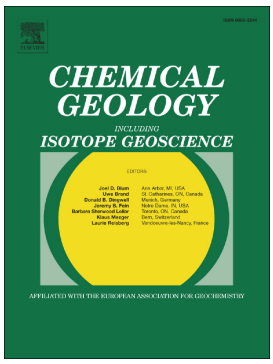

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Minimisation of pressure dependent mass discrimination in the ion source of the Helix MC *Plus* noble gas mass spectrometer

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Abstract

When tuned for maximum sensitivity, the electron bombardment ion source on the ANU (the Australian National University) Helix MC *Plus* noble gas mass spectrometer produces an Ar ion beam that is mass discriminated as a function of Ar partial pressure. This effect can be reduced substantially or eliminated by adjusting the repeller and trap voltages, although with a sensitivity loss of up to 50%. A recommended procedure for tuning an ion source to reduce pressure dependent mass discrimination is described. Similar procedures can be applied to other noble gases and other ion sources to ensure that pressure dependent mass discrimination is avoided.

Keywords: noble gas, Helix MC *Plus*, repeller, mass discrimination, pressure dependence

1. Introduction

The Helix MC *Plus* is a new generation, high mass resolution, multi-collector noble gas mass spectrometer manufactured by ThermoFisher Scientific. The high mass resolution (> 1,800) and mass resolving power (> 8,000) of this mass spectrometer are revolutionising research in the fields of noble gas cosmo-geochemistry and Ar geochronology (Honda et al., 2015; Caracausi et al., 2016; Phillips et al., 2017). The ^{21}Ne abundance in the atmosphere, for example, has now been determined much more accurately because ^{21}Ne could be measured free from the isobaric interference from ^{20}Ne^{1}H (Honda et al., 2015).

The Helix MC *Plus* achieves its high mass resolution using a newly designed ion source that is a modification of a Nier-type electron bombardment source (Nier, 1947). It has variable accelerating voltage (up to 9.9 kV) and a double focusing lens system (see On-Line

Resource 1 in Zhang et al., 2016). The Helix-MC *Plus* is relatively new to the market, and its performance is still being explored (Honda et al. 2015; Zhang et al. 2016).

To obtain reliable measurements of noble gas elemental and isotopic abundances in a geological sample it is essential that the mass discrimination (instrument-induced isotope fractionation) of the mass spectrometer remains constant over the working range of noble gas partial pressures. It is known, however, that there are pressure-dependent variations in sensitivity and mass discrimination, particularly for He, in conventional noble gas mass spectrometers such as the VG5400 (Honda et al., 1993), MAP 215-50 (Burnard and Farley, 2000) and GVI Helix SFT (Mabry et al., 2012). Further, it is known by the noble gas community that changing the repeller plate voltage (see, for example, Honda and Chivas, 2016) on a Nier-type source causes a large change in mass discrimination. The question is whether the Helix MC *Plus* shows some of the same effects. The short answer is yes. Here we discuss a practical approach to ensuring that those effects are minimised, and potentially eliminated.

2. Experiments

The isotopic composition of atmospheric Ar was measured on the Helix MC *Plus* at the Australian National University under a range of operating conditions to test the effects of different parameters on Ar mass discrimination. The gas used for the experiments was atmospheric Ar stored in the small Heavy Gas Pipette on the Helix MC *Plus* gas handling system (Online Resource 7 in Zhang et al., 2016). The small Heavy Gas Pipette contains a purified air standard which was further purified by two SAES C50 and two SAES NP10 getters prior to admission to the mass spectrometer for analyses. Ar was not separated from other noble gases. The amount of gas in the pipette was well-calibrated, one aliquot of the

standard containing 1.2×10^{-7} cc STP of ^{40}Ar, with atmospheric isotopic composition. The volume of each section of the gas handling system also was accurately determined.

Different fractions of atmospheric Ar were prepared to determine the pressure effect on Ar mass discrimination. The Ar partial pressure in the mass spectrometer during the Ar analyses was calculated based on the volumes of the gas handling system and the mass spectrometer. Vacuum valves separating individual sections of the gas handling system were tested for throughput leaks—no leaks were detected. Ar procedural blanks were negligible relative to the amounts of sample Ar introduced. Atmospheric ^{36}Ar, ^{38}Ar and ^{40}Ar were analysed using the L2 CDD (Compact Discrete Dynode Multiplier), Ax CDD and H2 Faraday (with 10^{12} Ω resistor) high resolution collectors, respectively, all with 300 μm collector slits. The source slit was set to either 100 or 250 μm.

Two source assemblies (Ion Source #22 and #27) were used in the experiments. They are identical ion sources manufactured by Thermo Fisher Scientific. Most of the data presented here are from Ion Source #22, but similar results were obtained using Ion Source #27. This suggests that the pressure dependent mass discrimination found in the

Group	Source parameter	
Ionisation chamber	Accelerating High Voltage	9.9 KV
	Trap Current	170.0 μA
	Trap Voltage	19.7 V
	Ion Repeller Voltage	-5.0 V
	Electron Energy	114.0 eV
Lens system for ion steering and focussing	Extraction Lens	36.4 %
	Horizontal Symmetry	37.1 %
	Extraction Focus	9.5 %
	Extraction Symmetry	18.9 %
Lens system for shaping ion beam	Flatapole	-9.0 V
	Rotation Quad	-6.0 %
	Vertical Deflection North	54.5 V
	Vertical Deflection South	72.6 V

Table 1. Parameters of the ion source of the Helix MC *Plus* with optimised settings for Ar sensitivity.

current study could be a behaviour common to all ion sources supplied with the Helix MC *Plus* mass spectrometers.

3. Optimisation of the ion source for sensitivity

There are 13 parameters that control the operating conditions of the Helix MC *Plus* ion source (Table 1). For the first experiment, having fixed the accelerating voltage at 9.9 kV and trap current at 170 μA, we optimised the other source parameters for maximum Ar sensitivity, and they are summarised in Table 1. Using Ion Source #27 with a source slit width of 250 μm and a trap current of 170 μA, the maximum Ar sensitivity achieved was 0.87×10^{-3} A/Torr. We then maximised Ar sensitivity for a range of trap currents, optimising the other source parameters for each. Overall, there is a linear relationship between trap current and Ar sensitivity over the range 130 to 300 μA (Fig. 1).

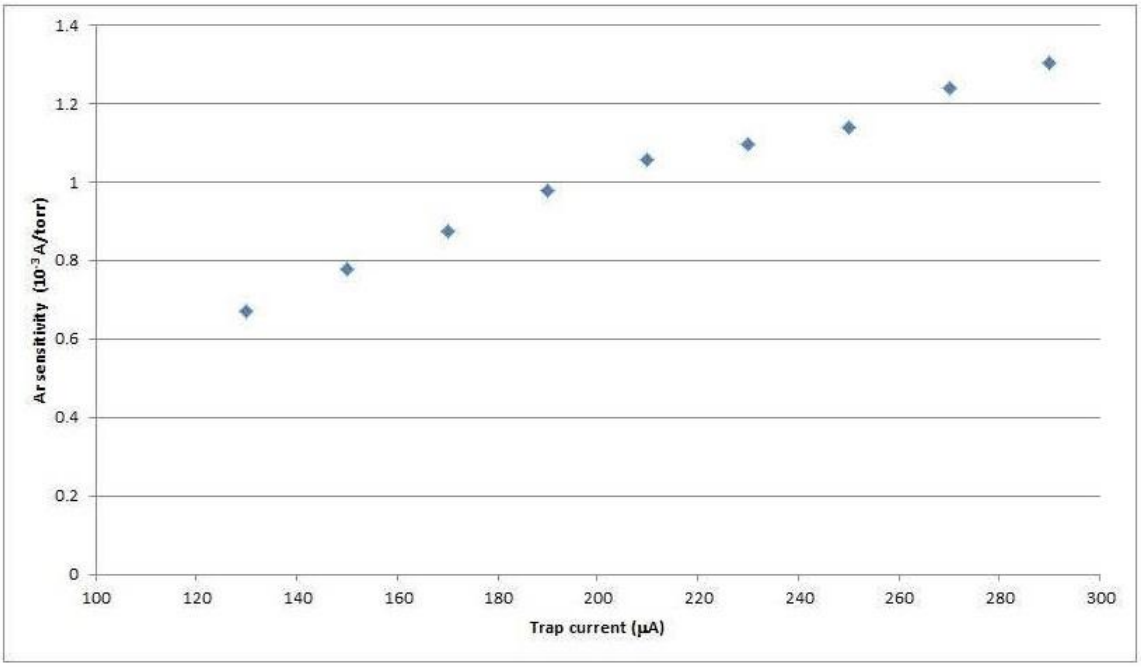

Fig.1. Ar sensitivities versus trap currents. Ion Source #27 with source slit width of 0.25 mm was used.

4. Pressure dependent Ar mass discrimination

Figure 2 shows the Ar mass discrimination as a function of Ar partial pressure over the range 0.2 to 1.3 x 10^{-8} Torr, corresponding to ^{40}Ar beam sizes ranging from 1.4 to 7.5 pA, respectively. The effect was similar, but not identical, in two separate experiments. The normalised ^{40}Ar/^{36}Ar ratio decreased by up to 12% as the partial pressure of Ar in the mass spectrometer increased.

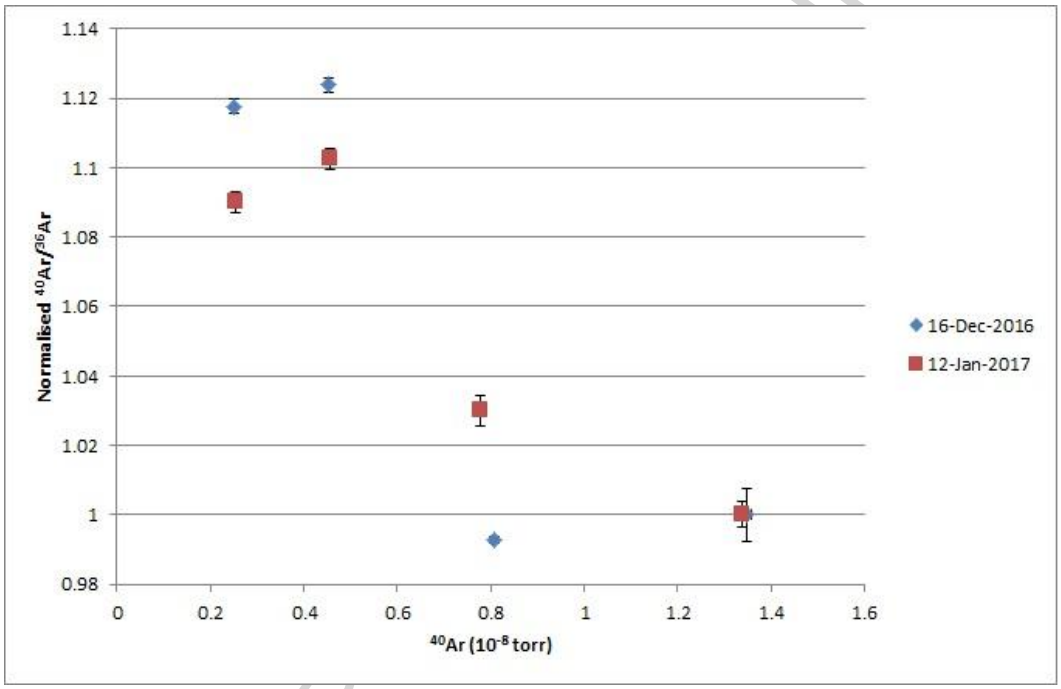

Fig.2. Atmospheric ^{40}Ar/^{36}Ar ratios measured with variable Ar partial pressures. The ion source settings were optimised for ^{40}Ar sensitivity using a full shot from one aliquot of the Small Heavy Gas Pipette, with the corresponding Ar partial pressure in the mass spectrometer of 1.35 x 10^{-8} Torr. For the analyses of diluted Ar shots the same source settings as determined for the full shot (Table 1) were used. Data are normalised to ^{40}Ar/^{36}Ar ratio measured for the full shot. Two repeated analyses were taken, both using Ion Source #27, with 0.1 mm source slit width and 170 μA trap current.

5. Effect of the repeller voltage

If the pressure effect on mass discrimination is to be minimised or eliminated, it is necessary to tune the Helix-MC *Plus* ion source to a condition that does not necessarily

maximise Ar sensitivity. Of the 13 source parameters listed in Table 1, those having the strongest influence on pressure dependent mass discrimination are electron energy, repeller voltage and trap voltage.

Zhang et al. (2016) investigated Ar beam intensity as a function of ion source repeller voltage and electron energy (see their Fig. 2). We found the highest beam intensities at electron energies over 120 eV and the second highest at about 80 eV. At higher electron energies the secondary electrons emitted from Ar atoms as they are ionised are able to ionise other Ar atoms, increasing total ion production. The efficiency of this process is probably a function of the Ar pressure in the ionisation chamber. To avoid the potential complexity of secondary electron ionisation, a lower electron energy of 80 eV was used in the experiments on the pressure effects on mass discrimination. Conventional noble gas mass spectrometers (e.g. the VG5400) use a fixed trap voltage of 20 V. This same voltage was used as a starting point in the search for source parameters that minimised pressure effects, but it was reduced to 18.4 V for the experiments in the present study.

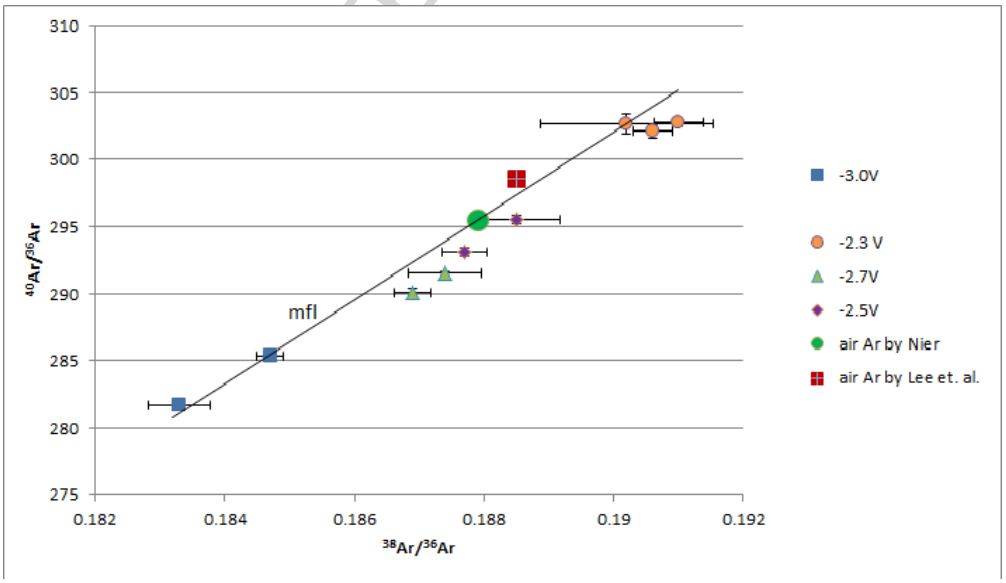

Fig. 3: Argon isotope plot ($^{40}Ar/^{36}Ar$ vs. $^{38}Ar/^{36}Ar$) for atmospheric Ar, with variable repeller voltages, as shown in the legend of the diagram. For comparison, atmospheric Ar isotope compositions determined by Nier (1950) and Lee et al. (2006), as well as an isotope fractionation line (mfl), are plotted. Source settings used for Ion Source #22 were 0.1 mm source slit width, 170 µA trap, 80 eV electron energy, and 18.4 V trap voltage. A range of Ar partial pressures for the analyses is indicated in Figure 4.

Figure 3 and Table 2 show the isotopic composition of atmospheric Ar measured over a range of repeller voltages from -2.3 to -3.0 V relative to the ionisation chamber. For a change of only 0.7 V in repeller voltage, the Ar isotopic composition changed by ~ 1.75% / AMU along a mass dependent fractionation line that passes through the reference composition of air Ar (Nier, 1950; Lee et al., 2006).

Repeller voltage (V)	Fraction	^{36}Ar (fA)	1σ	$^{40}Ar/^{36}Ar$	1σ	$^{38}Ar/^{36}Ar$	1σ
-3.0	100%	14.93	0.019	285.32	0.370916	0.1847	0.000314
-3.0	32%	4.83	0.004	281.7	0.22536	0.1833	0.000367
-2.7	100%	14	0.013	290.1	0.26109	0.1869	0.00028
-2.7	32%	4.49	0.003	291.51	0.174906	0.1874	0.000562
-2.5	100%	12.98	0.016	293.12	0.29312	0.1877	0.000357
-2.5	32%	4.17	0.004	295.53	0.29553	0.1885	0.000679
-2.3	100%	11.89	0.025	302.13	0.483408	0.1906	0.000305
-2.3	71%	8.44	0.011	302.76	0.333036	0.191	0.000382
-2.3	32%	3.85	0.011	302.69	0.756725	0.1902	0.001331
* Atmospheric Ar (Lee et.al. 2006)				298.6		0.1885	
* Atmospheric Ar (Nier 1950)				295.5		0.1879	

Table 2. Atmospheric Ar compositions measured with various settings of repeller voltages. Diluted fractions from one full aliquot of the standard pipette used for the analyses are listed in the table.

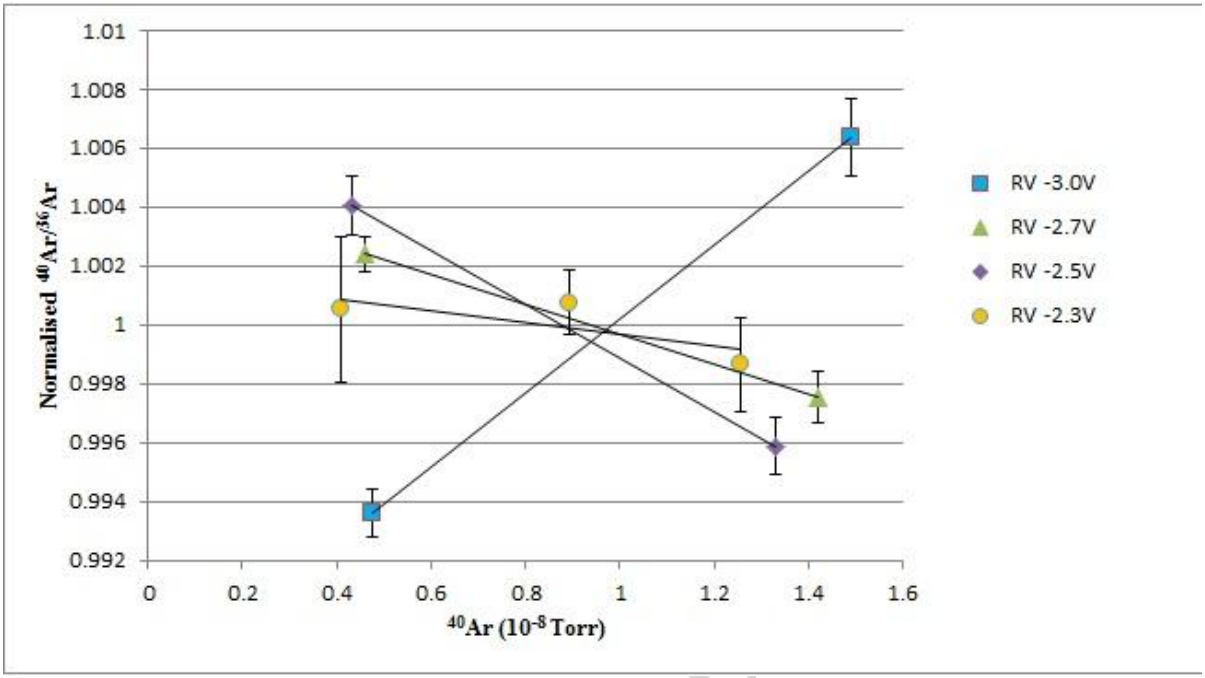

Fig.4: Normalised $^{40}Ar/^{36}Ar$ ratios versus ^{40}Ar partial pressures with different repeller voltage settings.

Group	Source parameter	
Ionization chamber	Accelerating High Voltage	9.9 KV
	Trap Current	170.0 µA
	Trap Voltage	18.4 V
	Ion Repeller Voltage	-2.3 V
	Electron Energy	80.0 eV
Lens system for ion steering and focussing	Extraction Lens	18.4 %
	Horizontal Symmetry	36.9 %
	Extraction Focus	9.9 %
	Extraction Symmetry	19.9 %
Lens system for shaping ion beam	Flatapole	-10.2 V
	Rotation Quad	-6.6 %
	Vertical Deflection North	54.5 V
	Vertical Deflection South	71.9 V

Table 3. The best optimised source parameters for constant mass discrimination on Ar isotopes independent from Ar partial pressure.

The effect of pressure as a function of repeller voltage is shown in Figure 4. At high repeller voltage (-3.0 V), the variation in normalised $^{40}Ar/^{36}Ar$ over an Ar partial pressure range of 0.4 – 1.5 x 10^{-8} Torr is about 1.2%. The pressure effect reverses and decreases at lower repeller voltage, becoming negligible (< 0.2%) at -2.3 V over the same pressure range. This is the optimised operating condition of the ion source under which the isotopic composition of Ar can be measured accurately and reliably, free from the Ar partial pressure effect.

Table 3 summarises the optimised source parameters for constant mass discrimination in Ar isotopic analyses at a trap current of 170 μA and 9.9 kV accelerating voltage. Operating with these parameters both ion source assemblies (#22 and #27) produced essentially constant Ar isotope mass discrimination over the wide range of Ar partial pressures from 0.2 to 1.3 × 10^{-8} Torr (Fig. 5). The variation in $^{40}Ar/^{36}Ar$ over the range of Ar partial pressure for the two sources is less than 0.2%. Such high accuracy is ideal when Ar isotope data obtained by a Helix MC *Plus* are applied to tackling various problems in the fields of earth and planetary sciences.

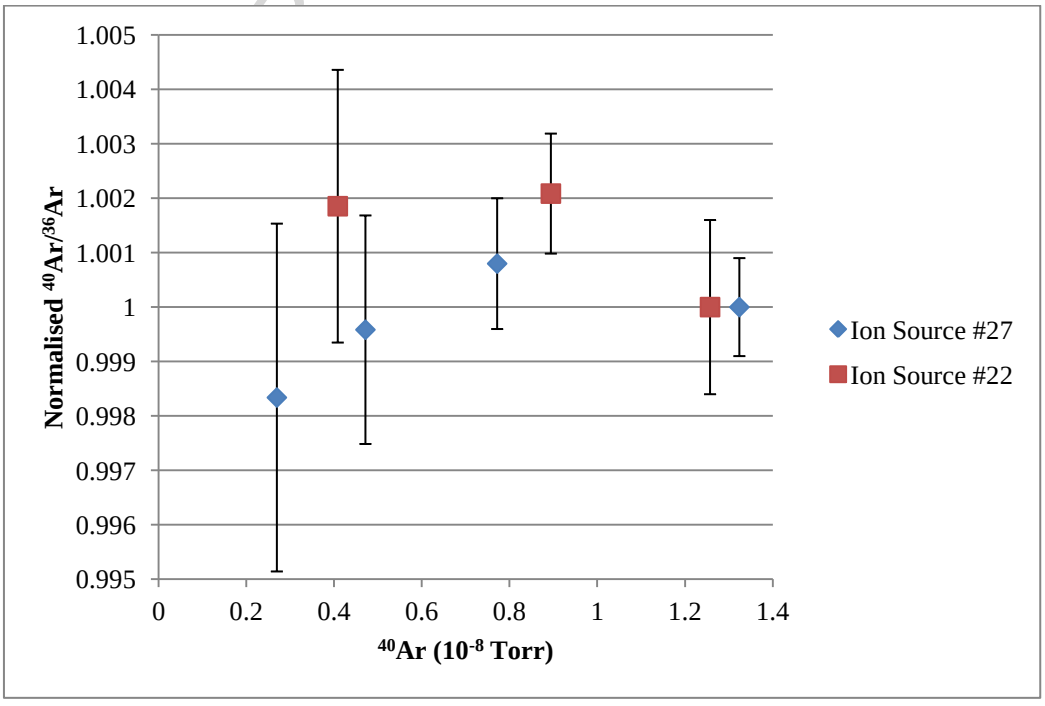

Fig. 5: $^{40}Ar/^{36}Ar$ ratios, normalised to the ratios measured for the highest Ar partial pressures, for variable Ar partial pressures (the same optimised source parameters as listed in Table 3 were used.)

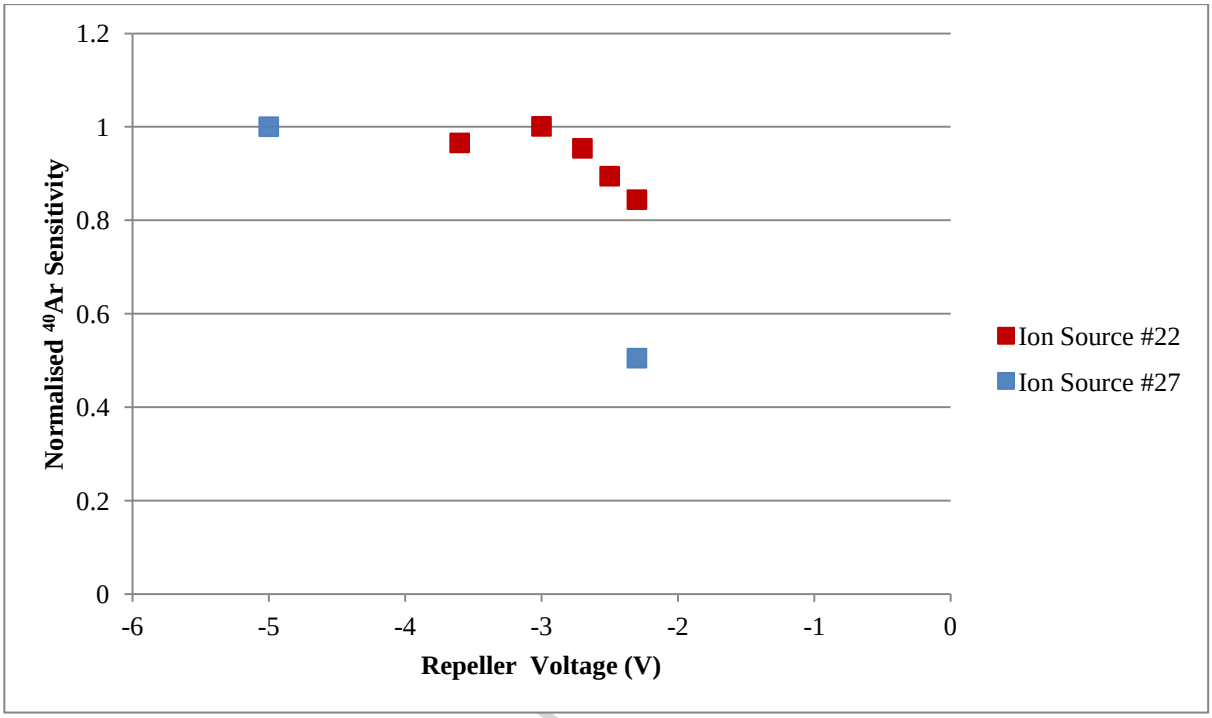

Fig. 6: Ar sensitivity versus repeller voltage. Source settings used were 0.1 mm source slit width, 170 μA trap, 80 eV electron energy, and 18.4 V trap voltage. The sensitivities are normalised to the maximum sensitivity for each data set.

A repeller voltage of -2.3 V does not give maximum Ar sensitivity (Fig. 6). In fact, for Ion Source #27, the sensitivity for a repeller voltage of -2.3 V is about half the maximum Ar sensitivity achievable at a repeller voltage of -5.0 V (Table 1). Although it would be desirable to maximise sensitivity and thereby reduce analytical uncertainties, sacrificing sensitivity to improve accuracy by eliminating the pressure effect provides the greater benefit. Ion Source #22 performed significantly better, Ar sensitivity at a repeller voltage of -2.3 V being only 20% less than the maximum achievable at higher voltage.

6. Effect of the trap voltage

Trap voltage is another important parameter in minimising the pressure effect on Ar mass discrimination. At a trap voltage of 5.0 V the variation in measured $^{40}Ar/^{36}Ar$ was nearly 4% over a ^{40}Ar partial pressure range of 1.3×10^{-8} to 2.6×10^{-8} Torr (Fig. 7). At a trap voltage of 18.4 V the pressure effect was negligible. The other source parameters were the same as those listed in Table 3.

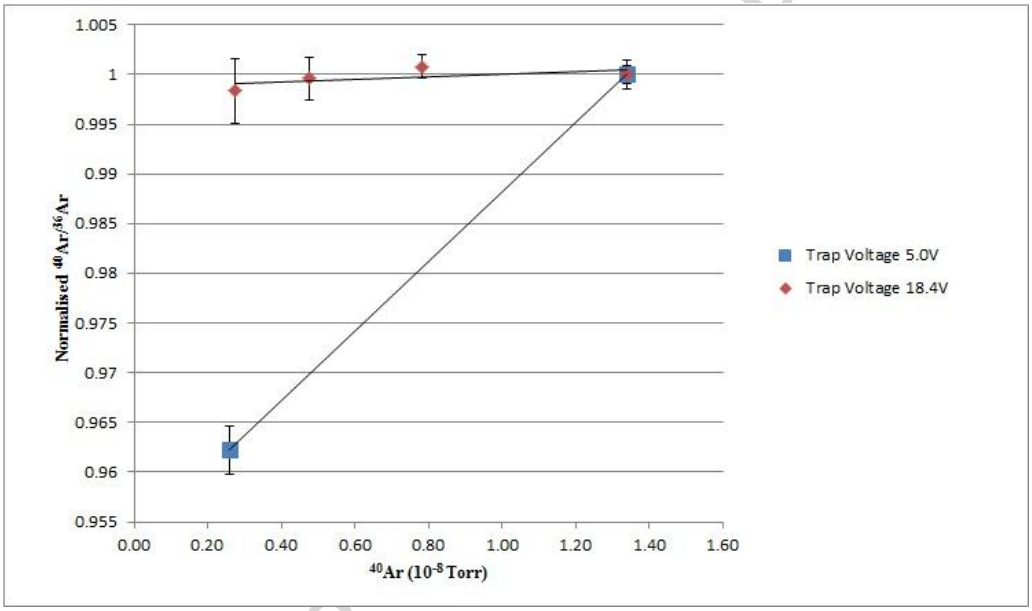

Fig. 7 Comparison of atmospheric $^{40}Ar/^{36}Ar$ ratios measured with 5.0V and 18.4V trap voltages at various partial pressures.

7. Discussion

To our knowledge, with a few exceptions, the effect of repeller voltage on sensitivity and mass discrimination in noble gas analyses has not been closely investigated either theoretically or experimentally. Using ray tracing, Wallington (1970) calculated that a conventional Nier-type ion source would produce maximum ion beam intensity at a repeller voltage of +18 V relative to the ionisation chamber, with a secondary maximum at -3 V.

Werner (1974) studied the effects of the repeller when it was set to positive voltages with respect to the ionisation chamber. In that case, the repeller voltage directs positive ions back to an exit slit in the ionisation chamber and/or neutralises the effect of negative space charge and focuses the ions onto the exit slit. More recently Mabry et al. (2012) studied the effect of repeller voltage on He sensitivity and peak shape, finding a correlation between repeller voltage, maximum sensitivity and best focus.

The repeller voltage used in noble gas mass spectrometers is generally set to negative with respect to the ionisation chamber. In that case, the repeller plate would neither repel positive ions out of the ionisation chamber (as suggested by the name of the electrode), nor neutralise the effect of negative space charge. Instead, changing the repeller voltage might change the shape of the ionising electron beam inside the ionisation chamber, causing it to curve, for example, thereby changing the position of the ionisation region in relation to the ion extraction system.

Burnard and Farley (2000) reported pressure-dependent mass discrimination of He in Nier-type noble gas ion sources. They pointed out that it might be possible to reduce the pressure effect by suitable tuning of the repeller, but did not investigate this option in practice. Mabry et al. (2013) reported a pressure effect on the $^{3}He/^{4}He$ ratio in the ThermoFisher Helix SFT mass spectrometer, showing a change of about 13% in the ratio for a 20-fold increase in ^{4}He sensitivity. A pressure effect on He mass discrimination has also been observed on the ThermoFisher Helix SFT mass spectrometer at IAEA (International Atomic Energy Agency), Vienna, and could be minimised by setting the repeller voltage to about -2.3 V, similar to the recommended value found for Ar in the present study (T. Matsumoto, *pers. com.*).

The physical processes responsible for the pressure effect on mass discrimination in these ion sources remains to be identified. Possibly the effect of pressure on the ionisation of

different isotopes (e.g., ^{36}Ar or ^{40}Ar) differs due to electron exchange between the isotopes of interest and other residual elements. This would depend on the partial pressure of the isotope in question, as well as the total gas pressure in the ionisation chamber. Alternatively, the repeller voltage might favour the focus of the ion beam of one isotope relative to another of the same element. Optimising the repeller voltage to remove the pressure effect on mass discrimination might achieve a balance between the mass discriminations of the different isotopes of interest.

8. Conclusion

The experimental data reported here demonstrate that it is possible to minimise pressure dependent mass discrimination in the Helix MC *Plus* ion source by selecting appropriate repeller and trap voltages. The recommended optimisation procedure is as follows:

1. With the sample pressure at the higher end of the range of interest, using 80 eV electron energy, 20 V trap voltage and -2.3 V repeller voltage, maximise the sensitivity by adjusting the remaining parameters of the lens system, and determine the mass discrimination.
2. Repeat the tuning procedure and measurement with the sample pressure at the lower end of the range of interest. If the isotope ratios are pressure dependent, change the repeller voltage by 0.1 to 0.2 V and repeat the measurement of isotope ratios at both ends of the sample pressure range.
3. Keep adjusting the repeller voltage incrementally until the measured isotope ratios show no pressure dependence. Perform more measurements of isotope ratios within the sample pressure range of interest to confirm the pressure independency of mass

discrimination. The repeller voltage determined in this way can be used for accurate isotope ratio analyses.

In summary, this work focuses on an investigation of the effect of repeller voltage on Ar mass discrimination. It demonstrates that, for Ar isotope analyses, the source conditions optimised for maximum sensitivity on the Helix MC *Plus* mass spectrometer are different from those which minimise the effect of Ar partial pressure on mass discrimination. Adjusting for minimum pressure dependence involves a sensitivity sacrifice of up to 50%. The optimised source parameters reported here are likely to be applicable to other Helix MC *Plus* mass spectrometers—both ion source assemblies tested yielded similar results. It is likely, however, that different ion source settings will be required to minimise pressure-dependent mass discrimination for different noble gases. It has already been found, for example, that the best repeller voltage for Ne is slightly different from that for Ar (Honda et al., 2015; Zhang et al. 2016).

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