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The PNL High-Transmission Three-Stage Mass Spectrometer

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December 1992

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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THE PNL HIGH-TRANSMISSION THREE-STAGE MASS SPECTROMETER

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MASTER

(a) VG Isotech, Middlewich, Cheshire CW10 OHT, U.K.
(b) Westinghouse Hanford Company, Richland, Washington

SUMMARY

We have constructed a three-stage isotope-ratio mass spectrometer of unique ion-optical design that achieves high ion transmission efficiency and high abundance sensitivity. The spectrometer has tandem 90°-deflection magnets with boundaries 18° off normal. The magnet drift lengths are 1.48 times the 27-cm radius of deflection. This extended geometry gives mass dispersion equivalent to a 40-cm-radius magnet with normal boundaries. The first magnet renders the ion beam parallel in the vertical plane and provides a focus in the horizontal plane of mass dispersion. The second magnet brings the beam to a stigmatic focus. This novel ion-optical design gives 100% transmission without the need for intermediate focusing lenses. It also provides a 16% increase in mass resolution over the traditional tandem geometry with normal magnet boundaries. Complete transmission of ions is maintained through a third-stage cylindrical electric sector of 38-cm radius, which provides increased isotope-abundance sensitivity.

The isotope-abundance sensitivity of the new mass spectrometer is an order of magnitude better than similar instruments with normal magnet boundaries. This is because the vertical focusing of the ion beam prevents ion scattering from the top and bottom of the flight tube. The measured values of the isotope-abundance sensitivity one-half mass unit away from the rhenium ion peaks at masses 185 and 187 are

$$M - \tfrac{1}{2} = (6.5 \pm 0.5) \times 10^{-10}$$
$$M + \tfrac{1}{2} = (3.1 \pm 0.8) \times 10^{-10}$$

By extrapolation, the uranium isotope-abundance sensitivity is

$$M - 1 = 1 \times 10^{-10}$$

Construction of the instrument was facilitated by using standard commercial mass spectrometer components.

CONTENTS

FIGURES

INTRODUCTION

The Pacific Northwest Laboratory (PNL)(a) has used three-stage mass spectrometers (Lagergren and Stoffel[s] 1970) for decades for high sensitivity measurements of large isotope ratios. Spurred by the increasing need to measure minor isotopes at sub-femtogram levels, we previously investigated the fundamental ion optics of multiple-sector mass analyzers. The primary purpose was to improve ion transmission through these long ion path instruments and, thereby, increase data yield from very small samples.

Our earlier studies produced a unique ion-optical design for mass spectrometers with tandem sector magnets that theoretically provides complete transmission of ions (Stoffel[s] and Laue 1991). We have now constructed a new three-stage isotope-ratio mass spectrometer according to that ion-optical design. In addition to fulfilling our primary purpose of high ion transmission efficiency, the instrument described here achieves an isotope-abundance sensitivity an order of magnitude better than similar instruments of conventional design.

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ION-OPTICAL DESIGN

To achieve high ion-transmission efficiency, the most favorable geometry found for tandem 90°-deflection magnets is a zero-dispersion or "C" configuration in which the magnet boundaries are 17° off normal and the symmetric drift lengths are 1.44 times the radius of deflection (Stoffel[s] and Laue 1991). The ion beam is rendered parallel in the vertical plane at the focus of the first magnet and is brought to a stigmatic focus by the second magnet. This parallel/stigmatic/tandem (PST) arrangement provides a 16% increase in mass resolution over normal geometry magnets and gives 100% transmission of ions without the need for intermediate focusing lenses. Complete transmission is also maintained through a cylindrical electric sector added as a third stage for greater isotope-abundance sensitivity.

To accommodate possible inaccuracy in the theoretical calculation and assure parallel/stigmatic focusing in the completed instrument, we increased the off-normal angle of the magnet boundaries to 18° and the magnet drift lengths to 1.48 times the radius of deflection. The instrument geometry as constructed is shown in Figure 1.

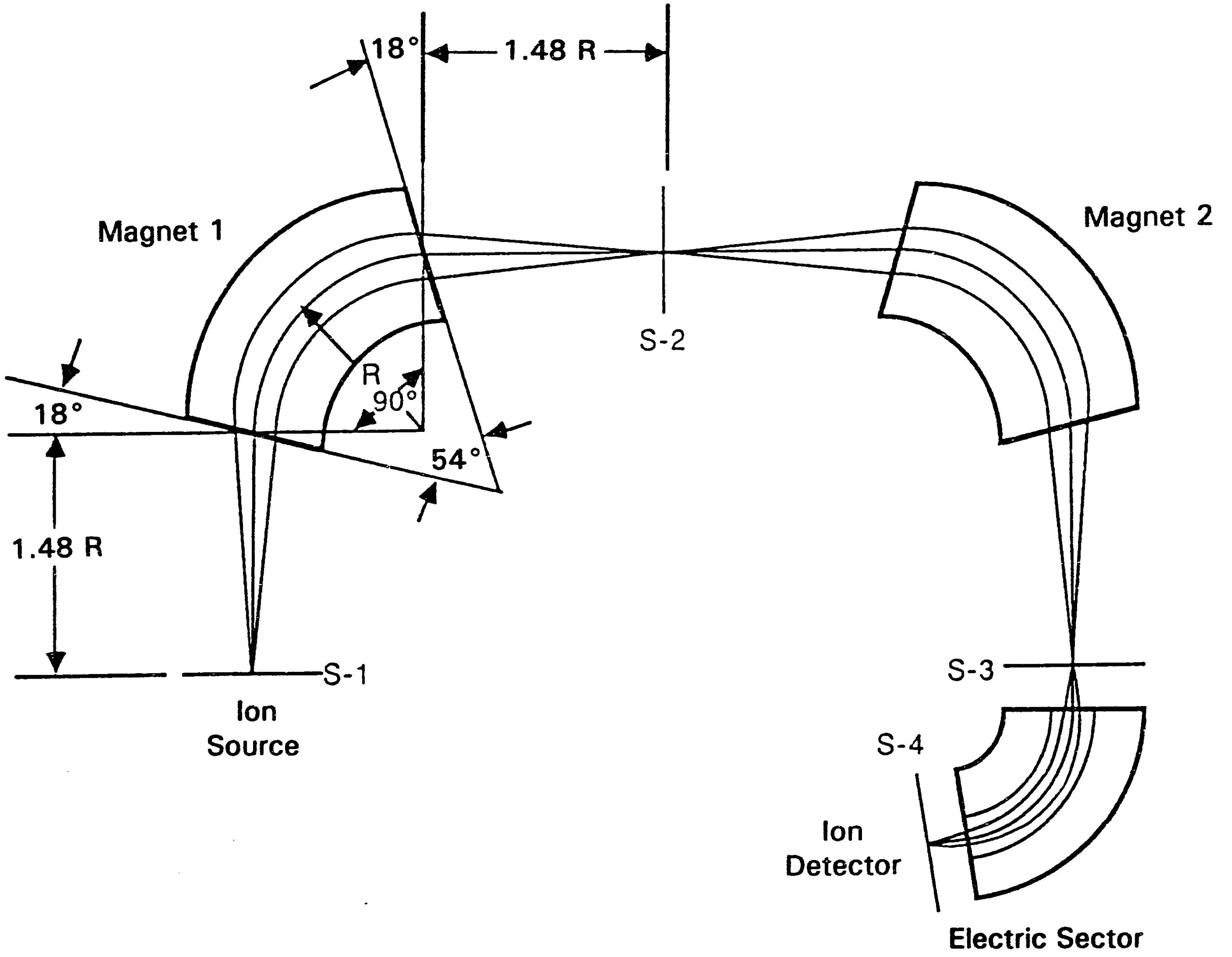

FIGURE 1. Ion-optical Design of a Triple-Sector Mass Spectrometer with Tandem Magnets that Gives a Parallel Ion Beam in the Vertical Plane at the Focus of the First Magnet and a Stigmatic Focus After the Second Magnet

CONSTRUCTION

The three-stage isotope-ratio mass spectrometer we have constructed according to the new PST geometry is shown in a plan-view drawing in Figure 2. One goal realized in the construction is that the major components are commercially available. Using standard components from a major mass spectrometer manufacturer is an important step in the direction of making commercially available complete instruments that satisfy advanced analytical requirements.

The bulk of the mechanical hardware for the spectrometer was built by the VG Isotech division of Fisons Instruments. Included are the complete ion source; two electromagnets with associated supplies, regulators, and controls; the magnet flight tubes; an electrostatic analyzer; and a bench to accommodate the complete instrument. PNL supplied from other sources the interstage housings and adjustable slits, vacuum system, ion detectors, electronic instrumentation, and computer control system.

The VG ion source is of the triple-filament, thermal ionization type. It uses very robust separable filament beads of VG design (Figure 3). The source is equipped with a 20-sample rotary turret (Figure 4) that can be positioned manually by a rotary motion feedthrough or automatically by an external motor drive under computer control. The source collimator lens uses thin plates similar to the NBS design. The lens is self-aligning upon assembly. Electrical connections to the lens are made automatically when it is plugged into place. Thus, the lens can be removed for cleaning and replaced without connecting or disconnecting any wiring--a user-friendly convenience.

The electromagnets (Figure 5) are standard magnets as used for VG single-sector isotope-ratio mass spectrometers. The magnets have rotatable pole tips that can be adjusted to the off-normal entrance and exit angles required for the PST geometry. The deflection radius is 27 cm. Because of the extended geometry, mass dispersion is equivalent to a 40-cm magnet with normal boundaries. The magnets produce a maximum flux density of 8000 gauss.

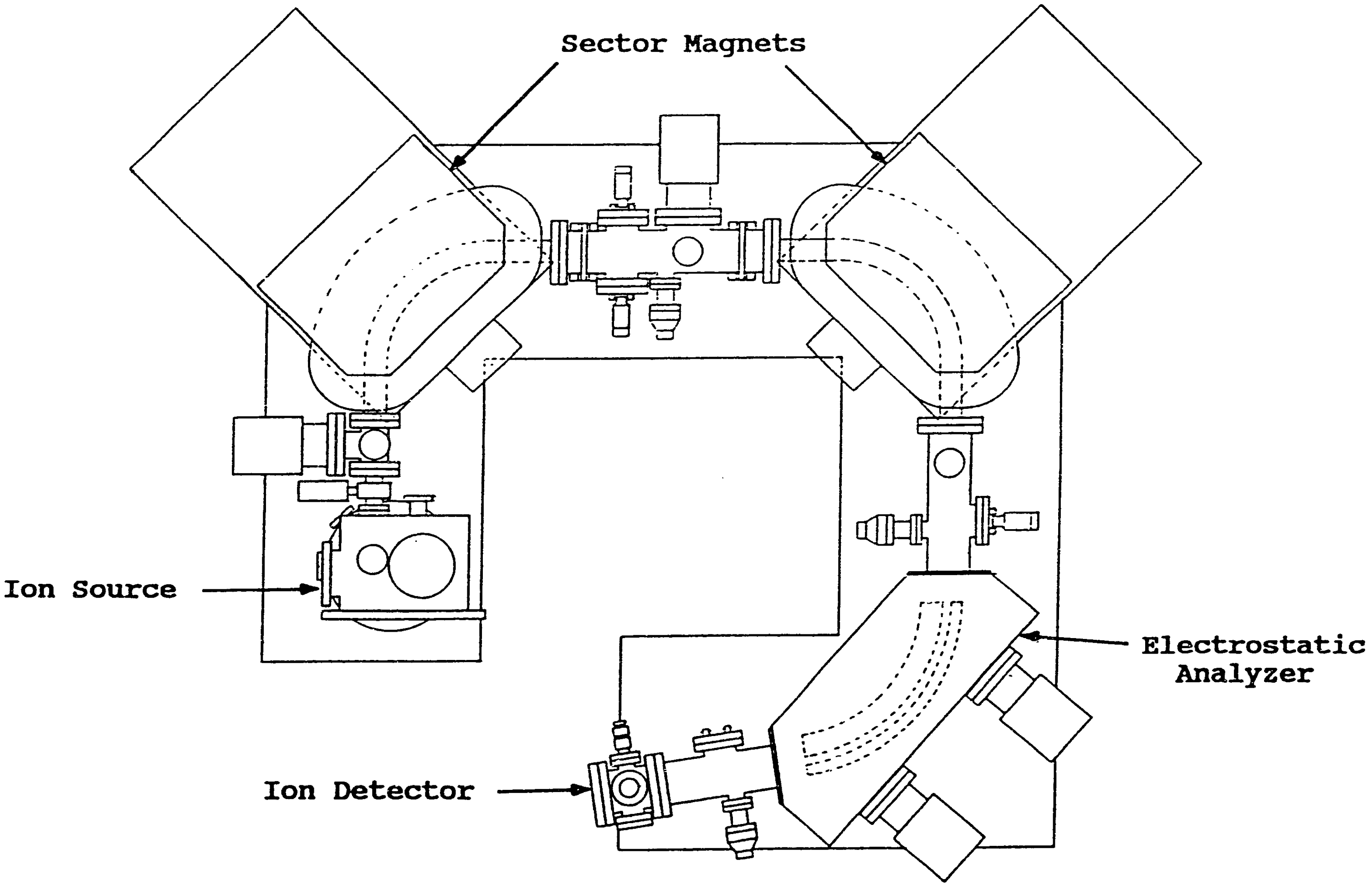

FIGURE 2. Plan-View Drawing of the Triple-Sector Mass Spectrometer Built According to the PST Geometry

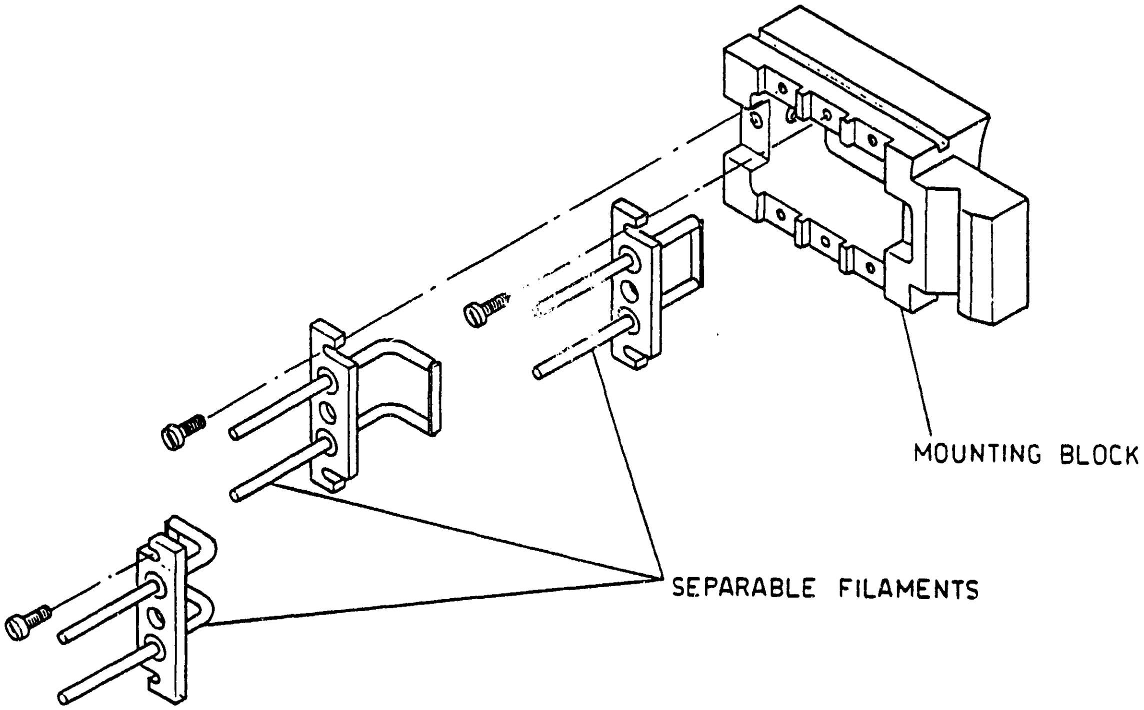

FIGURE 3. The VG Triple-Filament Assembly

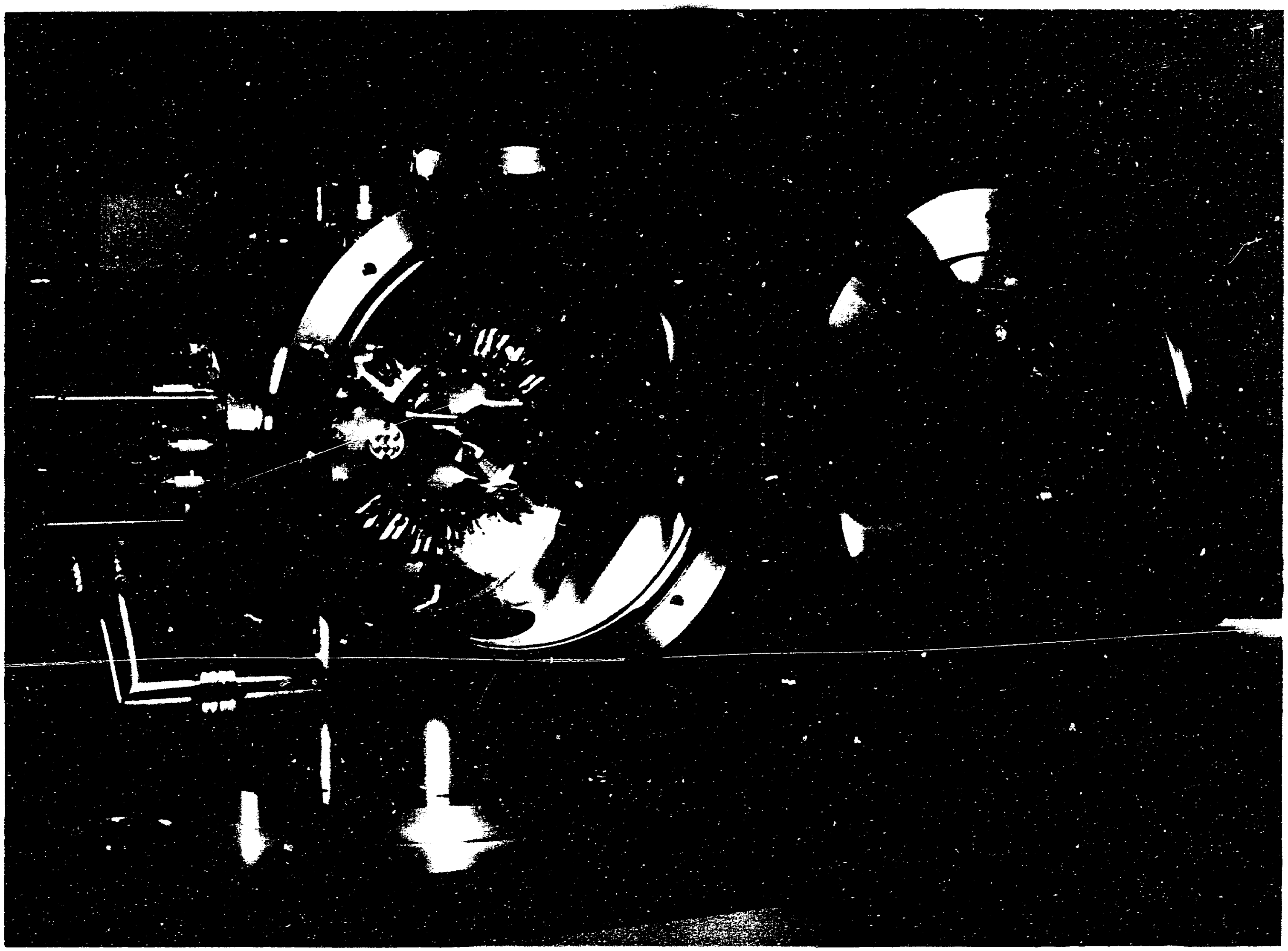

FIGURE 4. Ion Source with 20-Sample Rotary Turret

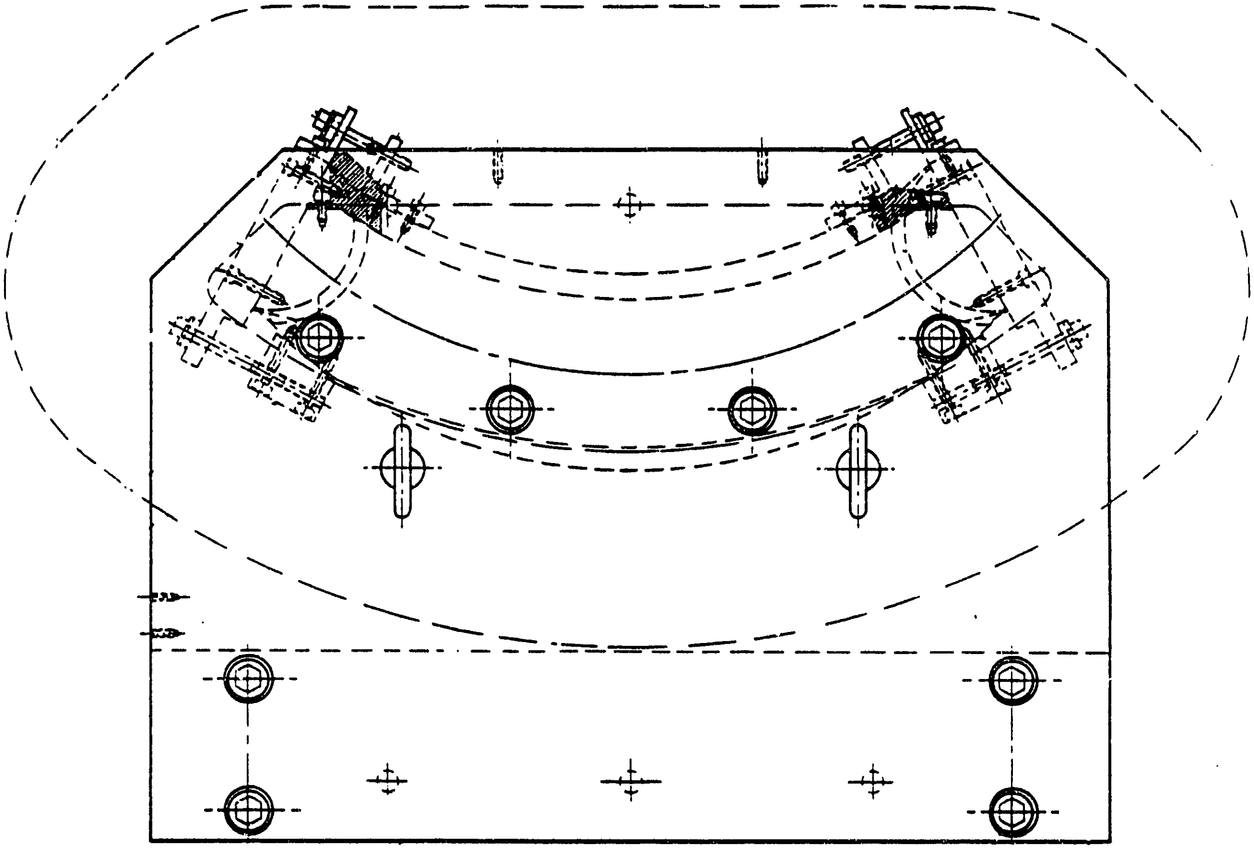

FIGURE 5. Electromagnet with Rotatable Pole Tips

The cylindrical electrostatic analyzer (Figure 6) is the same as used for the ZAB series of high resolution mass spectrometers manufactured by VG. It has a 38-cm radius of deflection and a deflection angle of 81.5°. The height of the analyzer plates is five times the separation to provide a highly uniform electric field in the region of the ion beam.

A Faraday cup detector is located near the focus of each magnetic sector, just ahead of the slits S-1 and S-2. The cups are mounted on linear motion feedthroughs so they can be inserted into the beam and are adjustable in position. The ion detector following the third stage has both a Faraday cup for DC measurement of ion signals greater than 10^6/s and an electron multiplier for ion pulse counting at rates up to 10^6/s (Figure 7). The Faraday cup is located on the ion beam axis, and the electron multiplier is located off axis. An electrostatic deflector under computer control switches the ion beam into the multiplier at appropriate times in the mass scanning sequence.

Measured ion signals are read into the computer from a dual-channel 100-MHz scaler. One channel counts ion pulses from the electron multiplier through a fast discriminator. The other channel is connected to the Faraday cup through an electrometer and voltage-to-frequency converter.

The above components are mounted on a bench with a welded frame. The frame members are thin-section fabricated steel angles. The benchtop comprises a 1-in.-thick aluminum honeycomb core epoxy bonded to two 0.1-in.-thick aluminum skins, which makes for a very light, strong, and rigid construction. The benchtop is flat to within ±0.125 mm.

The vacuum system for the instrument is completely oil free. Rough pumping is accomplished by a combination bellows, piston, and molecular drag pump. The high vacuum pump on the source chamber is an 8-in. cryopump rated at 1500 l/s. An air-operated gate valve maintains the cryopump at high vacuum while the source chamber is vented for sample changing. Four 60 l/s ion pumps are distributed along the ion flight tube. An air-operated minigate valve serves to isolate the flight tube under high vacuum when venting the source chamber to atmosphere.

The completed three-stage mass spectrometer is shown in Figure 8.

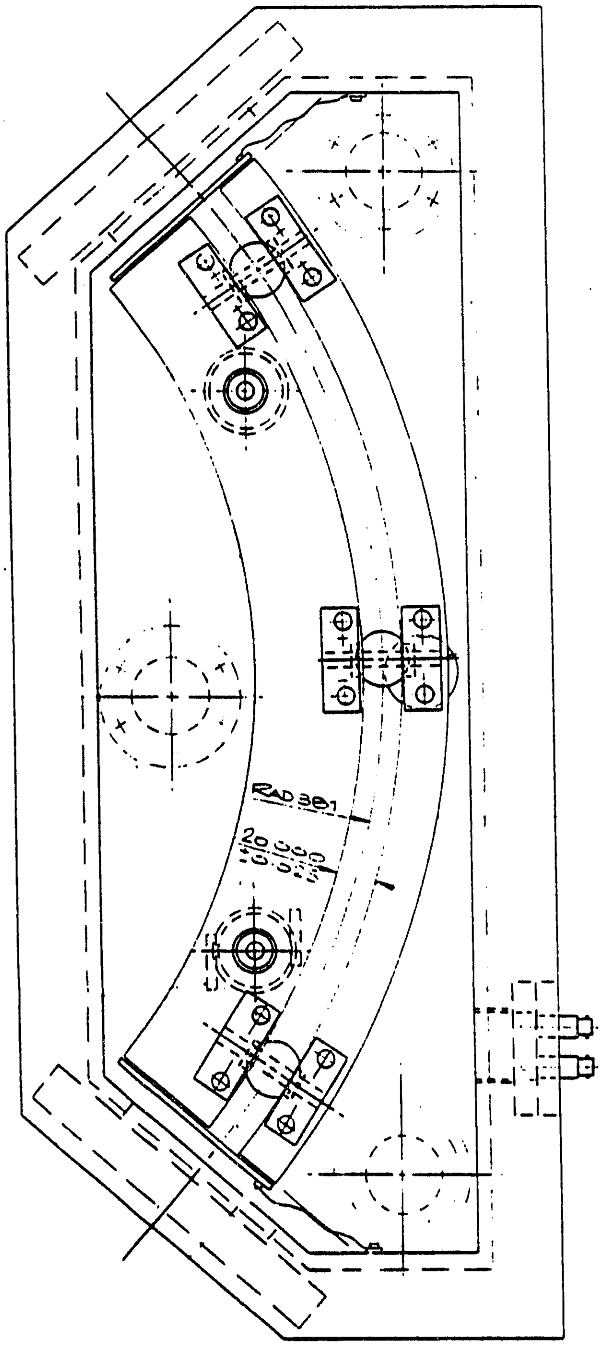

FIGURE 6. Electrostatic Analyzer

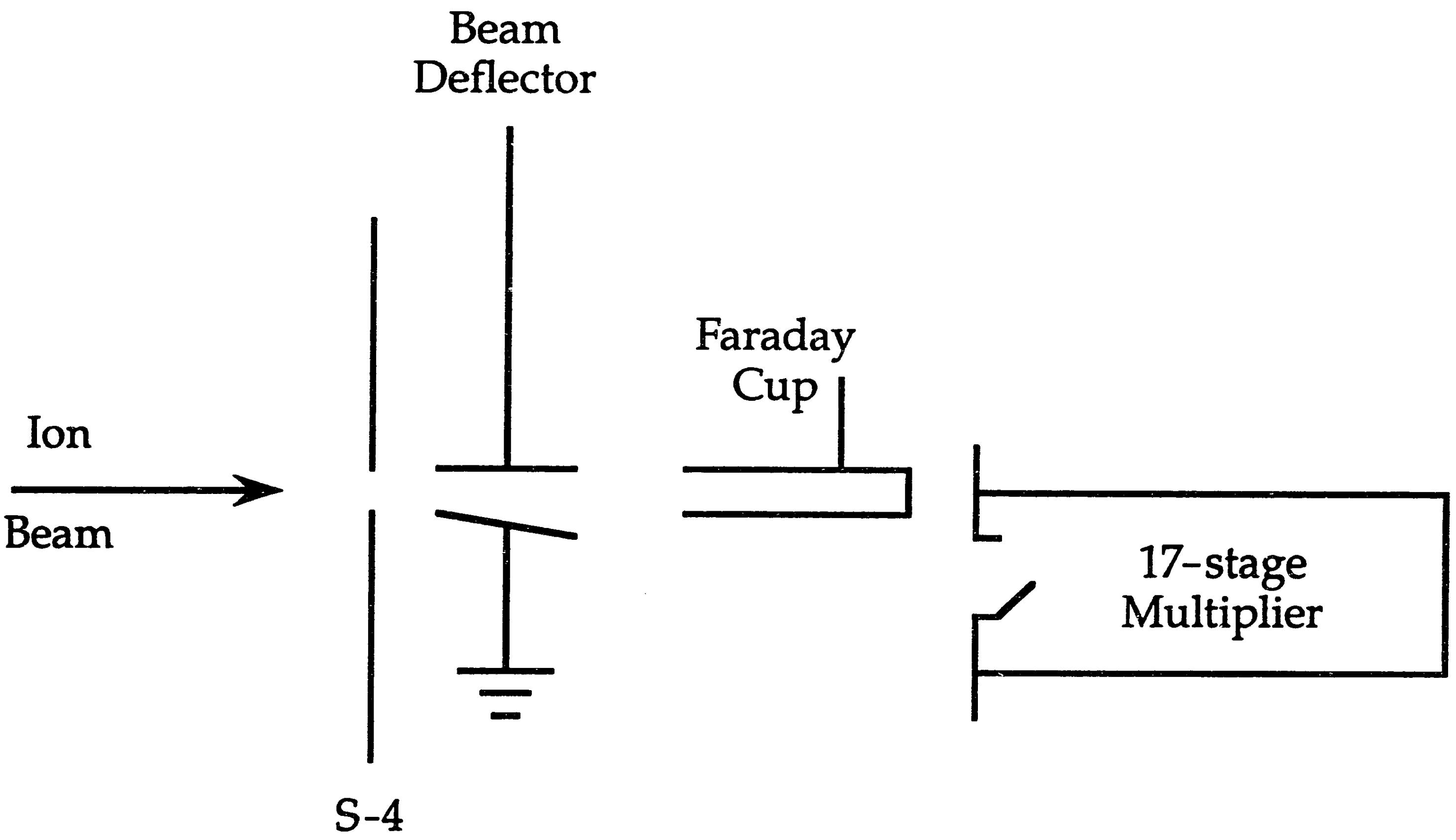

FIGURE 7. Schematic Diagram of Ion Detector with Electrostatic Switching Between Faraday Cup for DC Measurement and an Electron Multiplier for Pulse-Counting

The mass spectrometer is controlled by a 386-class personal computer through IEEE-488 and RS232 interfaces. Menu-driven operating software developed at PNL provides for scanning of the mass spectrum in the peak-hopping mode by control of the ion accelerating voltage. The ion source and electrostatic analyzer high-voltage supplies (see Appendix A) are of reversible polarity so that the instrument can be operated for both negative and positive thermal ionization.

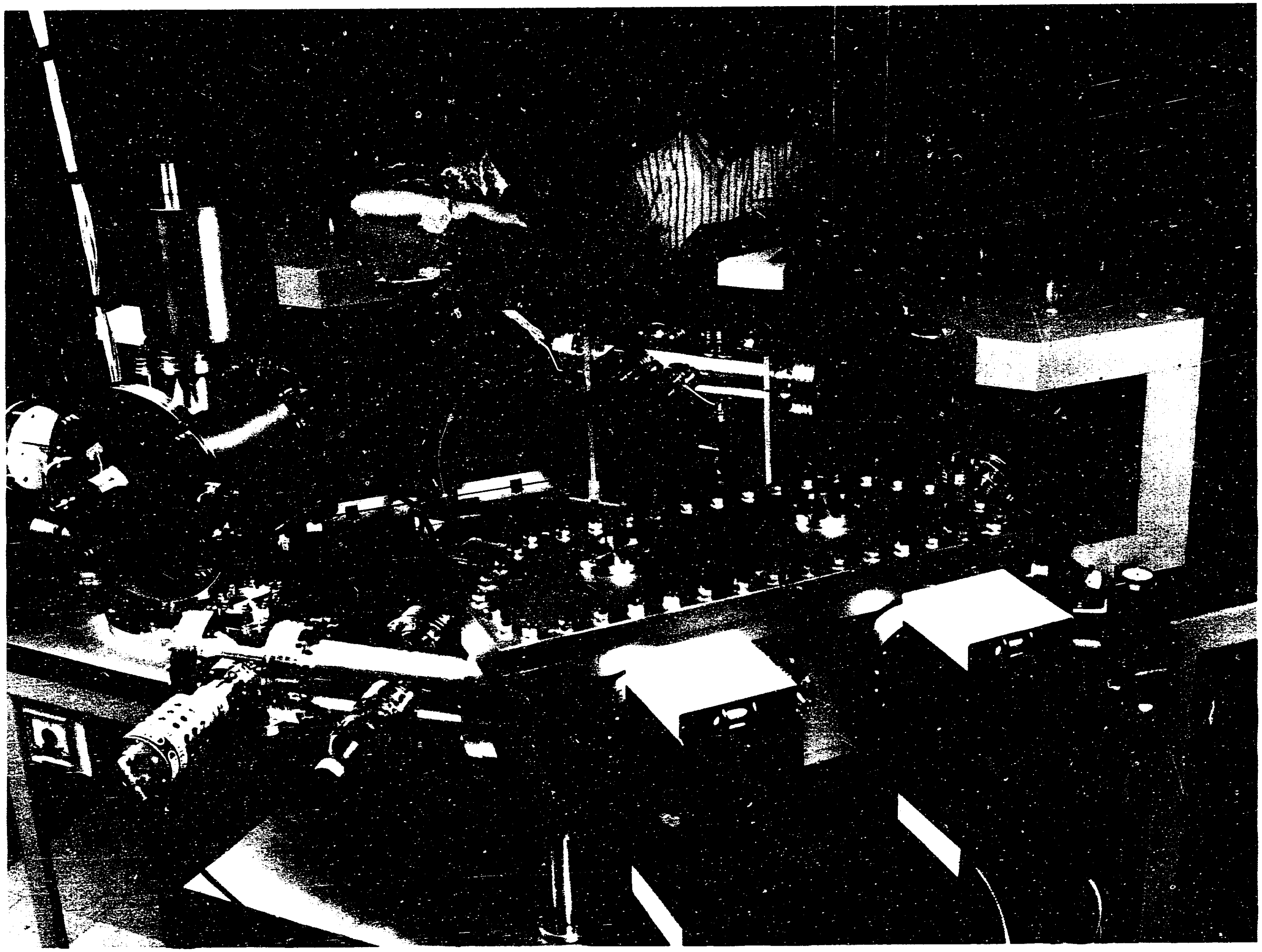

FIGURE 8. Completed Three-Stage Mass Spectrometer

PERFORMANCE

The validity of the PST ion-optical design was verified by measuring vertical ion beam profiles at the focal points of the two magnetic sectors (Figure 9). The beam height at S-2 is less than the 14-mm internal height of the flight tube in the magnet gap, demonstrating full transmission to that point. The beam height at S-3 is much less than that at S-2, which contrasts with the continuously diverging beam produced by normal geometry magnets (Stoffel[s] and Laue 1991). The beam height at S-4 (Figure 10), the focus of the electric sector, is entirely within the vertical aperture of the electron multiplier and the Faraday collector. Thus, the goal of 100% transmission through the three-stage analyzer has been achieved.

The isotope-abundance sensitivity of the new three-stage mass spectrometer is an order of magnitude better than similar instruments with normal magnetic field boundaries. This is due to our unique ion-optical design that provides vertical focusing of the ion beam and, thereby, prevents ion scattering from the top and bottom of the flight tube. Because an intense and stable ion beam was required to make the large dynamic range measurement of abundance sensitivity on the present instrument, rhenium ions were used rather than uranium ions. Due to the presence of background interferences at masses 184 and 186 from tungsten in the zone-refined rhenium and at mass 188 from osmium, the abundance sensitivity measurement was made one-half mass unit away from the rhenium ion peaks at masses 185 and 187. During the measurement, the ion source pressure was 2×10^{-8} torr and the analyzer pressure was 3×10^{-9} torr.

The average values of the rhenium abundance sensitivity are

$$M - \tfrac{1}{2} = (6.5 \pm 0.5) \times 10^{-10}$$
$$M + \tfrac{1}{2} = (3.1 \pm 0.8) \times 10^{-10}$$

These values are equivalent to the abundance sensitivity only two-thirds of a mass unit away from the major uranium isotope at mass 238, because abundance sensitivity is a function of physical distance from the peak (Belshaw and O'Nions 1990). By extrapolating the logarithmic shape of the tail on the

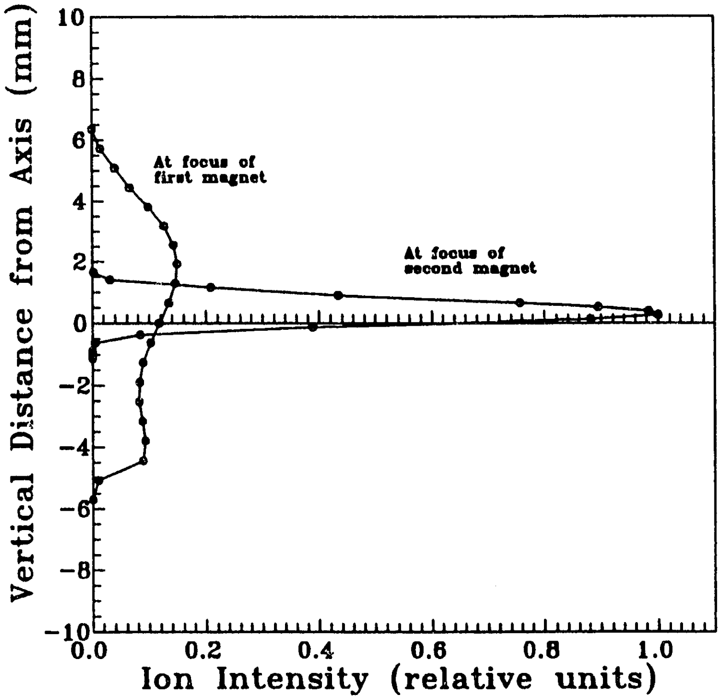

FIGURE 9. Vertical Ion Beam Profiles at S-2, the Focus of the First Magnetic Sector, and at S-3, the Focus of the Second Magnetic Sector. The beam is 8-kV Cs$^+$ ions from a single-filament source.

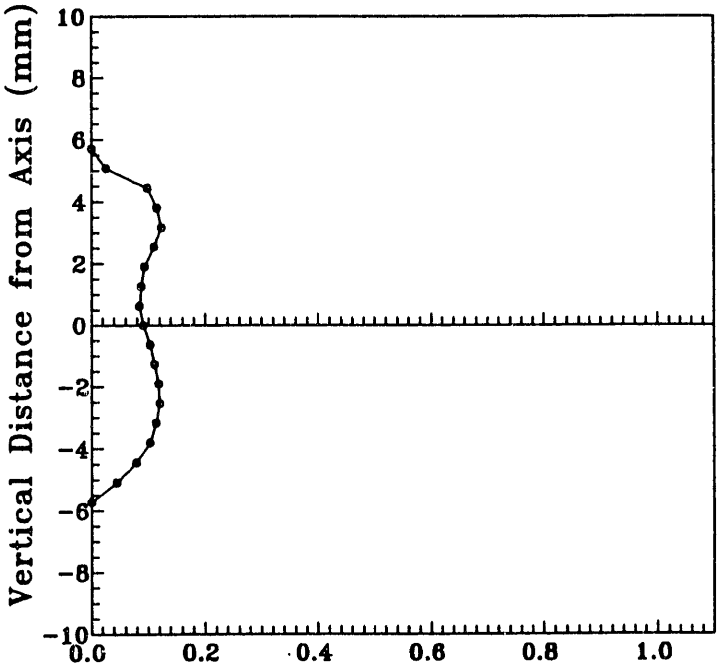

FIGURE 10. Vertical Ion Beam Profile at S-4, the Focus of the Third-Stage Electric Sector. The beam is 8-kV Cs$^+$ ions from a single-filament source.

rhenium peak, the abundance sensitivity at M - 0.79 is 1 x 10^{-10}, which is equivalent to the uranium abundance sensitivity at M - 1. In comparison, the uranium abundance sensitivity of a normal geometry three-stage mass spectrometer at M - 1 is 2 x 10^{-9} (Lagergren and Stoffels 1970).

The isotope-abundance sensitivity for negative ions is expected to be orders of magnitude better than for positive ions because negative ions are neutralized in a single scattering collision (Purser et al. 1981). A definitive measurement of the negative ion isotope-abundance sensitivity of this instrument has not yet been made.

However, the first background-limited measurement has been made by negative thermal ionization of the radionuclide ^{129}I in a natural iodine sample. Accelerator mass spectrometry, which eliminates molecular ion interferences in the mass spectrum, established a value of 7.5 x 10^{-13} for the $^{129}I/^{127}I$ ratio in this sample. The mass spectrometer reported here measured a ^{129}I concentration upper limit of 7.5 x 10^{-11}. This is a factor of four better than the upper limit measured at PNL on a three-stage mass spectrometer of normal geometry.

CONCLUSION

A three-stage isotope-ratio mass spectrometer of unique ion-optical design has been constructed. Non-normal magnet boundaries provide vertical focusing that achieves complete transmission of ions through the three-stage analyzer. The elimination of ion scattering from the top and bottom of the flight tube results in an exceptional isotope-abundance sensitivity of 1×10^{-10} for uranium. Construction of the instrument was facilitated by using commercially available standard mass spectrometer components.

ACKNOWLEDGMENTS

We are grateful to our co-workers at the Pacific Northwest Laboratory for their contributions to this project. Robert C. Thompson provided engineering support for the computer interface. Harry R. Emtman designed and fabricated custom electronic equipment. We also thank the Center for Accelerator Mass Spectrometry at the Lawrence Livermore National Laboratory for measurement of the natural iodine sample.

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APPENDIX A

A PROGRAMMABLE HIGH-VOLTAGE SYSTEM FOR A MASS SPECTROMETER ION SOURCE AND ELECTRIC SECTOR

A PROGRAMMABLE HIGH-VOLTAGE SYSTEM FOR A MASS SPECTROMETER ION SOURCE AND ELECTRIC SECTOR

Commercial power supplies have been used with a minimum of modification to provide a high voltage system for an isotope-ratio mass spectrometer with magnetic and electric sectors. The high-voltage system, which is programmable through an IEEE-488 interface, provides up to ±10 kV accelerating voltage for the ion source and slaved positive and negative voltages of the proper ratio for an electrostatic analyzer. Switching speeds are adequate for scanning the mass spectrum in the peak-hopping mode.

The cost of a system engineered and custom-built to our specifications would have been ~\$30,000. The cost of the system described here was ~\$5,500 plus a non-recurring engineering charge of \$2,700 and some in-house labor. Identification of a particular brand or model does not imply that the item specified is the best or only unit available for the purpose.

The high-voltage supply for the ion source is a Bertan model 2351 (Bertan Associates, Inc., 121 New South Road, Hicksville, NY 11801), a standard model 225-10R that has been factory modified to achieve high-speed voltage switching. The reversible polarity supply has an output of 0 to 10 kV, 2.5 mA, with voltage regulation of 0.001% for a ±10% line change and .005% for a 100% load change. It can make a 100 V step change in output voltage in <20 ms with an output current loading of at least 0.2 mA. To achieve this switching speed, the ripple specification was derated from 100 mV_{p-p} to 150 mV_{p-p} at full load. At 1 mA load, the ripple decreases to <50 mV.

The Bertan supply has full manual controls as well as remote programming by an IEEE-488 interface over the full range of output voltage. The voltage resolution is 1.0 V.

The electrostatic analyzer voltages are provided by two Trek model 601B high-voltage operational amplifiers (TREK, Inc., P.O. Box 231, Medina, NY 14103). The Trek op amps supply 0 to ±1000 V out for 0 to ±10 V in. Gain is adjustable. Ripple is <50 mV_{p-p} and slew rate is >35 V/µs.

A 1000:1 voltage divider (50MΩ in series with 50kΩ) is used on the Bertan HV output to provide a programming voltage for the Trek op amps.

Although the Bertan supply has a low voltage analog monitor output, it is not clean enough for the desired purpose. Impedance matching of the voltage divider to the Trek inputs is accomplished with buffer amplifiers designed and built in house. One of the buffer amplifiers includes an inverter to provide the opposite polarity programming voltage.

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