

MEMORANDUM

February 2, 1994

TO: Dr. Al Goodman
Office of Naval Research, Electronics Division

FROM: Floyd D. McDaniel
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University of North Texas
Denton, Texas 76203
Phone: 817-565-3251

REGARDING: Final Progress Report
ONR Grant No. N00014-90-J-1691

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GOALS OF RESEARCH PROGRAM

Development of sample charge compensation for the University of North Texas Accelerator Mass Spectrometry facility for characterization of impurities in semiconductor materials.

SUMMARY

Because of the high sensitivities and small sample size capabilities, an Accelerator Mass Spectrometry (AMS) system has been constructed at the Ion Beam Modification and Analysis Laboratory (IBMAL) at the University of North Texas.^{1,2} See figure 1. The AMS system, which has been developed³⁻⁴ through a collaboration with Texas Instruments Inc., the National Science Foundation, and the Office of Naval Research has been applied to trace element analysis of stable isotopes in electronic materials.⁵⁻⁶ The terminal charge stripping inherent with tandem accelerator operation allows molecular interferences to be removed.⁷⁻⁹ The interferences of molecules that have approximately the same mass as the element of interest (e.g. ²⁸Si₂ and ⁵⁶Fe) are one of the primary limits to high sensitivities for SIMS.¹⁰ Because AMS has increased sensitivities over SIMS for some elements by factors of 100 to 1000 due to the removal of molecular interferences, AMS is sometimes called "Super-SIMS".

The unique capabilities of AMS allow new and more sensitive methods for the characterization of trace impurities in electronic materials. Impurities in many cases determine the electrical properties of semiconductor materials. Impurities determine the carrier type as well as the resistivity, the mobility, and the carrier lifetimes. The control of unintentionally as well as intentionally added impurities is necessary for the development of advanced device processing of high performance, high reliability devices with lower unit cost through increased device yields. Understanding the materials science is essential for advancements in the device technology. At present, there are no other known laboratories in the world employing AMS for routine, trace element impurity determination in electronic materials.

While AMS has been applied in other laboratories to radioisotope determinations with sensitivities of 1 part in 10¹⁵ or better, existing AMS instruments are not designed for stable element analysis and cannot adequately perform these measurements without extensive modifications to the ion source. We have developed an ultra-low sample-contamination, UHV sputter ion source which injects mass-analyzed negative secondary ions from the sample into a 3 MV tandem accelerator. During acceleration, electrons are stripped from the ions. For charge states greater than 2+, most molecular species dissociate leaving only atomic ions. Momentum/charge and energy/charge discrimination, followed by total energy detection, provides unambiguous elemental identification. The AMS instrument, which operates under computer control, will provide automatic mass scans of stable isotopes in solid materials. The AMS instrument allows molecular interference-free mass scans to be obtained with a higher sensitivity than SIMS for some elements. The AMS instrument developed at the University of North Texas provides a super-sensitive trace analysis technique which is applicable to a large variety of samples.

We have made considerable progress in the development of the AMS system for stable elements, including

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University of North Texas

Industry University Cooperative
Research Center

February 7, 1994

Defense Technical Information Center
Building 5, Cameron Station
Alexandria, VA 22304-6145

Dear Sir or Madam:

Enclosed are two copies of the Final Progress Report for ONR Grant No. N00014-90-J-1691. If you need additional information, please call me at 817-565-3251 or write to the address below.

Sincerely,

Floyd D. McDaniel
Professor of Physics
Director, Ion Beam Modification and Analysis Laboratory
Director, Industry/University Cooperative Research Center

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the first computer automated, molecular interference free mass scan. We have achieved higher sensitivity than standard SIMS for P in Si. We have completed the installation of the new ultra-clean, microbeam UHV sputter ion source and it is being used to make bulk measurements at ppb sensitivity levels (1 part in 10^9 or 10^{13} atoms / cm^3) for many elements. At present, the AMS sensitivity is limited by sample contamination in the analysis chamber. Additional vacuum and sample cleaning techniques are being employed to reduce contamination. Microbeam and raster-scanning techniques are being tested at this time. When the ion source is fully operational, the AMS instrument should allow sensitivities of ppt (1 part in 10^{12} or 10^{10} atoms / cm^3) for almost any element in the periodic table as well as sputter depth profiling and secondary electron imaging of a sample.

Additional capabilities to be developed include microbeam imaging of lateral distributions of impurities; microbeam raster-scanned, sputter depth profiling of the impurity distribution as a function of depth; and the engineering of the instrument which provides for rapid turnaround of samples utilizing computer controlled data acquisition and analysis. The Accelerator Mass Spectrometry system at UNT is a powerful and sophisticated materials characterization tool ideal for providing the information needed for understanding the dynamics of impurities in semiconductor materials. AMS couples the sensitivity of a technique like Neutron Activation Analysis with the general applicability of SIMS. In addition, the surface sensitivity and depth profiling capabilities will allow this technique to accurately measure near surface features such as junction depths, diffusion profiles, etc.

PROGRESS TO DATE

The AMS system may be divided into three main components: (1) the ultra-clean, microbeam ion source, (2) the tandem accelerator, and (3) the detector system including the high energy beam transport line with magnetic and electrostatic analysis, and the particle detection system. A good portion of the past 12 months has been spent constructing and installing apparatus for the ultra-clean ion source and testing of the system. The high energy beam transport has been completed. A Si surface barrier detector is being used for particle detection while an ionization detector is being constructed. In the future, both will be available. The total energy detection system has been installed so that particle counting may be used for low intensity impurity ions. We have adapted and incorporated many of the best features of a variety of mass spectrometers of the past into a single powerful instrument which joins secondary ion mass spectrometry to a high energy electrostatic accelerator.

A. Ion Source

The ion source has been designed as a flexible, ultra-clean ion microprobe for the production of negative ions of stable, naturally occurring isotopes from samples of materials science interest. The primary ion beam was chosen to be Cs+ ions of approximately 10 keV. This ion species and energy has been shown to produce enhanced emission of negative secondary ions. Moreover, the tandem accelerator requires negative secondary ions in order to accelerate them with the positive terminal potential. The ionizer is maintained at approximately 1000°C. This corresponds to an energy spread of approximately $kT = 0.02$ eV. The fractional energy spread is approximately $dE/E = 2 \times 10^{-6}$. While the cesium ion beam may be very monoenergetic, it is not very pure. The unique feature of this source is its clean design. Most other ion source designs do not adequately discriminate between ions that arise from the sample of interest and ions that originate from spurious contamination. A schematic view of the Chimera source is shown in figure 2.

B. Computer Control of the AMS System

In addition, a considerable amount of time has been spent developing the software and hardware to allow computer control of the AMS system including the ion source, the accelerator, the magnetic and electrostatic analyzers, and the detection and data acquisition system. The computer control of these apparatus will allow fully automated mass scans which are necessary for AMS measurements. The AMS computer control system at North Texas is composed of three separate computer control subsystems communicating over a GPIB interface.

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 Al Goodman ONR/Code 1114
 Arlington, VA 22217-5000
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There are several advantages to a computer controlled AMS system. First, in order to remove molecular interferences, the accelerator system must be extremely stable. Magnets, lenses and electrostatic analyzers must be adjusted to compensate for changes in the accelerator terminal voltage due to beam loading effects. Also, electrostatic lenses must be adjusted for ions of different energy/charge ratios to insure uniform transmission. Secondly, in order to increase sensitivity, an ultra-clean ion source must be used. The various lenses, magnets, and electrostatic analyzers in the ion source may be floating at -50 kV with respect to ground. Computer control simplifies the operation of these components. Third, the computer system can be used for data display and analysis. Fourth, the system is more reliable and user-friendly.

C. Charge Compensation of the Sample

In order to take full advantage of the capabilities of the UNT AMS system, charge compensation is required. We are following the successful strategy used by Cameca (largest commercial vendor of SIMS systems) and shower the sample with very low energy electrons. This required the design and construction of several custom components for electron generation (electron gun, bias supply), electron transport (magnetic 90 degree deflector, electrostatic steerers, quadrupole focussing, power supplies), and ion transport (corrector magnet for ions, power supplies). The magnetic deflection of the electrons removes the electron source from line of sight of the sample, so there is no possibility of sample contamination by the electron source materials. Although the field required for electron deflection is small there will still be some effect on trajectories for low mass ions, and a corrector magnet will most likely be required.

Electron and ion optics calculations have been performed to address various current, current density and electron/ion overlap issues. In addition the fields generated for electron transport are designed to avoid any compromise of the primary beam optics on the existing AMS chamber. Mechanical integration of the system hardware with existing sample holder, extraction lenses, etc. has been considered.

Computer control of the various supply voltages will also be implemented. This allows computer controlled searches of optimum conditions as well as rapid reset of appropriate conditions for special samples and/or experiments. This control will be integrated into the existing AMS ion source control system in the future.

The charge compensation system has been designed. The components for the charge compensation system have been ordered and received. The components have not yet been installed in the chamber because of a sample contamination problem that has not yet been solved. We are reluctant to add any more equipment inside the chamber until we reduce the sample contamination to an acceptable level. Contamination of samples in the analysis chamber has proven to be the limiting factor in attaining higher sensitivities. Additional vacuum and cleaning techniques are being employed to reduce contamination. In addition a class 100 portable clean room has been purchased which is 6 feet by 8 feet in size to help keep samples clean during preparation and before insertion into the chamber.

D. Calibration of the AMS System

The computer software development for calibration of the AMS magnets and electrostatic analyzer has been completed. Reproducible calibration procedures for the AMS system have been developed and tested. The calibration of the AMS system, which has remained valid for over six months, is rechecked each time samples are analyzed. The AMS system is calibrated by running mass scans of elements of known concentration, i.e. the elements of the matrix for the sample to be analyzed. The calibrations are run sequentially through the 90° magnet, the 40° magnet, and the 45° electrostatic analyzer for a fixed terminal voltage. A calibration file is constructed for each magnet and the ESA from the isotopic mass and the magnetic or electrostatic rigidity. After obtaining mass and magnetic rigidity data over the mass range of interest, a cubic polynomial fit is made to the data and the fit is used for future mass analyses of unknown masses.

The magnetic rigidity is given by

$$Br = mv/q = (2mE/q^2)^{1/2}, \quad (1)$$

where B is the magnetic field strength, r is the radius of curvature in the magnetic field, m is the mass of the ion exiting the accelerator, v is its velocity, E is its kinetic energy, and q is its charge. The electrostatic rigidity is given by

$$\epsilon r = mv^2/q = 2E/q, \quad (2)$$

where ϵ is the electric field strength and r is the radius of curvature in the electric field. After the singly charged negative ions are accelerated to the tandem accelerator terminal, which is at a potential of V_T (~3 MV maximum), the ions have energies of

$$E = e(U_0 + V_T), \quad (3)$$

where e is the electronic charge and U_0 is the negative ion injection potential from the ion source. For the present work, the negative ions are passed through an N_2 gas stripper canal. The N_2 gas is differentially pumped in the terminal of the accelerator. Collisions with the gas stripper may remove several electrons from the atomic or molecular ions leaving the ions in charge state q . The mass m of the ion exiting the accelerator may be less than (if dissociation occurs) or equal to the mass m_0 injected into the accelerator. The energy of the ion of mass m is given by

$$E = eqV_T + e(m/m_0)(V_T + U_0), \quad (4)$$

where the first term is the energy from post-stripping acceleration and the second term is the residual energy of the dissociated ion at the terminal. This expression neglects the ion's energy loss in the stripper gas which can vary from 0.1 kV for H to 7.0 kV for Si and must be taken into account. After exiting the accelerator, ions may reach energies/mass of ~1 MeV/u. Atomic and molecular ions as well as dissociated ions may be used for calibration. Figure 3 shows a SIMS spectrum of Ga and As molecules taken after the 90° injection magnet that provides calibration points for the mass 213–224 region. For each mass shown, a magnetic rigidity Br was recorded. After obtaining mass and magnetic rigidity data over the mass range of interest, a cubic polynomial fit is made to the data and the fit is used for future mass analyses of unknown masses. A plot of the data and calculated fit for the 90° magnet is shown in fig. 4. Here, the magnetic field strength B is plotted versus $\chi = Br$ which depends on m , E , and q of the ion as given in eq. (1). The right hand vertical axis gives a measure of the goodness of fit, the residual fraction $\Delta B/B$. Similar procedures for the 40° magnet and the 45° ESA calibrate the AMS system so that ions from the sample may be produced, scanned, and analyzed through the entire spectrometer under computer control. A precision of 0.1% in $\Delta B/B$ is required for both magnets for preservation of isotopic ratios.

E. Data acquisition

Data is acquired under computer control utilizing the previously mentioned calibration fits. Attenuators may be inserted into the beam to reduce loading of the accelerator and to enable measurements with the particle detector. In order to protect the surface barrier (particle) detector, the AMS system automatically switches from current mode to particle counting only when the ion current is less than a user selected threshold. However, at present the Faraday cup system can only measure currents larger than approximately 1 pA due to system noise. Thus, a possibility for detector damage still exists if the ion beam current is only slightly below the pA level. To improve current measuring sensitivity to $< 10^{-14}$ A, a microchannel plate detector is being added to the existing system. Also, an ionization chamber has been built to replace the surface barrier detector and thus improve the ruggedness of the system.

Since magnetic and electric field analyses define a unique value of m/q rather than a unique m , interferences

may occur using different charge states. In some cases, elemental dissociation fragments from a molecular breakup have the same m/q as the element of interest and will pass through the magnetic and electrostatic analyzers (e.g. $(^{28}\text{Si}_2)^- \Rightarrow ^{28}\text{Si}^+$ has the same mv/q and E/q as $^{56}\text{Fe}^- \Rightarrow ^{56}\text{Fe}^{2+}$). This interference can be removed by total energy detection since the breakup ion and the ion of interest clearly have different energies.

RESULTS OF RECENT MEASUREMENTS

Si, InP, GaAs, and HgCdTe samples have been analyzed over the past few months. Sensitivities of ppb (1 part in 10^9 or 10^{13} atoms per cm^3) and slightly better have been obtained for selected elements. Figure 5, which shows an AMS current scan over the mass region for the Si isotopes, indicates the correct isotopic abundances for ^{28}Si (92.2%), ^{29}Si (4.67%), ^{30}Si (3.1%) to within 1 percent, which indicates the calibration is accurate.

Figure 6 shows an AMS particle scan of the mass region 55–82 for a contaminated Si sample which indicates Co, Ni, Cu, Ge, Se, and Br in the few ppb range, Fe and Ga in the few hundred ppb range, and As in the 1 ppm range. Again, the isotopic ratios are in agreement for Ni, Ga, Se, and Br. For ^{80}Se , 200 cps were obtained, which corresponding to ~ 2 ppb. A single count of Se at a ppt concentration could be measured in 10 s. Therefore, count rates are sufficient to make ppt measurements in a reasonable time.

• Figure 7 shows an AMS particle scan of the Cu region for a CdZnTe sample which indicates Cu is present in the 1 ppm range. Cu in II–VI semiconductor materials is a p-type dopant and rapidly diffuses through the material. Since Cu is fairly common in starting materials, its rapid movement can adversely affect n-type dopants.

Figure 8 shows an AMS particle scan of mass region 16–65 for a contaminated InP sample. Data are ratioed to the $^{31}\text{P}^{3+}$ signal for comparison. Counting time was 5 s/mass. Concentrations of impurities vary from 4.6 parts-per-thousand for Si, to a few ppm for F, S, Cl, and Fe, to a few ppb for Cr. Concentrations for Na, Al, K, Ca, and Cu are not given because Relative Sensitivity Factors are not yet available.¹

SUMMARY

The University of North Texas AMS facility builds on existing instrumentation science, but extends it beyond any instrument available today. We have developed an AMS instrument ultimately capable of parts-per-trillion (ppt) sensitivities for stable isotopes in solid materials. Such an AMS instrument has general applicability for the characterization of materials and special applications to important materials science issues concerning electronic materials.

During the past three years, we have made a great deal of progress in the development of AMS for stable elements in electronic materials. We have made the first computer automated, molecular interference free mass scan of AMS. We have achieved a higher sensitivity than Secondary Ion Mass Spectrometry (SIMS) for P in Si and also for other dopants and impurities. These initial measurements are about a factor of 100 to 1000 times better than conventional day-to-day SIMS.

Although AMS as applied to stable element detection is still under development, the basic principles should allow resolution and system yields similar to or better than conventional SIMS while also removing the major sources of molecular interference. High sensitivity impurity scans and depth profiles are being implemented in a straightforward fashion by careful attention to ion source design (good primary beam optics and control, low levels of sample contamination during sputtering) as well as charge state selection during analysis.

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UNT Accelerator Mass Spectrometer

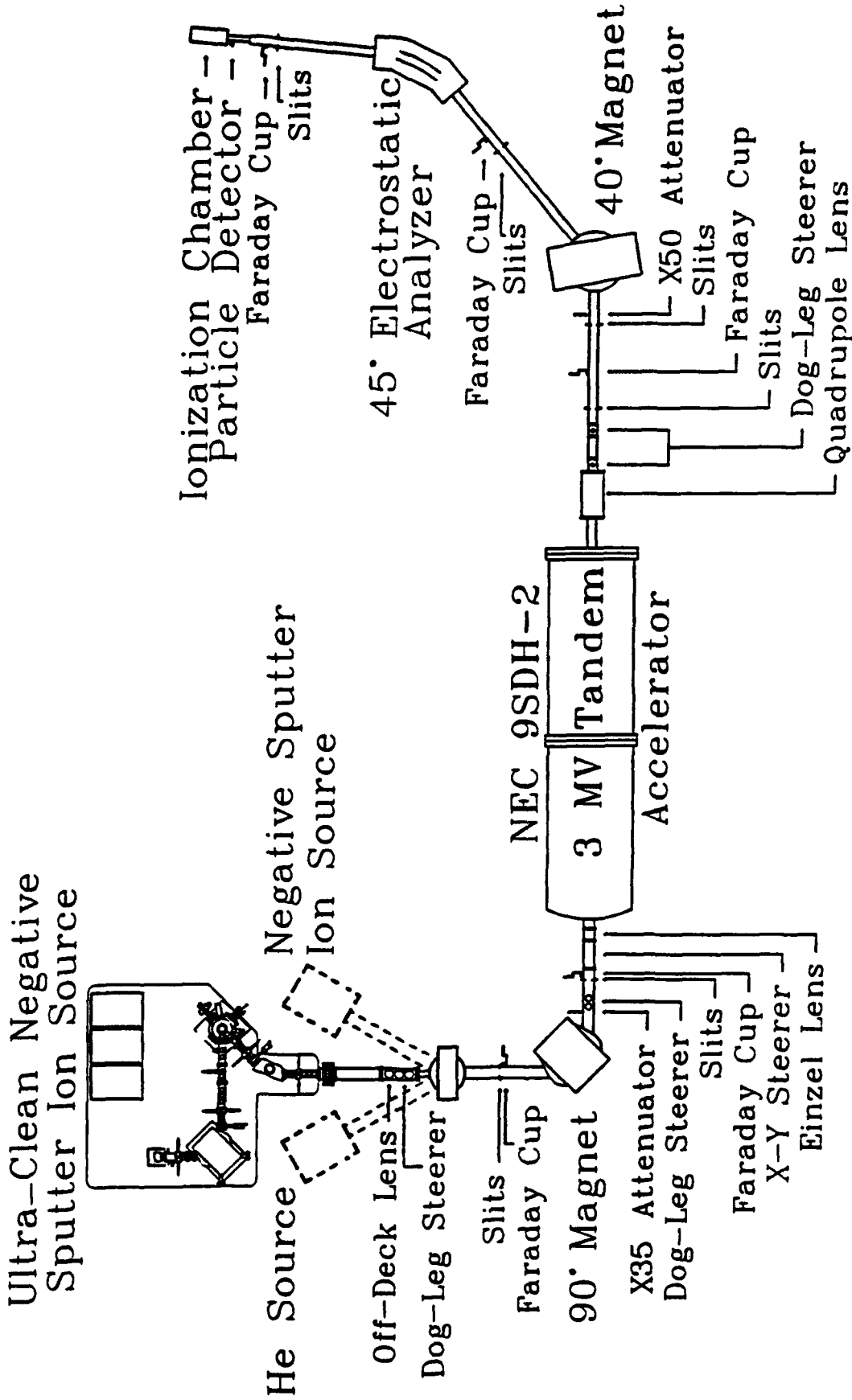


Figure 1. The University of North Texas accelerator mass spectrometry facility showing the ultra-clean negative sputter ion source, the 90° injection magnet, the 3 MV tandem accelerator, the 40° analyzing magnet, the 45° electrostatic analyzer, the particle detector, and other associated beamline components such as X-Y slits, Faraday cups, beam steerers, focusing lenses, and ion beam attenuators.

Ultra-Clean Negative Sputter Ion Source

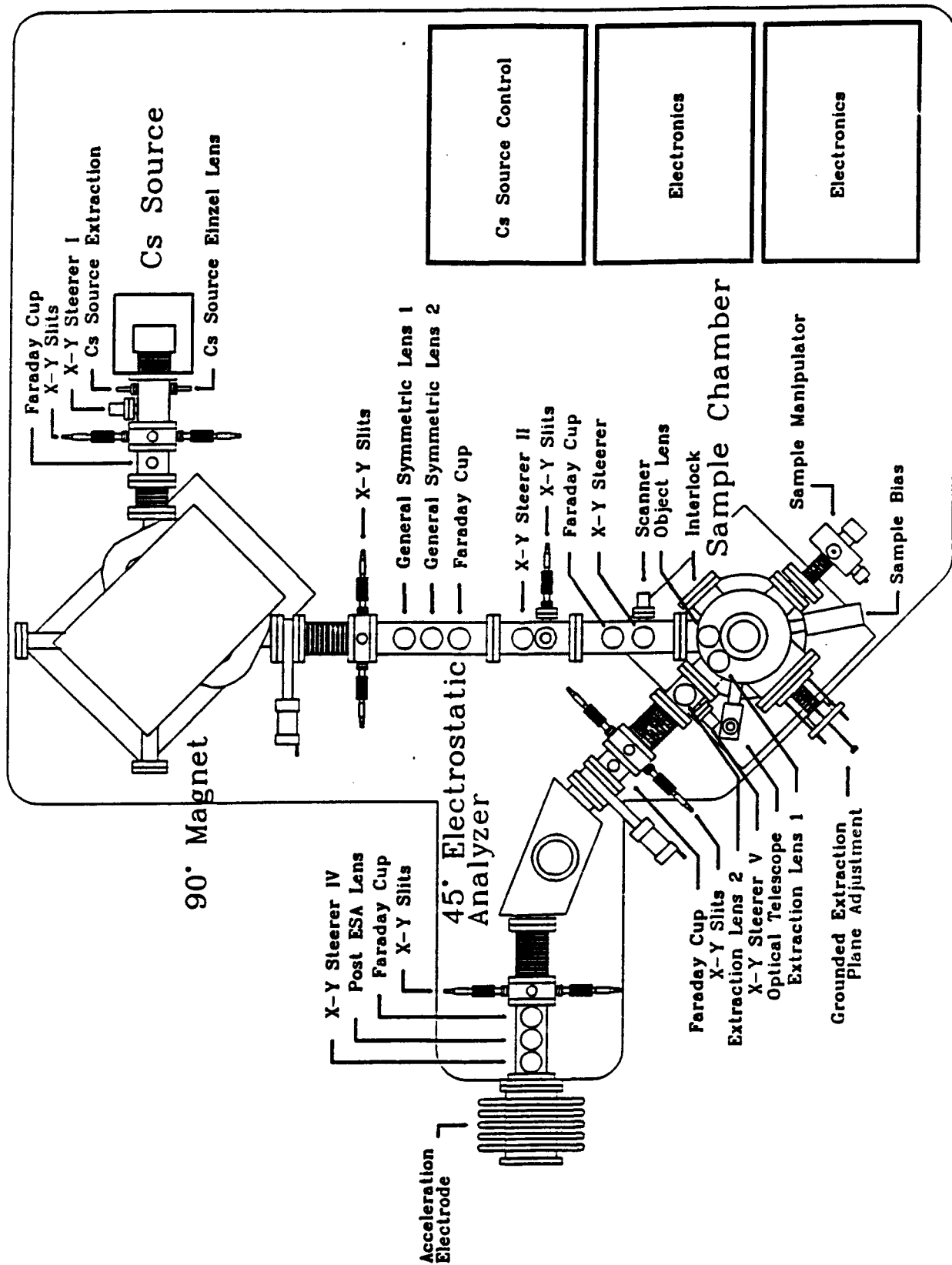


Figure 2. Schematic of the ultra-clean negative ion source showing the Cs source, 90° source magnet, sample chamber, 45° source electrostatic analyzer, and other associated beamline components such as einzel focussing lenses, beam steerers, X-Y slits, and Faraday cups. Also seen are sample manipulators, extraction optics, and an optical telescope for viewing the sample in the chamber.

SIMS SCAN GaAs

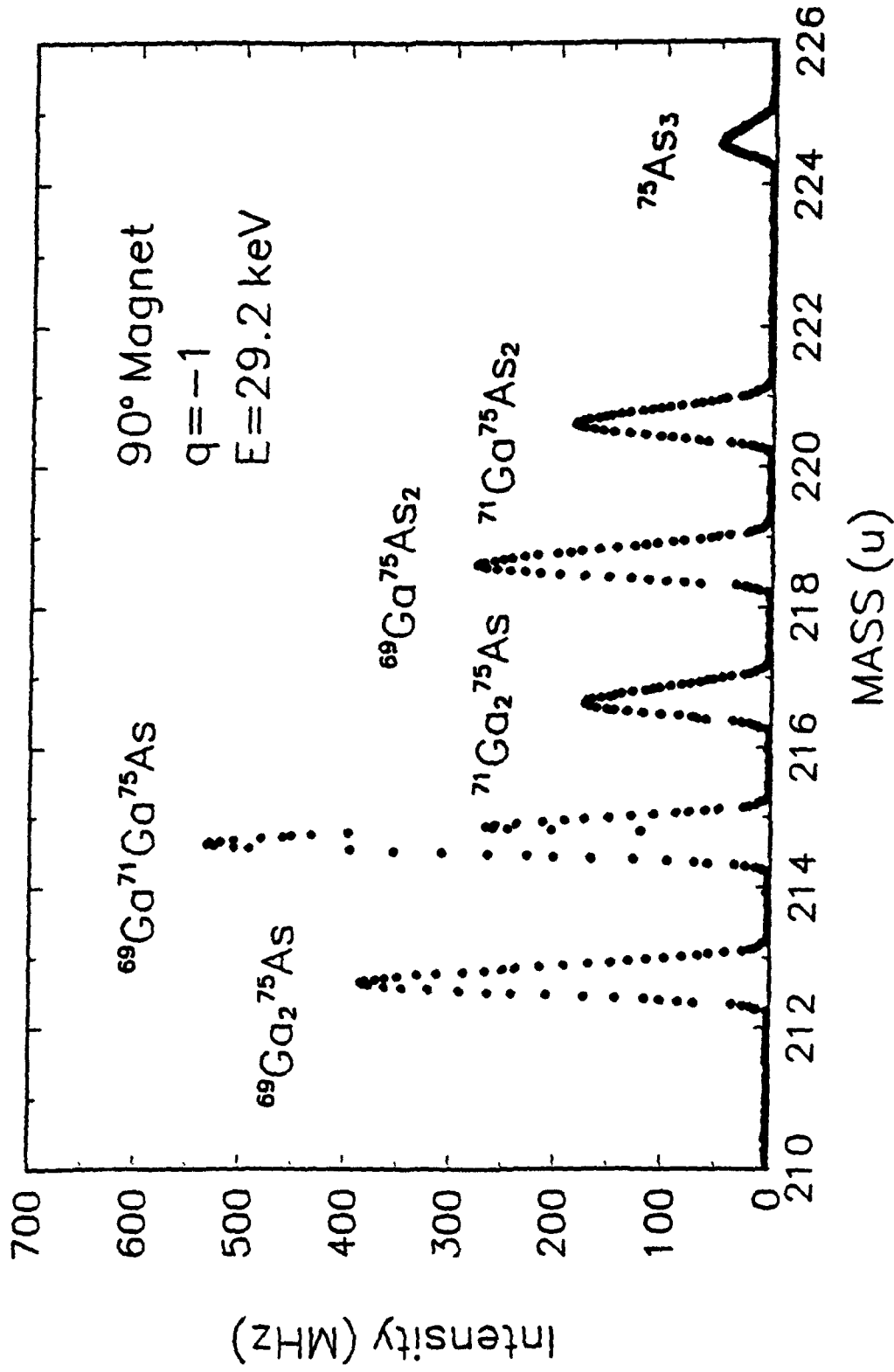


Figure 3. Secondary ion mass spectrometry (SIMS) current scan of a GaAs sample used for constructing a calibration file. The mass spectrum shows a number of molecular species formed in a charge state $q = -1$ from a GaAs sample in the ion source. The peak heights are related to the natural abundances of the ^{69}Ga (60.1%) and ^{71}Ga (39.9%) isotopes.

90° MAGNET CALIBRATION

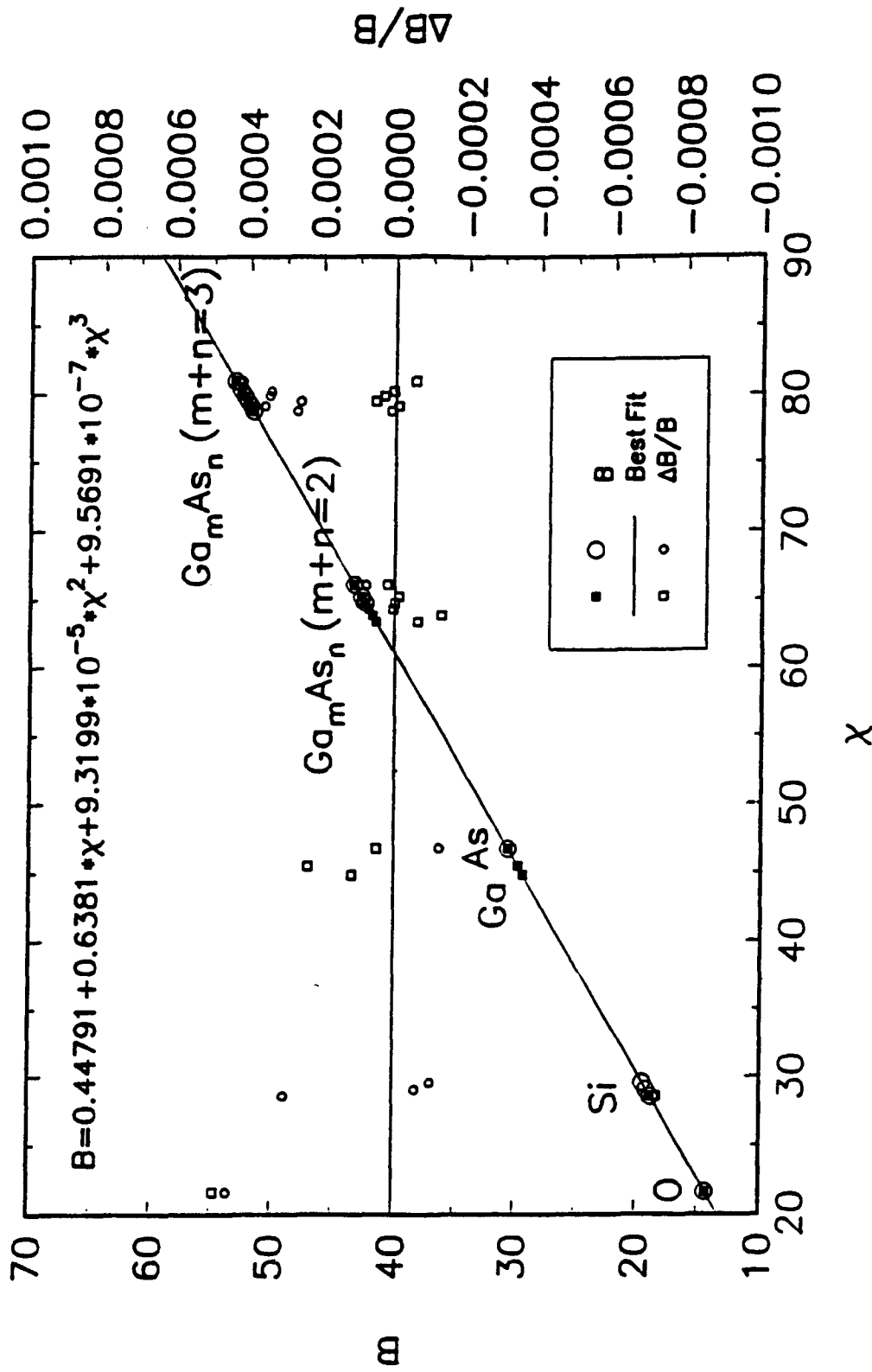


Figure 4. A plot of the 90° injection magnet calibration file showing magnetic field strength B versus $\chi = Br$, the magnetic rigidity, which is dependent on m, E, and q of the analyzed ion. No measurements of B were more than a data point thickness from the calculated fit. The right hand axis is a measure of the goodness of fit, the residual $\Delta B/B$, and in all cases is less than 0.0006. The calculated fit is given at the top of the figure.

AMS SCAN Si

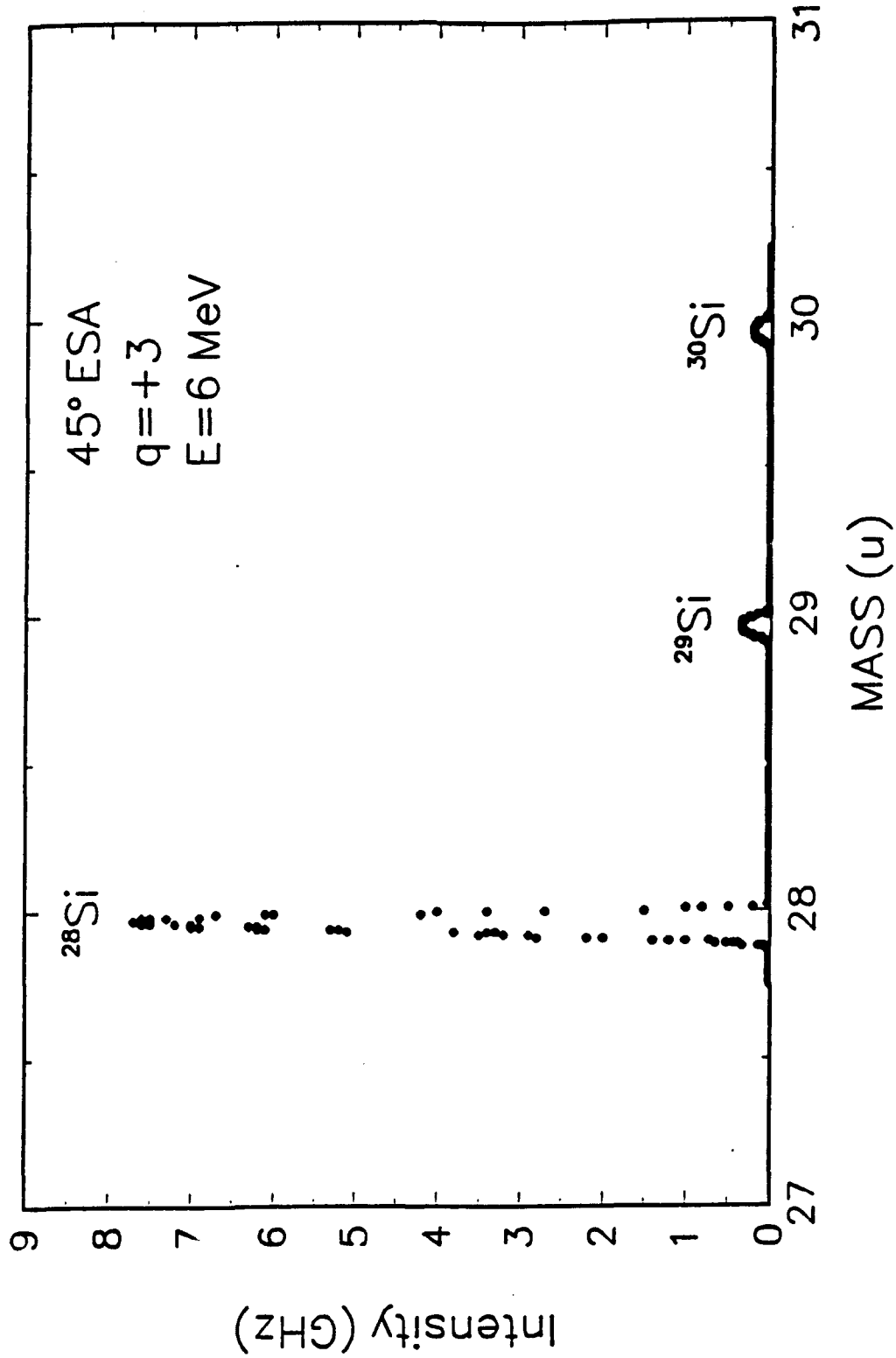


Figure 5. Accelerator mass spectrometry current scan of the silicon isotopes measured after the 45° electrostatic analyzer. The peaks indicate the correct isotopic ratios as expected for an accurate calibration.

AMS SCAN Si
Sample TS1

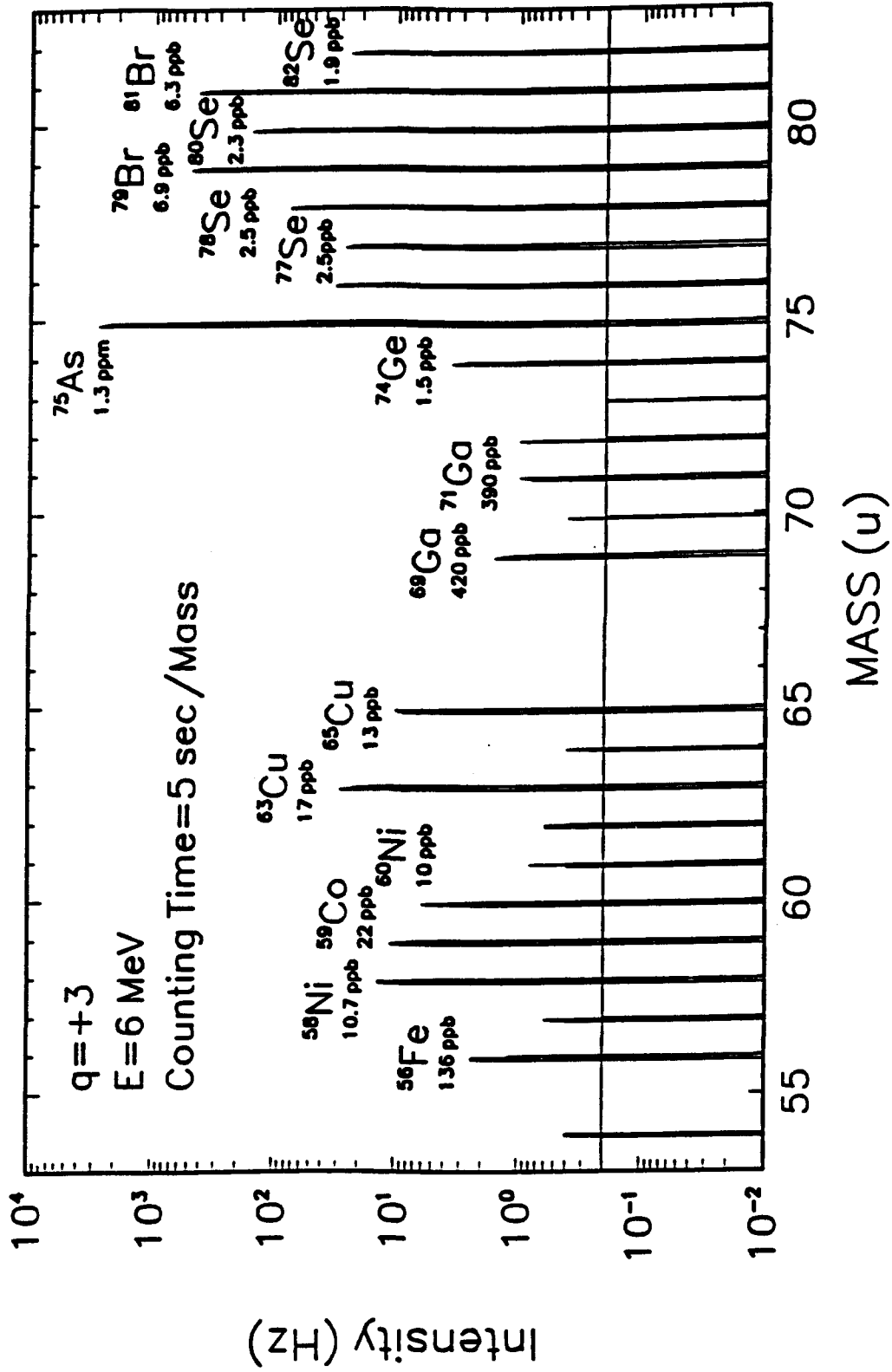


Figure 6. Accelerator mass spectrometry particle scan of a silicon sample for elements from Fe to Se. Isotopic identification and predicted total contamination level are given for each element. The horizontal line at 0.2 Hz corresponds to the minimum detectable counting rate for the chosen counting time per mass of 5 s (i.e. one count detected in 5 s).

AMS SCAN
Sample CZT2

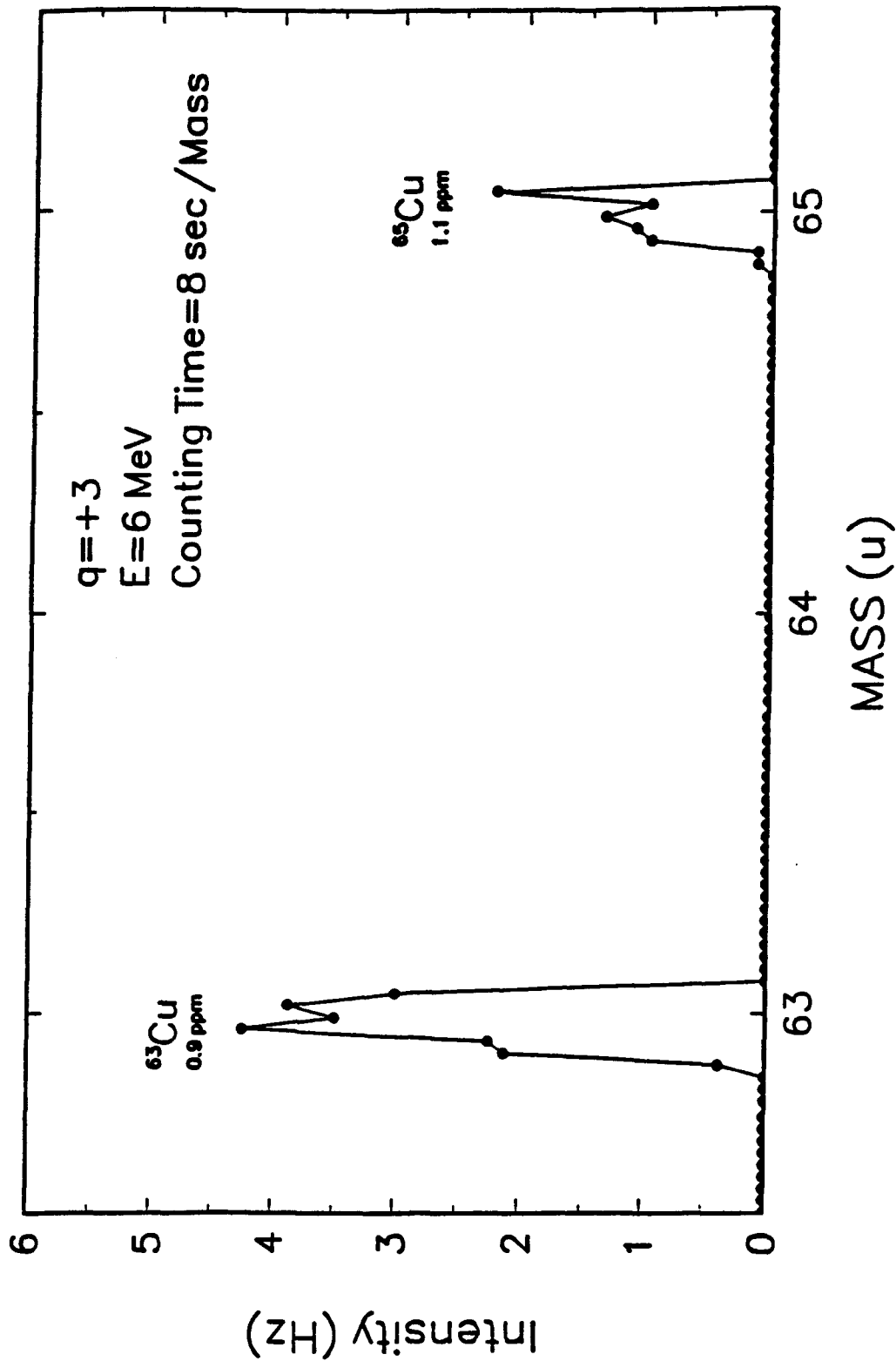


Figure 7. Accelerator mass spectrometry particle scan of $^{63,65}\text{Cu}$ isotopes in a CdZnTe sample. Predicted concentration levels are indicated for both Cu isotopes and are in agreement within statistics indicating correct isotopic ratios.

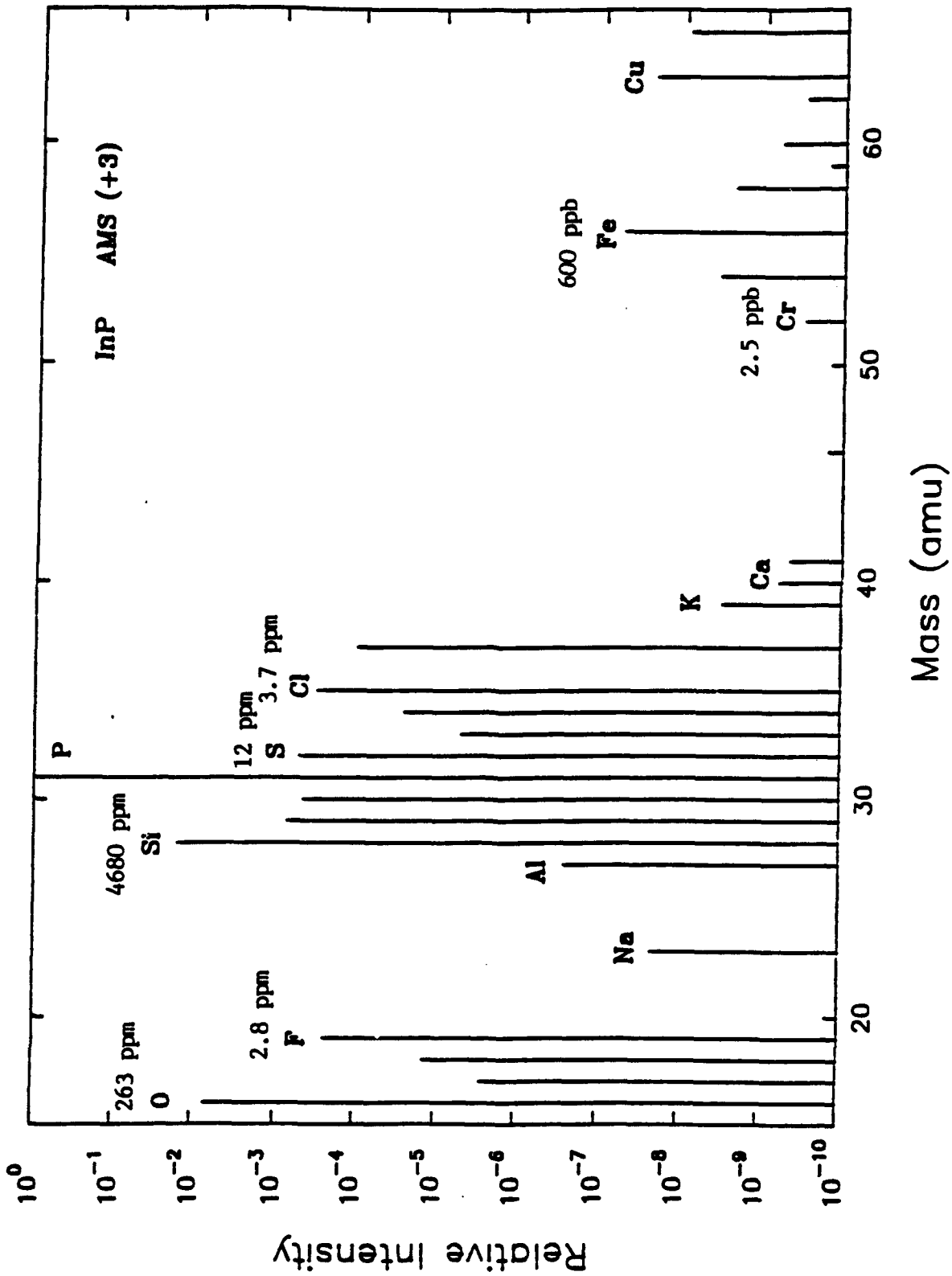


Figure 8. Full AMS scan of InP using charge state +3 to dissociate molecular ions. Data are ratioed to the $^{31}\text{P}^{+3}$ signal.