



Calibration of pressure-dependent sensitivity and discrimination in Nier-type noble gas ion sources

P. G. Burnard and K. A. Farley

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125
(peteb@gps.caltech.edu; farley@gps.caltech.edu)

[1] **Abstract:** The efficiency of many noble gas mass spectrometers to ionize gas species is known to be a function of the pressure of gas in the spectrometer. This work shows how the half plate voltage for maximum He or Ar signal depends on the spectrometer pressure and shows that the half plate voltage for maximum ⁴He sensitivity does not coincide with the half plate voltage for maximum ³He sensitivity. In addition, half plate voltage has a greater control on sensitivity at higher spectrometer pressures. Variations in He and Ar sensitivity and isotopic discrimination as a function of pressure are due, at least in part, to these variations in the position of maximum sensitivity with respect to half plate voltage. The maximum sensitivity settings shift to lower half plate voltage at high spectrometer pressures, irrespective of if the pressure increase is due to the gas being investigated or a different species. Therefore noble gas mass spectrometers should always be tuned at the maximum possible pressure; measurements at higher pressures should be avoided. Significant errors in the spectrometer sensitivity and discrimination can result from improper tuning and calibration of noble gas mass spectrometers.

Keywords: Mass spectrometer; noble gases.

Index terms: Instruments and techniques; isotopic composition/chemistry; geochronology.

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1. Introduction

[2] Many noble gas mass spectrometers generate ions by electron bombardment in “Nier-type” ion sources. Neutral species in the spectrometer are ionized by an electron beam that strips an electron (or electrons) from molecules or atoms, producing positive ions. A magnetic field is applied to the source region in order to increase the path of electrons through the ionization chamber using

small magnets, usually external to the evacuated source housing. The ions are produced at a potential of 3–5 KV, then extracted by a lower voltage focusing plate (the “half plate”) and an exit slit at ground potential before magnetic sector mass analysis (Figure 1) [Wallington, 1970]. Nier-type sources are standard on the commercially available noble gas mass spectrometers manufactured by Mass Analyser Products (e.g., MAP 215-50) and VG (e.g., the 5400 and 3600).

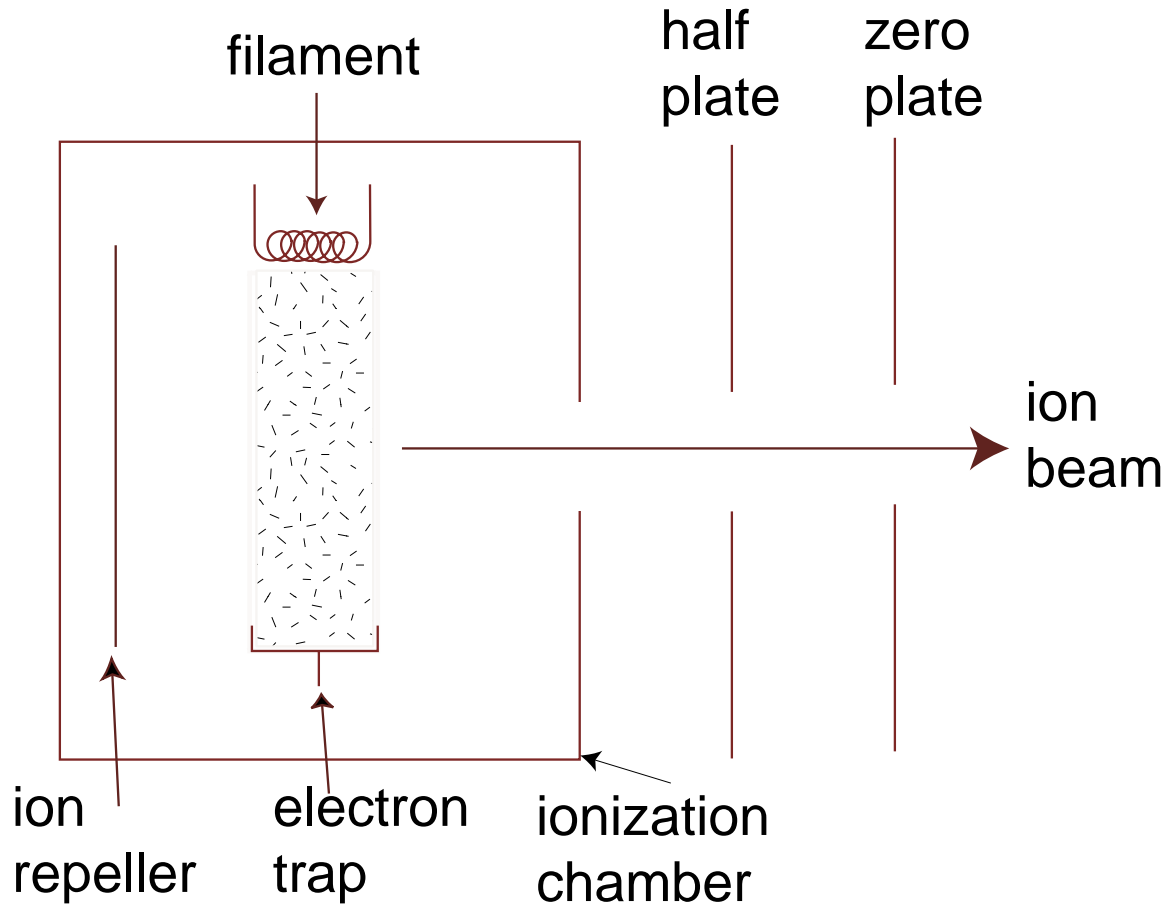


Figure 1. Schematic section through a Nier-type source, illustrating relative positions of the ionization chamber and accelerating plates. These experiments were conducted with a constant ionization chamber voltage of ~ 3 KV while the half plate voltage was adjusted between 2.4 and 2.5 KV. The electron current in the trap was set at $500 \mu\text{A}$ with an electron potential of 58 eV and repeller plate (drawout) voltage of -9 V. The spectrometer volume is $\sim 1800 \text{ cm}^3$.

[3] The efficiency with which ions are produced in Nier-type sources is a function of the gas pressure in the mass spectrometer. As a result, isotopic discrimination and spectrometer sensitivity depend on sample size or total gas pressure. The sources of these pressure-dependent effects are not well known or characterized and must depend, to a certain degree, on different protocols used in various laboratories: some laboratories retune the spectrometer source voltages for optimum

sensitivity prior to each analysis, whereas standard practice elsewhere is to “tune up” the source only rarely, for example, only after a power-down. *Honda et al.* [1993] showed that the $^3\text{He}/^4\text{He}$ discrimination in a VG5400 increased by $\sim 10\%$ between low (2×10^{-8} torr) and high ($\sim 1 \times 10^{-6}$ torr) He pressure in the mass spectrometer. Similarly, discrimination and sensitivity of He and Ar increase with pressure in the Caltech MAP 215-50 (see below).

[4] The calibrations required to correct for pressure-dependent isotopic discrimination are relatively straightforward. In order to perform these corrections, it is sufficient to characterize discrimination as a function of the spectrometer signal; therefore absolute calibration volumes are not required. For example, adequate corrections for pressure-dependent $^3\text{He}/^4\text{He}$ discrimination can be performed by calibrating the He isotopic discrimination as a function of the ^4He signal; absolute calibration of the volume of ^4He pipetted into the spectrometer is not required. More complex are the calibrations required to determine spectrometer sensitivity as a function of pressure. These require accurately known calibration aliquots that vary in size over a range similar to that encountered during sample analysis, i.e., by a factor of at least 100. These aliquot volumes have to be independently determined (for example, by a manometer), which is not possible on some noble gas mass spectrometer systems. Failure to account for the pressure dependence of the spectrometer sensitivity can result in serious (>20%) errors in determination of the absolute amount of He (or Ne or Ar) in a sample.

[5] While many of these effects are recognized by noble gas analysts, these issues have rarely been addressed in the literature. Despite the difficulty in obtaining reliable noble gas abundances, there is an increasing demand for high-quality noble gas abundance data. For example, exposure dating using cosmogenic noble gases relies on accurate absolute abundances of ^3He and ^{21}Ne [Cerling and Craig, 1994], and noble gas studies are increasingly focusing on the relative abundances of He, Ne, and Ar in geological fluids and rocks [Harrison *et al.*, 1999; Honda and Patterson, 1999], requiring accurate abundance data for each of the noble gases.

[6] This contribution outlines the performance of the Caltech MAP 215-50 noble gas mass

spectrometer as a function of pressure and how source tuning affects this performance. We do not attempt to reconcile these observations with the ion optics of the source. The aim of this paper is to highlight the importance of pressure-dependent effects when measuring noble gas abundances and isotopic compositions and to outline how spectrometers may be operated in order to minimize errors. Readers interested in more detailed discussion of the electron impact source optics are encouraged to read Holst *et al.* [1999] and Brown [1989].

2. Caltech MAP 215-50

[7] Variations in sensitivity and mass discrimination must reflect the efficiency with which ions are produced in and extracted from the ion source; variations in detector sensitivity cannot account for these variations. Our goal was to map out source-focusing characteristics at different pressures, to determine if source focusing can be used to control the sensitivity and discrimination variations with pressure.

2.1. Method

[8] Two calibration gases were used: The first is “Murdering Mudpots” (MM), which is Yellowstone He gas with $^3\text{He}/^4\text{He}$ ratio of 2.29×10^{-5} ($16.5 R_a$). The MM standard was not used for Ar calibration. The second is an air standard (modified air) that has had He added such that $^3\text{He}/^4\text{He} = 2.86 \times 10^{-6}$ ($2.06 R_a$) and $^4\text{He}/^{40}\text{Ar} = 1.45$. With the exception of He, all other noble gases in this standard have air isotopic compositions and relative abundances.

[9] The volumes of the gas-handling manifold at Caltech have been accurately determined (relative to a known volume) using a 0–1 torr type 270C MKS Baratron capacitance manometer. The well-calibrated line volumes allow accurate subdivision of calibration aliquots,

essential for the determination of spectrometer response with pressure.

[10] Prior to analysis in the MAP 215-50 mass spectrometer, the calibration gases were first split to the desired size in the extraction system, then purified using two (one hot, one cold) SAES NP10 Zr-Al getters. The purified gases were condensed onto charcoal at 16 K; He was released at 32 K (at which temperature Ne is quantitatively retained on the charcoal); the charcoal was then heated to 75 K and the Ne was discarded. Ar was released at 190 K, at which temperature Kr and Xe are retained on the charcoal, ensuring that the pure gases were analyzed on the MAP. The ^3He and ^4He were measured on a Galileo Channeltron and Faraday cup ($10^{11} \Omega$ resistor), respectively.

2.2. Response to Half Plate Voltage and Bias at Constant Pressure

[11] The primary focusing of Nier-type sources is achieved through the voltage and bias of the half plates (where the bias is the voltage difference across the two half plates). These voltages have been placed under computer-control on the Caltech MAP 215-50, which allows the signal response as a function of half plate voltage and half plate bias to be analyzed more readily than in conventional spectrometers that do not have automated source focusing. The bias voltages reported below are absolute voltages (i.e., are the actual voltage difference across the plates), whereas average half plate voltage is reported relative to an arbitrary fixed voltage of ~ 2.4 KV. The actual voltages on the half plates are not accurately known. The remaining source conditions, including orientation of the source magnets, were held constant (see Figure 1 caption for details) throughout the experiment.

[12] An aliquot of ~ 250 ncc (ncc = $1e^{-9}$ cm³ STP) of ^4He was introduced into the mass

spectrometer. The ^4He was measured at ~ 150 different half plate voltage and bias settings on a well-defined grid. Each measurement was corrected for ion consumption during the experiment using a decay constant determined from 10 repeated measurements at the center of the grid at regular intervals during the experiment. The results of the experiment are shown as sensitivity contours in half plate voltage-bias space in Figure 2. A similar experiment was conducted for Ar (not shown). The Ar signal response to the half plate and bias is broadly similar to that of He, except that the maximum occurs at a lower bias (-18 V).

[13] The position of the bias maximum is largely independent of half plate voltage (Figure 2). This is important, as it is therefore possible to maximize bias and then investigate the response to half plate voltage in the knowledge that bias will be maximized. Spectrometer tuning would be considerably more problematic if the position of the bias maximum were a function of the half plate voltage (i.e., if the "ridge" in Figure 2 were not approximately parallel to the X axis).

2.3. Response to Half Plate Voltage at Different Pressures

[14] The ^3He and ^4He response as a function of half plate voltage was determined at different pressures of gas in the spectrometer. The results of the experiment for two representative pressures are shown in Figure 3. These experiments demonstrate that (1) at a given pressure, the half plate voltages for ^3He and ^4He maximum sensitivity are not coincident; (2) at a given pressure, the sensitivity with changing half plate voltage has a different curve for each isotope, i.e., there are different shapes to the "peaks" in Figure 3 (typically, the ^3He curve is steeper than that of ^4He); and (3) the position and slope of the ^3He and ^4He sensitivities as a

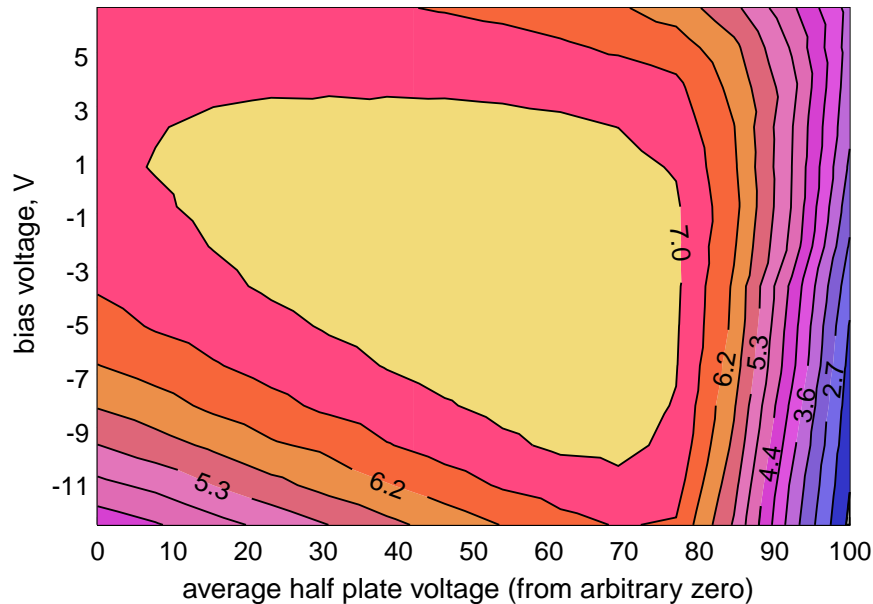


Figure 2. The ^4He sensitivity (mV ncc) as a function of half plate voltage and bias ($\text{ncc} = 1\text{e}^{-9} \text{cm}^3 \text{STP}$). A total of $250 \text{ ncc } ^4\text{He}$ was introduced into the spectrometer, and the signal on the Faraday was recorded at ~ 150 different half plate voltage and bias settings. All half plate voltages are reported with a constant offset of $\sim 2400 \text{ V}$. The contour interval is 0.2 mV ncc^{-1} on the Faraday cup ($10^{11} \Omega$ resistor). A well-defined plateau is produced with a sharp drop-off in sensitivity at high half plate voltage. A crucial feature of this plateau is that the bias maximum is insensitive to the average half plate voltage. This means that the bias maximum applies to all half plate voltages (in the range investigated) and it is not necessary to iteratively maximize half plate voltage and bias.

function of half plate voltage are not constant but depend on the gas pressure within the spectrometer.

[15] Similar experiments show that the positions of the ^{36}Ar and ^{40}Ar maximum sensitivity also shift to lower half plate voltages at high mass spectrometer pressures (not shown), although, unlike for He, the ^{36}Ar and ^{40}Ar sensitivity curves as functions of half plate voltage were similar in shape.

[16] In a separate experiment the amount of He admitted into the spectrometer was held constant while the pressure within the mass spectrometer was increased by adding Ar. The same effect was observed; that is, ^4He maximum sensitivity occurred at lower half plate

voltages in the presence of a high partial pressure of Ar. Therefore the changes in the He sensitivity as a function of half plate voltage result from changes in the total pressure (as opposed to the partial pressure of He) in the spectrometer.

[17] As a result of the different ^3He and ^4He sensitivity curves as a function of pressure (Figure 3), the discrimination (the relative ^3He and ^4He sensitivities) is a function of both half plate voltage and spectrometer pressure, illustrated in Figure 4.

2.4. Sensitivity as a Function of Pressure

[18] Pressure-dependent sensitivity variations result, at least in part, from the changes in half

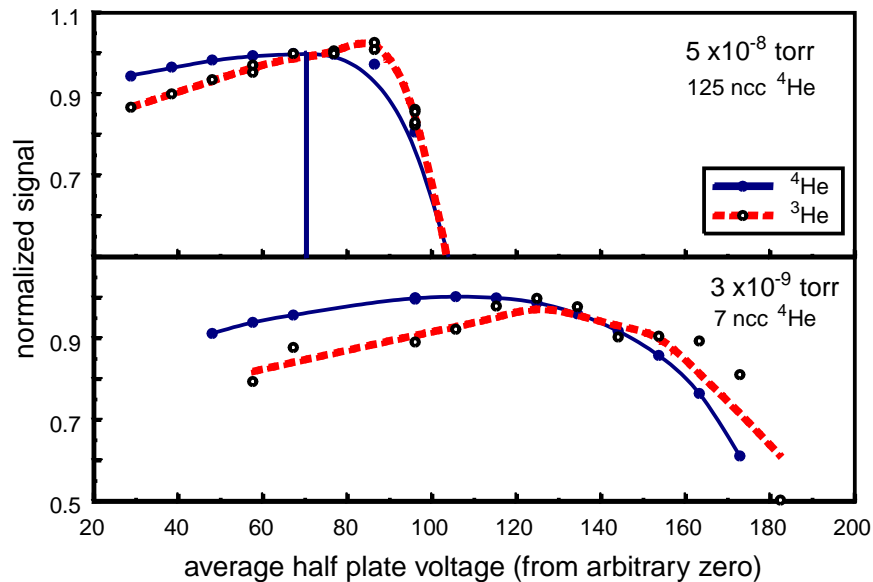


Figure 3. Variations in the ^3He and ^4He response to half plate voltage at different pressures. Half plate voltages are as in Figure 2. Variable aliquots of the MM standard were introduced into the spectrometer. The position of maximum He sensitivity depends on the He pressure in the spectrometer: at low pressures (bottom) the He maximum occurs at approximately +50 V relative to the higher-pressure He maximum (top). Furthermore, a higher gas pressure in the mass spectrometer (top) results in a narrow region of maximum sensitivity (e.g., 90% sensitivity corresponds to ~ 100 V) with a sharp drop in sensitivity on the high voltage side of the He maximum sensitivity. At low He pressures the He sensitivity curve is broader (e.g., 90% sensitivity corresponds to 160 V) with a more gentle drop in sensitivity on the high-voltage side.

plate voltage for maximum sensitivity at different pressures. Calibrations performed at constant half plate voltage and bias (one setting used for He, a separate setting for Ar) result in a log-linear relationship between spectrometer sensitivity and pressure (Figures 5 and 6). It seems likely that these relationships result from the systematic changes in the sensitivity versus half plate voltage curves as a function of pressure; essentially, the curves in the top panels of Figures 5 and 6 mirror the shape of the curve as the maximum sensitivity “peak” migrates to higher voltage at lower pressures (shown as a function of half plate voltage in Figure 3).

[19] In contrast, Ar isotope discrimination is largely independent of spectrometer pressure.

This behavior is expected for two similarly shaped sensitivity versus half plate voltage curves (i.e., ^{36}Ar and ^{40}Ar) that vary only in position and not in shape; at any given pressure, the difference between ^{36}Ar and ^{40}Ar sensitivity is constant. However, this pattern does not apply to He isotope discrimination, where it appears that there is a step function at a spectrometer pressure of between 4 and 8×10^{-9} torr. This step function is due to the different shapes of the ^3He and ^4He curves as a function of half plate voltage (Figure 3). Helium isotope discrimination is also known to vary over time in the Caltech MAP 215-50 (independent of tuning), increasing with the age of the source filament, suggesting that the curves in Figure 3 change as the shape of the ion cloud within the

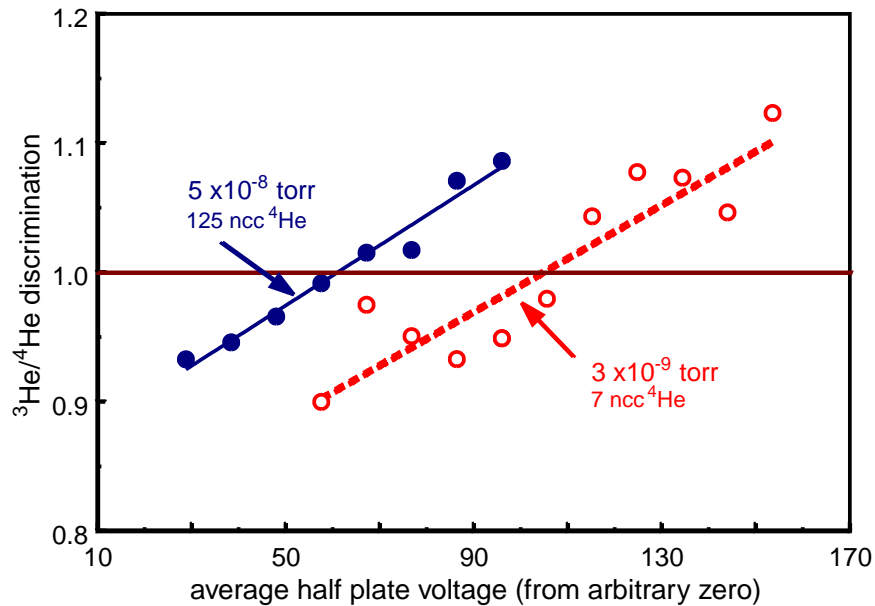


Figure 4. He isotope discrimination as a function of half plate voltage at different pressures (half plate voltage reported as in Figure 2). Because of the differences in the ³He and ⁴He sensitivity versus half plate voltage curves, discrimination progressively increases with increasing half plate voltage. The discrimination changes dramatically at half plate voltages greater than approximately +10 V relative to the maximum signal (not shown). As a result, the correlation between discrimination and half plate voltage does not continue to higher voltages than shown here. For a given pressure of He in the spectrometer, it is possible to set the half plate voltage such that there is constant discrimination irrespective of pressure, although this will be at the penalty of a slight (~5%) reduction in sensitivity.

source changes because of the progressively deforming filament.

2.4.1. Recommendations

[20] These pressure-dependent variations in sensitivity likely result from space-charge effects in the source: all other source parameters were held constant during the experiments; therefore these variations cannot be due to (for example) changes in mass discrimination induced by the source magnets. Therefore reducing space charge in the source could potentially reduce some of these effects. However, reducing the source space charge usually involves decreasing the intensity of the electron beam (for example, by reducing the fila-

ment emission or tuning the source magnets for minimum emission), with an accompanying reduction in sensitivity; it is likely that pressure effects in sources running at lower trap current (for example, mass spectrometers optimized for analyzing Ar isotopes frequently operate at ~50% of the trap current used here) will be less extreme than those described here. In this section we outline how noble gas mass spectrometers operating at high trap currents can be tuned to minimize pressure-dependent effects without significantly compromising sensitivity. Nevertheless, there are likely to be significant differences in each instrument's discrimination and sensitivity as a function of pressure, as well as temporal variations for the same instrument.

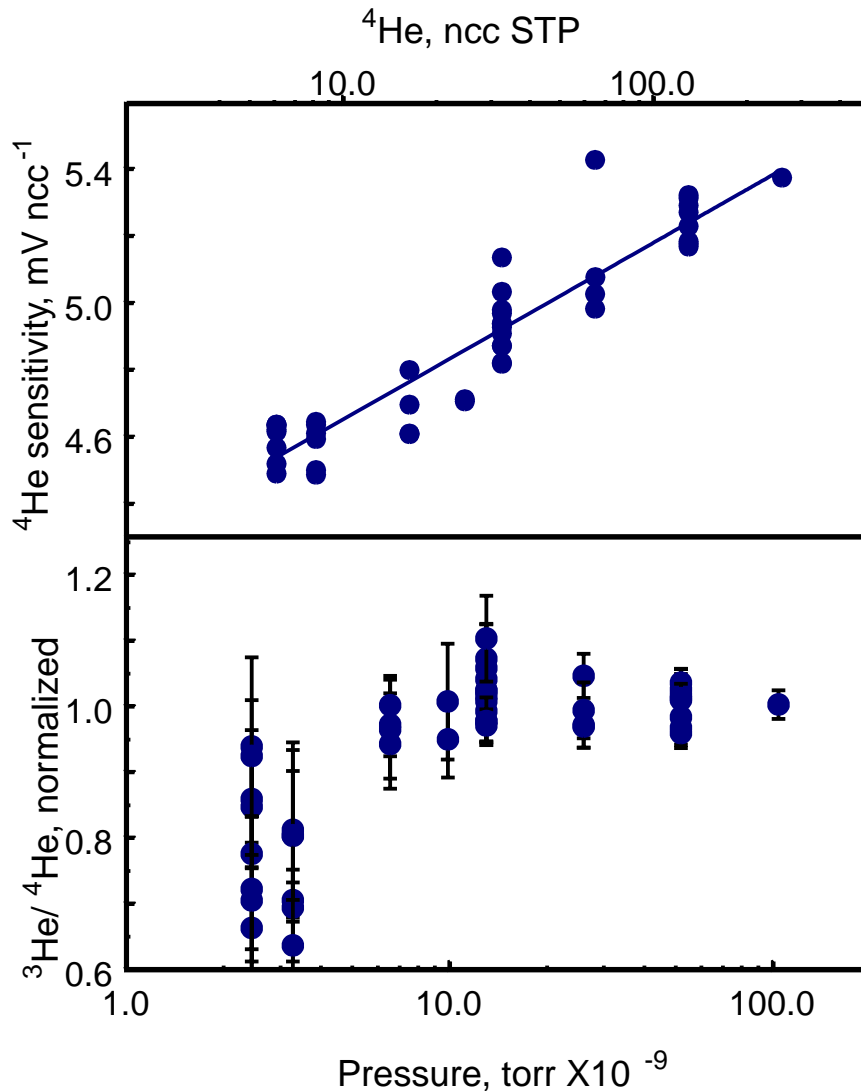


Figure 5. Repeated He calibrations using the modified air standard at differing pressures with fixed half plate voltages. (top) Helium sensitivity and (bottom) discrimination depend on spectrometer pressure. He sensitivity is approximately linear with the log of He pressure. He discrimination is approximately constant for pressures over $\sim 8 \times 10^{-9}$ torr, but there is an abrupt step at lower pressure such that ³He is ionized less efficiently than ⁴He. The variation in He sensitivity over this pressure range is $\sim 10\%$, which is typical for this instrument when well tuned; discrimination may be lower than that reported here, depending on filament age and on source tuning. Increased He isotope discrimination occurs with older filaments, irrespective of tuning. Note that sensitivity and discrimination are not measured at pressures higher than the “tune-up pressure” of 100×10^{-9} torr.

[21] The effects of pressure-dependent sensitivity and discrimination can be reduced by careful tuning. For example, maximizing signal by

tuning the half plate voltage and bias for every individual sample will reduce pressure-dependent sensitivity variations but could conceiva-

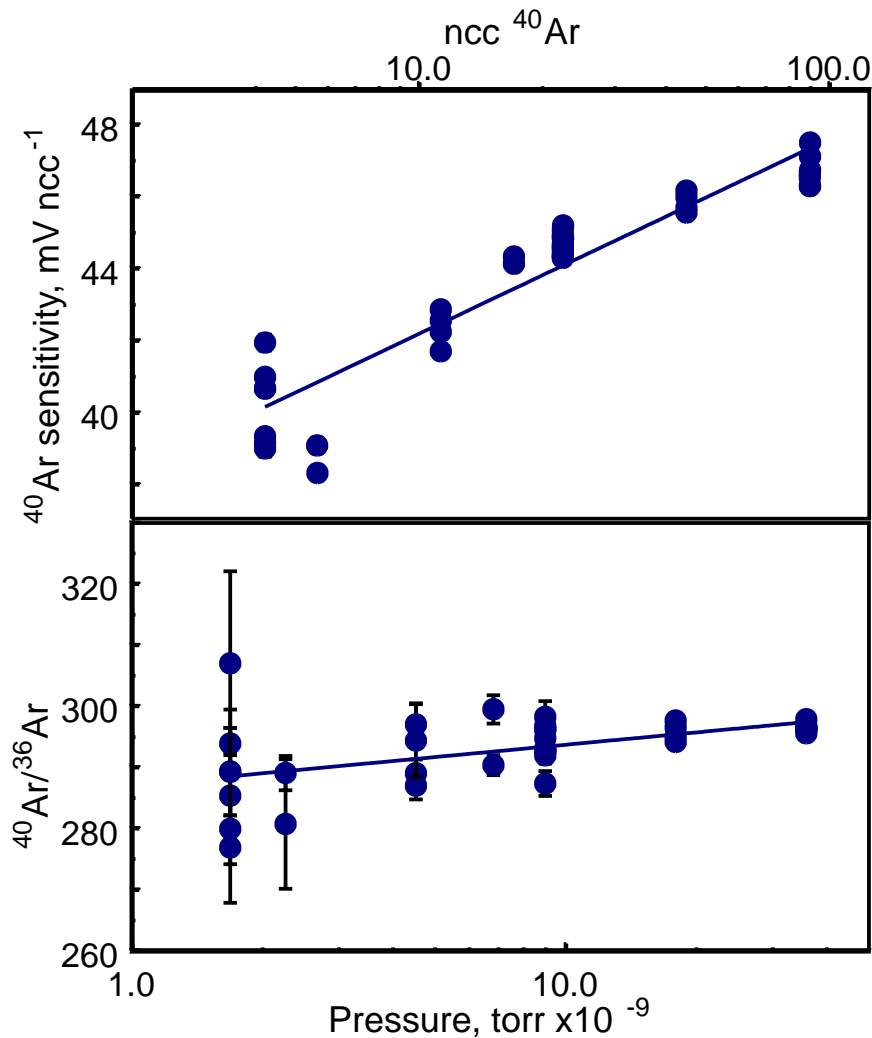


Figure 6. As for Figure 5 except for Ar. Different, but fixed, half plate voltage and bias are used to analyze Ar from those used for He calibrations. Ar sensitivity is a linear function of the log of the spectrometer pressure, while the ⁴⁰Ar/³⁶Ar discrimination is apparently independent of pressure.

bly increase pressure-dependent discrimination. Rather than tuning half plate voltages for maximum sensitivity, it is possible to tune these for constant discrimination for a given pressure of gas in the spectrometer. For example, constant discrimination over the range 5×10^{-8} to 3×10^{-9} torr can be achieved by adjusting half plate voltage between 60 and 110 V (relative; see Figure 4) for each sample.

[22] Increasing pressure in the spectrometer results in steep sensitivity versus half plate voltage curves (Figure 3). At these pressures, minor shifts in the position of maximum sensitivity as a function of half plate voltage, particularly to lower half plate voltages, will result in dramatic changes in sensitivity, yet high pressures will result in a shift to lower half plate voltage, increasing the probability of

missing the region of maximum sensitivity. Consider the following scenario. A spectrometer is tuned for maximum sensitivity on 50 ncc of ^4He . This would result in a half plate voltage of ~ 100 V (on the scale in Figures 2, 3, and 4). A sample of 125 ncc ^4He is then analyzed. Because of the increased pressure in the spectrometer, the position of the half plate maximum will have shifted to ~ 75 V (on the same scale). Analyzing this sample at 100 V on the half plate (the previous best tune) results in a loss in sensitivity of $\sim 35\%$; analyzing a 250 ncc sample would result in $>90\%$ loss in sensitivity! The same principle applies whenever the spectrometer pressure during sample analysis exceeds the pressure at which the source was tuned, irrespective of whether the high pressure is due to inadequate gas separation or cleanup, or simply due to large samples.

[23] Therefore the spectrometer should always be tuned at the maximum possible pressure; measurements at higher pressures should be avoided. The same arguments apply to Ar tuning and measurement of Ar isotopes and abundances. We have not investigated the effects of source magnets or repeller plate on the source performance; the source magnet positions were adjusted to minimize filament emission (while holding trap current constant) in order to extend the filament lifetime. It may be possible to reduce pressure dependency of Nier-type source sensitivity and/or discrimination by suitable source magnet or repeller plate tuning, as these have a significant effect on space charge distribution in the source. Experiments on Ne sensitivity and discrimination

as a function of spectrometer pressure will be performed in the near future. The effects of pressure-dependent Ne sensitivity and discrimination need to be deconvolved from the effects of pressure on isobaric interferences on ^{20}Ne and ^{22}Ne .

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