
Cu	0.10	0.35	0.102
Fe	0.154	0.479	0.678
Hg	0.00076	0.0085	0.0094
Mn	Interference		0.397
Pb	<1.0	<10.0	0.352
Se	<1.0	<4.0	0.044
V	<0.05	<0.1	0.157

used, and the current stage of development of the CHCIS. All the elements fall under the detection limit or fall roughly within the factor of 3 limit of a semiquantitative survey, except aluminum which is within a factor of 3.4. The results of the tap water samples indicated measurable levels of Fe, Al, Na, Cl, and Cr in both samples. The Lake Laverne natural water sample produced similar trace element results with somewhat higher levels than the tap water. The significant result from the Lake Laverne sample was the lack of interference from organic compounds and biological particles. Very few mass spectral lines were traceable to organic compounds and the lines traceable to organic compounds were easily resolved from the trace elements by the high resolution mass analyzer used in the experiment.

The data gathered during these experiments indicate the feasibility of a glow discharge plasma as an ion source for the mass spectral determination of trace elements in aqueous media. The CHCIS in its present stage of development does not fulfill all of the requirements for an analytical tool. The CHCIS is usable over a wide concentration range for most elements, has a minimum number of intereferences for semi-quantitative survey analysis, and requires relatively small sensitivity corrections for many elements. Problems remaining to be solved involve control of ion source parameters, basically pressure and temperature; some results indicate that higher ion source currents in the glow discharge would improve sensitivity of elements which exhibited poor sensitivity in this study. Source current for this study was limited to 4-6 mA because higher current would raise the cathode temperature and increase the water vapor pressure in the ion source housing to greater than 1×10^{-4} torr (1.3×10^{-2} Pa). High source housing pressure resulted in ion current loss in the cylindrical lens assembly and creates the potential of accelerating voltage breakdown in the source housing which could damage equipment. Figure 24 shows cathode temperature versus time at various ion source current settings. The CHCIS used in this study has three primary problems which result in the large changes in ion source temperature. The copper cooling strap used in these experiments is too long thereby creating problems with that conduction. The thermal conductance of the copper strap could be improved by increasing the thickness of the strap; however, the length should also be decreased to improve thermal conductance. The second cause of poor thermal conductance is the junction of the copper strap with the borosilicate glass cold finger. When the copper strap is warmed by heat from the cathode, the loop around the glass cold finger expands slightly, thus reducing the thermal conductance. The third possible problem concerns the thermal conductance of the glass cold finger itself. These problems combined to create a situation where the copper strap was warm to the touch after an experiment at 25 mA of source current, while the glass cold finger still contained liquid nitrogen. This was observed two to three minutes after the discharge had been shut off and the electronic circuits turned off and the source housing vented. A metal cold finger with an attached conducting strap could solve the

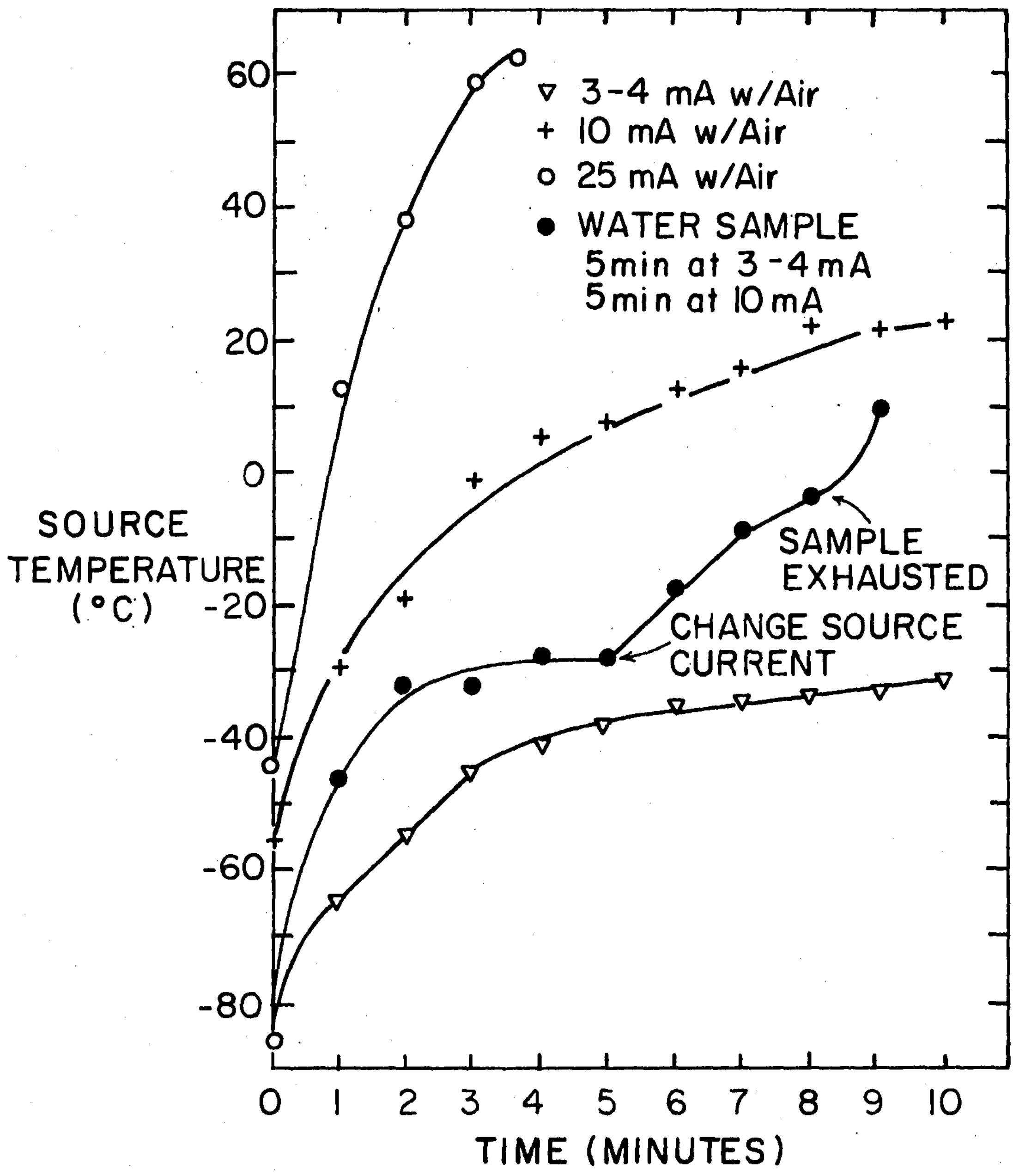


Figure 24. Cathode temperature vs. time at various ion source current settings

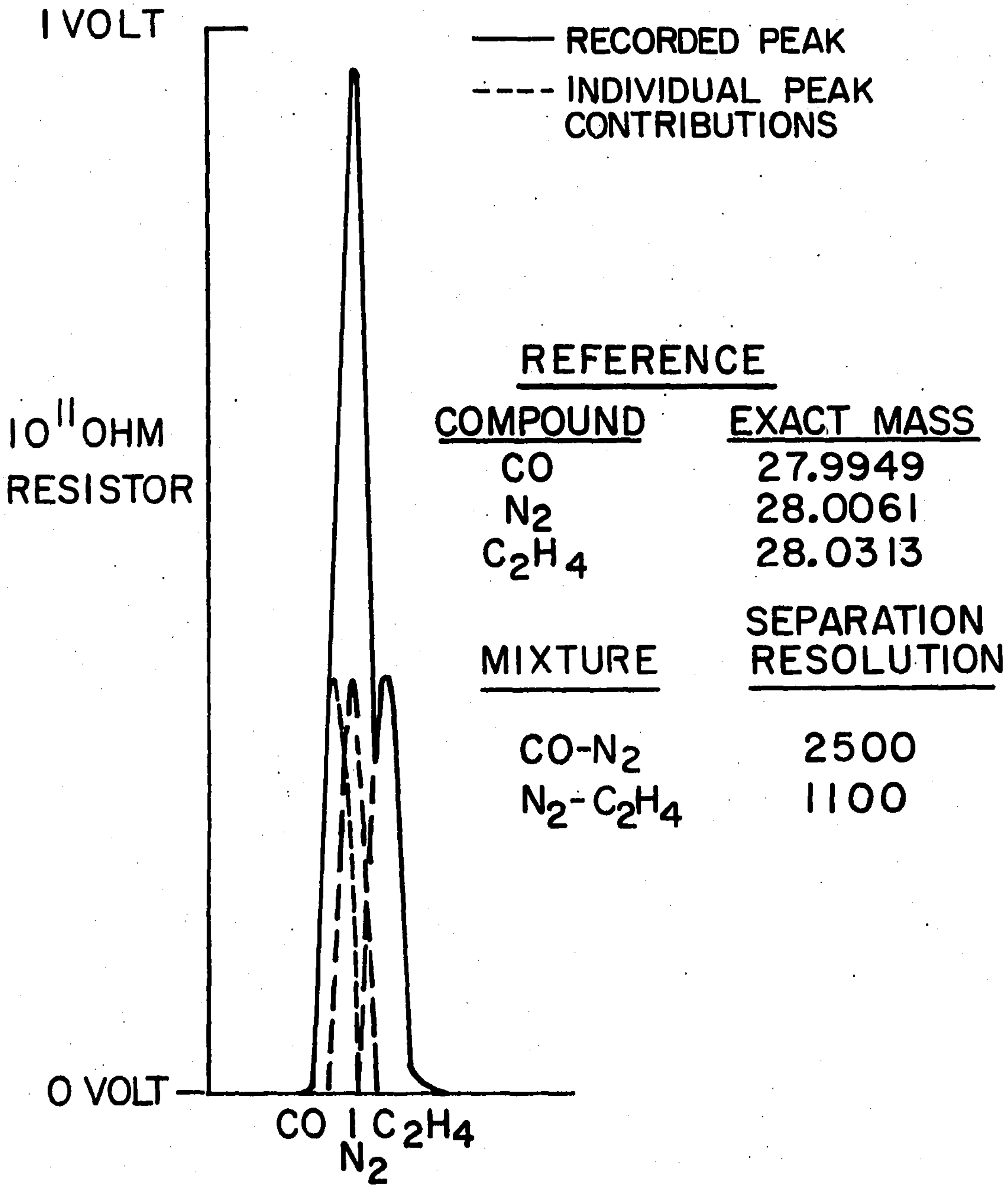
problems with the borosilicate glass cold finger, but the design of a metal cold finger is complicated by the requirement for nearly 24,000 volts of accelerating potential on the cathode of the CHCIS. Problems with the control of cathode temperature in the CHCIS make accurate control of the pressure in the ion source difficult. Analytical data from this study and others (17,18) indicate the need for accurate ion source pressure control. When the cathode temperature problems and pressure control problems have been solved, reagent gases other than water should be studied to evaluate the best reagent gas. Argon and oxygen were tested during the initial stages of this study and showed no advantages over water vapor. However, improved ion source temperature control may require a reagent gas be used to control the glow discharge. Variations in ion source geometry may also improve sensitivity for elements which exhibited poor sensitivity in this study.

The use of the CHCIS for analyzing small aqueous samples has several positive aspects which are important when considering the feasibility of using it as an ion source. In addition to good analytical sensitivity, the CHCIS produces intense, continuous ion beams (about 5×10^{-6} A at the object slit) which produce narrow, well-defined lines at the image of the mass spectrograph. The CHCIS is also a mechanically simple ion source which is easy to assemble and maintain. The positive aspects of the CHCIS are the sensitivity for a large number of elements, the small sensitivity corrections required for most elements, a simple design resulting in easy assembly and maintenance, a minimum number of interferences, and intense continuous ion current. These positive aspects make it desirable to solve the temperature and pressure control problems which will allow the other problems with the CHCIS to be studied.

B. The Research Ion Optical System

The RIOS was designed to be a flexible instrument for ion source research and development. The adjustable slit assemblies allow the instrument to be set for low resolution with higher sensitivity for initial ion source development and then be retuned for medium to high resolution with decreased sensitivity for final ion source evaluation. The higher sensitivity at low resolution settings is also a useful feature for routine analytical applications where high resolution is not required. The extra flanges on the mass analyzer housing also add flexibility to the detection system which allows the addition of electron multipliers to increase sensitivity and a photographic detection system to utilize fully the capabilities of the mass spectrograph ion optics.

The RIOS is a double focussing mass spectrograph with a spherical electric sector in the "Mattauch-Herzog" geometry. The theoretical resolving power of the mass analyzer is defined as the radius of the electric sector (a_e) divided by the object slit width (s_o). The RIOS electric sector has a radius of 12" (30.48 cm) and the theoretical resolving power with an object slit width of 0.0005" (0.0013 cm) would be 24,000. The highest observed resolution under test conditions used in this work was approximately 1000. Figure 25 shows the resolution obtained at M/z 28 with an equal mixture of CO, N_2, and C_2H_4. There are several reasons for the low observed resolution of the RIOS. The externally adjustable slit mechanisms are not as precise as fixed slits would be and the object slit in particular must be machined to tighter tolerances than were held on the RIOS in its present stage of development. A second important factor in both the alignment of the instrument and the measure of resolution is the CHCIS. The CHCIS is a marginal ion source for instrument alignment as details of its characteristics are not yet known and it is impossible to predict the fragmentation patterns of complex organic molecules which are desirable to use for alignment. The organic molecules are likely to decompose completely in the CHCIS. The resolution study with the CHCIS was complicated by the formation of carbon deposits on the anode which plugged the ion extraction hole after a few minutes of operation. A third factor in the resolution study involves



REFERENCE

COMPOUND	EXACT MASS
CO	27.9949
N_2	28.0061
C_2H_4	28.0313

MIXTURE	SEPARATION RESOLUTION
CO-N_2	2500
N_2-C_2H_4	1100

Figure 25. Resolution at M/z = 28 with CO, N_2 and C_2H_4

the detection system and the sensitivity loss with increased resolution caused by a narrowed object slit. The vibrating reed electrometers measuring the ion current at the Faraday cup detectors are not sensitive enough to do a satisfactory resolution study.

Another important measure of a mass analyzer is the ion transmission efficiency. The CHCIS produces a continuous ion current of 5 x 10^{-6} A as measured at the object slit of the RIOS. An object slit width of 0.007" (0.018 cm) transmits approximately 1.8 percent of the ion current (9 x 10^{-8} A) to the mass analyzer. The total ion current monitor which intercepts 20 percent of the ion current measured 1.6 x 10^{-9} A indicating a total of 8 x 10^{-9} A of ion current reached the monitor with 6.4 x 10^{-9} A of ion current transmitted to the magnetic sector. Most of the ion current lost in the electric sector is captured by the ion beam defining slit assemblies (α, β, and 2 z limiting slit assemblies). The sum of the mass analyzed ion currents was 1.2 x 10^{-10} A. The ion transmission efficiency for the magnetic sector is 2 percent and the total ion transmission efficiency for the RIOS is 0.0024 percent.

V. CONCLUSIONS

The cryogenic hollow cathode ion source has been developed to a point where it proves the feasibility of a low pressure glow discharge ion source for the direct determination of trace impurities from small volumes of aqueous samples. The accuracy of semiquantitative survey analysis with the CHCIS is similar to that possible with a spark source mass spectrograph. Improved accuracy for specific elements can be achieved as the CHCIS will adapt easily to isotope dilution techniques. There are serious problems to solve, however, before the CHCIS can be used as a routine analytical tool. An improved system must be developed to maintain the cathode at liquid nitrogen temperatures. An improved ion current deflection system should be developed to make the ion source easier to operate and the reagent gas pressure in the ion source must be regulated more accurately. The best reagent gas suitable for the analysis of general or specific trace elements in aqueous media should also be ascertained after improvements are made on the ion source.

The RIOS has proven to be a flexible instrument for ion source research and development. The present RIOS can be improved by replacing the tube type magnet power supply with a more stable solid state power supply. The detection system can be improved by replacing the Faraday cup detectors with an electron multiplier. The RIOS can be made more flexible by adapting it for photographic detection to augment the electronic detectors. If a more accurate determination of the ion optical parameters of the RIOS is desired, an electron bombardment ion source should be developed to provide a well-defined ion beam for mass resolution studies. It may be necessary to refine the object slit assembly to achieve maximum resolving power of the RIOS.

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VIII. APPENDIX

A. Listing of Manufacturers and Trade Names

1. Manufacturers

ARMCO, Inc.,
Box 600, Dept. E-1963, Middletown, Ohio 45042

Cole-Parmer Instrument Co.
7424 N. Oak Park, Chicago, Illinois 60648

Dell Electronics Corp.
250 E. Sandford Blvd., Mount Vernon, New York 10550

Kepco, Inc.,
131-38 Stanford Ave., Flushing, New York 11352

Leybold-Heraeus Vacuum Products Inc.,
200 Seco Rd., Monroeville, Pennsylvania 15146

Miller Laboratories,
Latham, New York 12110

Nuclide Corp.,
642 E. College Ave., State College, Pennsylvania
16801

Nupro Co.,
4800 East 345th St., Willoughby, Ohio 44094

Perkin-Elmer Ultek Inc.,
Box 10920, Dept. BB, Palo Alto, California 94303

Sargent-Welch Scientific Co.,
7300 North Linden Avenue, Skokie, Illinois 60076

2. Trade names

Cary
Varian Instrument Group
611 Hansen Way, Palo Alto, California 94303

CFF
Perkin-Elmer Ultek Inc.

CURVAC
Perkin-Elmer Ultek Inc.

Hastings-Raydist
Teledyne Hastings-Raydist
PO Box 1275, Hampton, Virginia 23661

Mykroy
Mykroy Ceramics Corp., An Alco Standard Corp.
Partner, Orben Dr., Box 399, Ledgewood, New Jersey
07852

Swagelock
Crawford Fitting Company
29500 Solon Rd., Cleveland, Ohio 44139

Teflon
E. I. du Pont de Nemours and Co., Inc., Plastic
Products and Resins Dept., 1007 Market St.,
Wilmington, Delaware 19898