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RESEARCH ARTICLE

Performance of the High Resolution, Multi-collector Helix MC *Plus* Noble Gas Mass Spectrometer at the Australian National University

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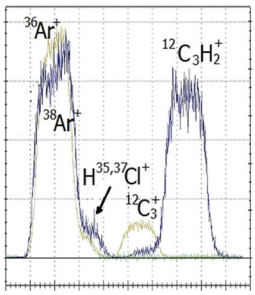

Abstract. Performance of the Helix MC *Plus* noble gas mass spectrometer installed at the Australian National University (ANU) is reported. Results for sensitivity, mass discrimination and their linearity against partial pressure of noble gases, and mass resolution of the mass spectrometer are presented, and the results are compared with those of conventional noble gas mass spectrometers. The application of the five detectors on the Helix MC *Plus* in measuring various noble gas isotopes in multi-collector modes and the integration of the software drivers of peripheral hardware devices into the controlling program Qtegra of the mass spectrometer are discussed. High mass resolution (>1800) and mass resolving power (>8000) make this mass spectrometer unique in noble gas cosmo-geochemistry. It provides the capability to measure isobaric interference-free noble gas isotopes in multi-collector mode, significantly improves the accuracy to determine isotopic ratios, and greatly increases the efficiency of data acquisition.

Keywords: Noble gas isotope, Geochemistry, Multi-collector, Mass resolution, Mass resolving power

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Introduction

The Helix-MC *Plus* noble gas mass spectrometer manufactured by Thermo Fisher Scientific is a 350 mm sector, 120° extended geometry, high resolution, multi-collector mass spectrometer for the simultaneous acquisition of data of noble gas isotopes, which provides substantial benefits in analytical precision and shortens the time of analysis. This paper presents details of commissioning the Helix MC *Plus* installed at the Australian National University (ANU), and reports its performance in terms of mass resolution, sensitivity, linearity, and mass discrimination.

The first production Helix MC *Plus* was installed in the Research School of Earth Sciences at the ANU in March 2013. The detector array of this mass spectrometer includes a fixed axial (Ax) detector, two adjustable high mass (H1 and H2) detectors, and two adjustable low mass (L1 and L2) detectors. Each detector is equipped with a Faraday/ion counting multiplier CFM (Combined Faraday and CDD (Compact Discrete Diode) Multiplier) collector. The Helix MC *Plus* installed at the ANU is unique in that it is equipped with three high resolution collectors with 0.3 mm collector slits: the axial (Ax), the high mass (H2), and the low mass (L2) detectors. In contrast, the H1 and L1 detectors are equipped with low mass resolution collector slits of 0.6 mm. In this work, the mass resolution is defined as m/Δm, where m is the mass of a peak and Δm is the width of the peak at 5% of its peak height. The high mass resolution collectors have a specified mass resolution of 1500 but routinely give in excess of 1800. A specified mass resolving power is 5000 but routinely in excess of 8000 can be achieved. Here, the mass resolving power is defined as m/Δm, where m is the mass of a peak and Δm is the mass difference at 95% and at 5% of the maximum peak height. The H1 and L1 detectors have a specified mass resolution of 1200 and a specified mass resolving power in excess of 6000. In addition, the L2 Faraday detector is equipped with a 1×10^{13} Ω amplifier with a noise level less than 5×10^{-18} A, whereas the other Faraday detectors are equipped with the 1×10^{12} Ω amplifiers. Figure 1 shows a comparison of noise levels from the 1×10^{13} Ω amplifier, the 1×10^{12} Ω amplifier, and a secondary electron multiplier.

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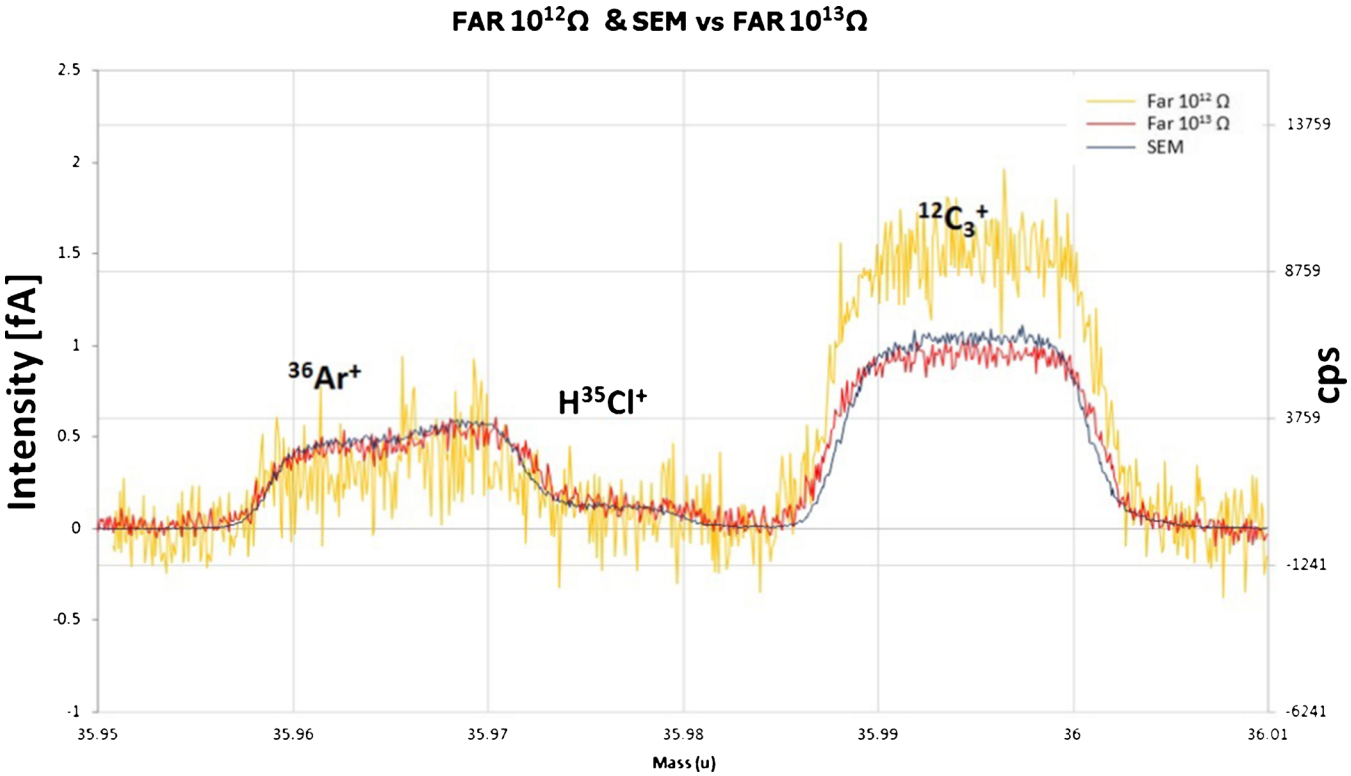

Figure 1. A comparison of noise levels from the 1×10^{13} Ω amplifier, the 1×10^{12} Ω amplifier, and the SEM detector. Beam intensity (fA) and the corresponding count rate (cps) measured by the three detectors are indicated on both sides of the Y axis

In order to achieve the desired high mass resolution capability, Thermo Fisher Scientific designed a new ion source with a variable accelerating voltage between 2 and 9.9 kV, in contrast to the typical 4.5 kV accelerating voltage of conventional noble gas mass spectrometers, such as VG5400. In addition, this ion source has a double lens system for beam

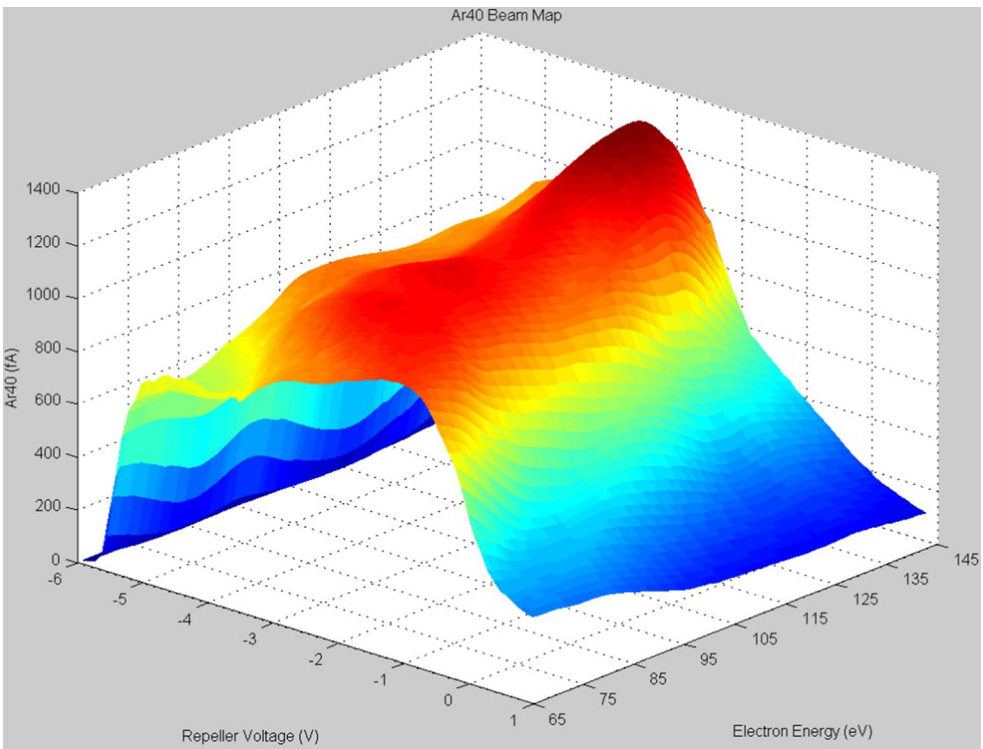

Figure 2. ^{40}Ar beam intensity map as a function of repeller voltage and electron energy

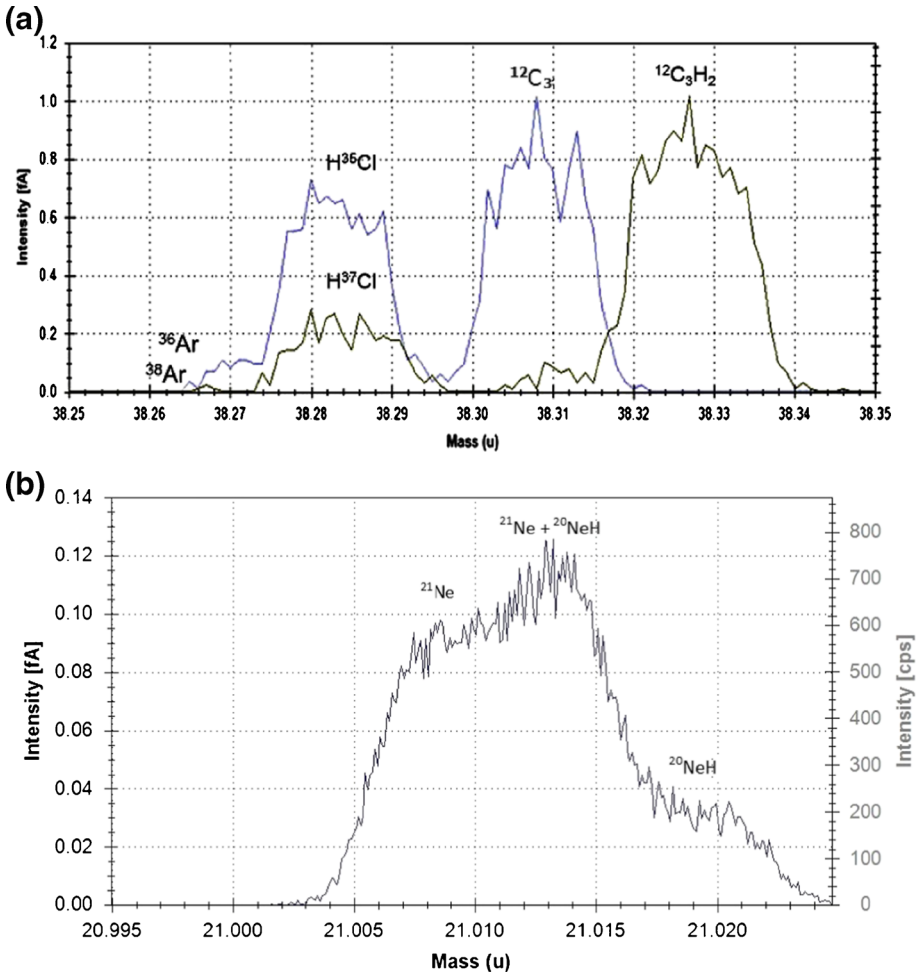

Figure 3. (**a**) Partial separations of the ^{36}Ar peak and ^{38}Ar from the $H^{35}Cl$ and $H^{37}Cl$ interference peaks, respectively; (**b**) partial separation of the ^{21}Ne peak from the ^{20}NeH peak

steering and focussing. The mass spectrometer is also equipped with Multipole and Flatapole lenses for shaping the ion beam. These new features contribute to high mass resolution and high mass resolving power of the Helix MC *Plus*. A schematic of the ion source is shown in On-line Resource 1.

Experimental

The Helix MC *Plus* at the ANU is equipped with an on-line noble gas extraction and purification system under ultrahigh vacuum with a base pressure of better than 1×10^{-7} Pa. The gas handling system consists of (1) a resistively-heated, double-vacuum, tantalum furnace (max. 2000 °C), (2) an air actuated vacuum crusher, (3) a Photon-Machines Fusion 970 diode laser heating system, (4) a Janis He cryogenic trap assembly (10 to 475 K), (5) a quadrupole gas analyser (Stanford Research Systems SRS100), (6) a gas purification system with SAES NP10, SAES C50, and Ti bulk getters, (7) standard gas pipette tanks, and (8) Nupro pneumatic valves.

This hardware is automated and controlled using computer serial ports and RS-232 protocol. We have integrated the

Table 1. Cup Assignments for Kr Measurements (Positions Relative to the Center of the Ax Faraday Cup)

Detector	L2 CDD (–30.488 mm)	L1 CDD (–16.936 mm)	AX CDD (0.6 mm)	H1 CDD (17.204 mm)	H2 CDD (32.401 mm)
Method 1	^{78}Kr	^{80}Kr	^{82}Kr	^{84}Kr	^{86}Kr
Method 2			^{83}Kr		

Table 2. Cup Assignments for Xe Measurements (Positions Relative to the Center of the Ax Faraday Cup)

Detector	L2 CDD (–27.029 mm)	L1 CDD (–8.155 mm)	Ax CDD (0.6 mm)	H1 CDD (10.318 mm)	H2 CDD (24.645 mm)
Method 1	^{126}Xe	^{130}Xe	^{132}Xe	^{134}Xe	
Method 2	^{124}Xe	^{128}Xe	^{130}Xe	^{132}Xe	
Method 3		^{129}Xe	^{131}Xe		^{136}Xe

associated software drivers into the Qtegra platform of Thermo Fisher Scientific, which controls both the mass spectrometer and auxiliary devices via scripts written in C#. On-line Resource 7 shows the control panel of our gas handling system in Qtegra.

The noble gas standards used for this study are the Heavy Gas standard and the HESJ helium standard [1]. The Heavy Gas standard was prepared in the noble gas laboratory at ANU from a clean air sample collected from the Canberra Airport. One aliquot of the Heavy Gas standard contains 1.2×10^{-6} cc STP of ^{40}Ar and 2.1×10^{-9} cc STP of ^{20}Ne with atmospheric noble gas abundances. One aliquot of the HESJ helium standard delivers 3.9×10^{-7} cc STP of ^{4}He isotope with a $^{3}He/^{4}He$ ratio of 2.9×10^{-5} [1]. For He measurements, a full shot of the HESJ standard was used. For Ne measurements, a full shot of the air standard was used, with LN_2 charcoal traps or the Janis cryogenic trap running to adsorb the heavier noble gases and other gases such as CO_2 and water. For Ar, a 10% split of a full shot of the Heavy Gas standard was used in order to keep the ^{40}Ar beam intensity less than 5×10^{-11} A (or 50,000 fA). For Kr and Xe, the Janis cryogenic trap was used to separate the lighter noble gases, with desorption temperatures for Kr and Xe being 220 and 340 K, respectively. One aliquot of our Heavy Gas standard contains 8.3×10^{-11} cc STP of ^{84}Kr and 3.0×10^{-12} cc STP of ^{132}Xe.

To test the effect of pressure on noble gas isotope discrimination, variable fractions of the standards were prepared. Four different fractions over a wide range of partial pressures were used to check the linearity of the isotope ratios.

To optimise the performance of the ion source, we developed a C# program to produce beam intensity maps as a function of various source parameters. A $^{40}Ar^{+}$ beam intensity map as a function of repeller voltage and electron energy is shown in Figure 2. An intensity plateau is observed around –2.5 V repeller voltage (relative to the ionisation box) and 85 eV electron energy. The optimised repeller voltage and electron energy determined in this way maximizes the ion source stability.

As the Helix MC *Plus* has a double lens system, tuning is more complicated than for a conventional single lens ion source. Our beam mapping program was used to generate a beam intensity map as a function of the Horizontal and Extraction Symmetries responsible for steering the ion beam in the ion source. In On-line Resource 2, such a beam intensity map for $^{20}Ne^{+}$ is shown, where a linear correlation between the Horizontal and Extraction Symmetries is observed. A global maximum $^{20}Ne^{+}$ beam of 42 fA. is found at around 23% of Horizontal Symmetry and 21% of Extraction Symmetry. Thus, to achieve the global maximum beam intensity, one needs to adjust both Extraction and Horizontal Symmetries simultaneously. For example, if one adjusts only Extraction Symmetry while the Horizontal Symmetry is held constant at 10%, the maximum beam intensity is only 29 fA. This is illustrated by a chart of beam intensity against Extraction Symmetry extracted from the beam map at 10% of Horizontal Symmetry, as shown in On-line Resource 3.

After the ion acceleration high voltage and the source slit width are set, the Multipole and Flatapole are the main parameters for optimizing mass resolution and mass resolving power. When properly optimized, a mass resolution of 1900 can be achieved, which makes it simple to separate $^{40}Ar^{++}$ from $^{20}Ne^{+}$, and to also partially separate $^{21}Ne^{+}$ from $^{20}NeH^{+}$ [2], and $H^{35}Cl^{+}$, $H^{37}Cl^{+}$ from $^{36,\ 38}Ar^{+}$. This enables interference-free measurements of $^{36,\ 38}Ar^{+}$ and $^{21}Ne^{+}$, as will be demonstrated in later sections.

We have determined the cup configurations for measurements of the isotopes of He, Ne, Ar, Kr, and Xe. For He measurements, peak jumping is used because the dispersion of ^{4}He and ^{3}He physically exceeds the maximum separation of the collectors, making simultaneous measurements in multi-collector mode impossible. For Ne measurements, the detectors of H2 CDD, AX CDD, and L2 CDD are used for $^{22}Ne^{+}$, $^{21}Ne^{+}$, and $^{20}Ne^{+}$, respectively. With the L2 CDD detector, $^{20}Ne^{+}$ can be measured without isobaric interferences from $^{40}Ar^{++}$, $H_2{}^{18}O^{+}$, and $H^{19}F^{+}$. Similarly, due to the high mass resolution of AX CDD, we are able to partially separate $^{20}NeH^{+}$ from $^{21}Ne^{+}$ allowing a high precision redetermination of the ^{21}Ne abundance in air [2]. For Ar measurements, the detectors of H2 Faraday, AX CDD, and L2 CDD are used for $^{40}Ar^{+}$, $^{38}Ar^{+}$, and $^{36}Ar^{+}$, respectively. Given the L2 CDD detector has a resolution of 1800, it can partially separate $H^{35}Cl^{+}$ from $^{36}Ar^{+}$, making it possible to measure interference free ^{36}Ar (Figure 3a).

For measuring the six Kr isotopes, we used a combination of multi-collector and peak jumping modes. Table 1 shows the

Table 3. Mass Resolutions and Mass Resolving Powers of the Detectors of the Helix MC *Plus*, Observed with $^{40}Ar^{++}$. For definitions of mass resolution and mass resolving power, see the text

Detector	Resolution	MRP (L)	MRP (R)
H2 (0.3 mm)	1815	8620	8316
H1 (0.6 mm)	1071	7763	8046
Ax (0.3 mm)	1892	8391	8774
L1 (0.6 mm)	1016	6516	6213
L2 (0.3 mm)	1792	6814	6235

Table 4. Sensitivities of the Helix MC *Plus* for Five Noble Gases, Under Various Conditions of High Voltage, Trap Current, and Source Slit Width

Source slit Noble gas	0.25 mm (10^{-4} A/Torr)	0.1 mm (10^{-4} A/Torr)
^{4}He	0.86 (9.9 KV, 400 μA)	0.53 (9.9 KV, 400 μA)
^{20}Ne	2.14 (9.9KV, 200 μA)	1.81 (9.9KV, 200 μA)
	2.0 (8 KV, 200 μA)	
^{40}Ar	8.43 (8 KV, 200 μA)	5.8 (9.9 KV, 200 μA)
	11.25 (9.9 KV, 300 μA)	8.94 (9.9 KV, 300 μA)
^{84}Kr		5.92 (9.9 KV, 200 μA)
^{132}Xe		17.46 (6.0 KV, 200 μA)

cup assignments for Kr measurements. For each cycle of measurement, Method 1 is used first in a multi-collector mode to measure $^{78}Kr^+$, $^{80}Kr^+$, $^{82}Kr^+$, $^{84}Kr^+$, and $^{86}Kr^+$. Then, the main magnetic field is changed in Method 2 so that $^{83}Kr^+$ is measured on the AX CDD detector.

With nine isotopes, the measurement of Xe is more complicated (Table 2). For each cycle of Xe measurement, three Methods are used. Each Method has a different mass assigned to the Ax Faraday detector, which is a reference detector in Qtegra. With this Cup Configuration, no detector movement is required among different Methods. In addition, $^{130}Xe^+$ and $^{132}Xe^+$ are measured in both Method 1 and Method 2; therefore, they can be used for cross-calibration between Method 1 and Method 2.

We have performed sequential analyses from Ar to Xe using the Heavy Gas Standard. A Cup Configuration was created for each noble gas; this includes detector positions, source settings, the mass assigned for the Ax Faraday detector, and the assignment of the isotopes to the detectors. Using these Cup Configurations, a Template is created for each noble gas that specifies the number of cycles, integration time, peak centering parameters, the Methods, and the Sample List. The Sample list determines whether the measurement is a background, standard, or sample measurement. A LabBook for each noble gas is created from the appropriate Template and then loaded into the Qtegra scheduler, where they are initiated and run sequentially.

We have created a Virtual Instrument (VI), called ANUPrepOnHelixMC, which includes all automated devices in the gas extraction line together with the mass spectrometer. In Qtegra, there are several steps to define an analysis, which include Prepare, Acquire, and PostAcquisition steps. A C# script of ANUPrepOnHelixMC-Prepare.cs was developed to automatically prepare a sample before it is admitted to the mass spectrometer. This script includes automatic operation of valves, furnace, and the Janis cryogenic charcoal system. This allows full automation of various analyses types such as Background, Blank, Heavy Gas Standard, HESJ standard, and Furnace Extraction. Similarly, a C# script ANUPrepOnHelixMC-PostAcquisition.cs was developed to pump away gases after sample analysis and to automatically reinitialize the gas extraction line for next measurement.

Results

Resolution

On-line Resource 4 shows the highest mass resolution achieved by the Helix MC *Plus* by scanning $^{40}Ar^{++}$ peak with a trap current of 130 μA and a source slit of 0.1 mm. The observed mass resolution of 1945 completely separates $^{40}Ar^{++}$ from $^{20}Ne^+$ (On-line Resource 5), allowing interference-free determination of ^{20}Ne. The mass resolutions and mass resolving powers with the five detectors determined using $^{40}Ar^{++}$ are listed in Table 3, which shows even the lower resolution detectors (H1 and L1) have higher mass resolutions (~1000) than a conventional noble gas mass spectrometer (~600), such as VG5400.

Complete separation of $^{36}Ar^+$ from its interference $H^{35}Cl^+$ requires a mass resolution of 3940. Similarly, a mass resolution of 3450 is required to completely separate $^{38}Ar^+$ from $H^{37}Cl^+$. The Helix MC *Plus* does not have such high mass resolution; however, owing to its high mass resolving power, it can effectively separate $^{36}Ar^+$ and $^{38}Ar^+$ from their isobaric interferences. Figure 3a displays mass spectra of $^{36}Ar^+$ and $^{38}Ar^+$ taken in multi-collector mode, and shows that interference free measurements of ^{36}Ar and ^{38}Ar can be achieved at mass 38.27 u. This capability will significantly improve accuracy of the air Ar correction in Ar-Ar dating, and be particularly useful for accurate determination of ages of young rocks. We will explore this topic in future work.

Similarly, $^{21}Ne^+$ and $^{20}NeH^+$ peaks can be partially separated (Figure 3b). Setting the mass at 21.01 u, we were able to

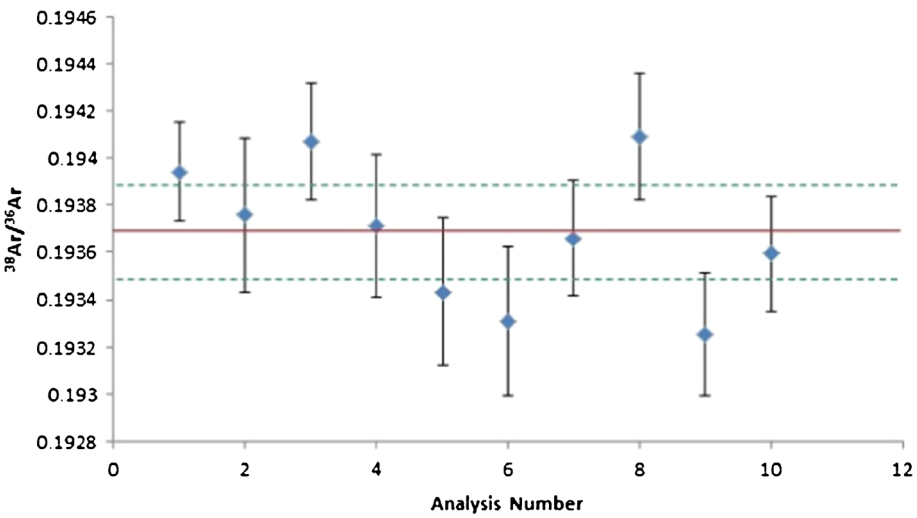

Figure 4. Repeat measurements of atmospheric $^{38}Ar/^{36}Ar$ ratio. The red line shows the average of 0.1937, and the green lines indicate ± 1σ. One aliquot of the standard gas contains ^{36}Ar and ^{38}Ar of 4.0×10^{-10} and 7.5×10^{-11} cm^3STP, respectively

measure interference free ^{21}Ne and to redetermine ^{21}Ne abundance in air [2]. This has significance for cosmogenic ^{21}Ne surface exposure dating, which involves the calculation of cosmogenic ^{21}Ne concentrations relative to the atmospheric $^{21}Ne/^{20}Ne$ ratio. For young samples, where cosmogenic ^{21}Ne contents are small and the observed $^{21}Ne/^{20}Ne$ ratio is close to the atmospheric value, the revised atmospheric composition could increase cosmogenic ^{21}Ne ages significantly. Further investigation on this matter is required.

Complete separation of Kr and Xe isotopes from isobaric hydrocarbon interferences requires mass resolutions around 600 and 550, respectively. Even the low resolution detectors of Helix MC *Plus* with mass resolutions around 1000 are sufficient for this task.

We also observed that the mass resolution is dependent on the trap current; the lower the trap current, the higher the mass resolution. Finally, optimal source settings for mass resolution may not be exactly the same as for sensitivity.

Sensitivity

Table 4 shows that the sensitivities for all five noble gases depend on the width of the source slit and show a positive correlation with the trap current. The ^{40}Ar sensitivity reaches 1.1×10^{-3} A/Torr at a trap current of 300 μA with a 0.25 mm source slit, where the total emission current is three times, which is around 900 μA, of the trap current. In contrast, a conventional noble gas mass spectrometer has a typical ratio of total emission current to trap current of 4 ~ 5 times. Our Helix MC *Plus* has similar ^{40}Ar sensitivity as that of the Thermo Fisher ARGUS VI mass spectrometer (~1×10^{-3} A/Torr at 200 μA trap current) [3].

Statistical Uncertainty

We have determined the statistical uncertainties in terms of sensitivity and mass discrimination by performing repeated air Ar measurements. Figure 4 shows $^{38}Ar/^{36}Ar$ ratios of 10 air Ar

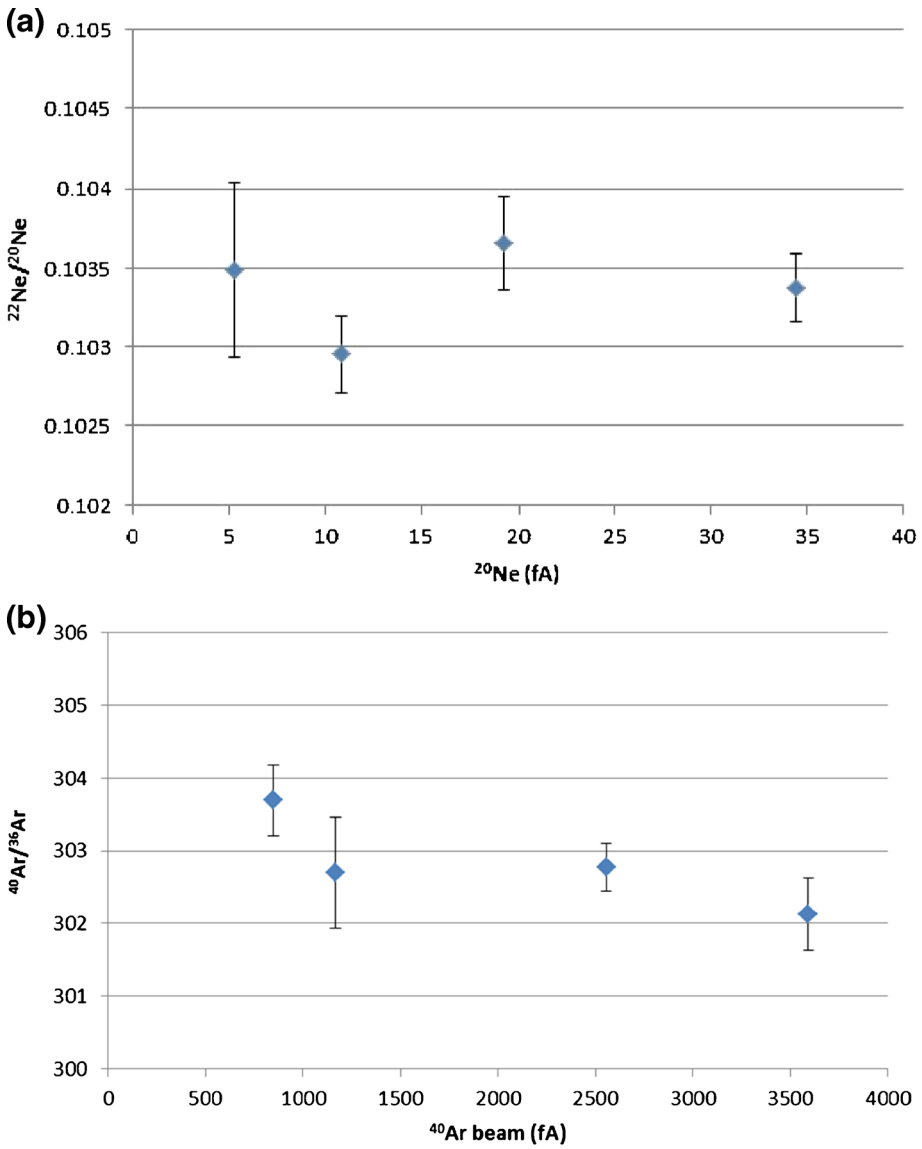

Figure 5. (**a**) Variation of $^{22}Ne/^{20}Ne$ over a range of ^{20}Ne beams. (**b**) Linearity of $^{40}Ar/^{36}Ar$ over a range of ^{40}Ar beams

measurements, with the red line showing the average measured $^{38}Ar/^{36}Ar$ ratio of 0.19368 and the green dash lines indicating the range of one standard deviation. The relative uncertainty for $^{38}Ar/^{36}Ar$ was 0.055%. The average $^{38}Ar/^{36}Ar$ and the relative uncertainty of $^{38}Ar/^{36}Ar$ were calculated using the public domain software ISOPLOT, developed by Kenneth R Ludwig at Berkeley Geochronology Center [4]. In the calculation of the average $^{38}Ar/^{36}Ar$, the uncertainty of each individual measurement has been taken into account.

This uncertainty is comparable to, or slightly better than, recent work in high-precision measurements of the isotopic composition of atmospheric argon. For example, Mark et al. [5] reported a relative uncertainty of 0.045% for $^{40}Ar/^{36}Ar$ and a relative uncertainty of 0.13% for $^{38}Ar/^{36}Ar$ from 180 air Ar measurements using a GVI ARGUS V multi-collector mass spectrometer.

Linearity

A map of $^{22}Ne/^{20}Ne$ ratios as a function of the repeller voltage and electron energy shows their dependence (On-line Resource 6). A relatively flat plateau around –3.7 V of repeller voltage and 110 eV of electron energy provides stable $^{22}Ne/^{20}Ne$ ratios. Using these settings, Ne isotope ratios were measured with various ^{20}Ne partial pressures. Figure 5a shows that the variation in the $^{22}Ne/^{20}Ne$ ratio is about 0.67% over a range of ^{20}Ne beam intensities from 5 to 35 fA. A trap current of 100 μA and a source slit of 0.25 mm were used in these measurements.

Similarly, the linearity of Ar isotope ratios was examined over a range of ^{40}Ar beams from 700 to 3600 fA. (Figure 5b), which covers the expected beam sizes of our potential geological samples to be analyzed, for example, MORB (Mid Ocean Ridge Basalt) samples. These measurements were performed at 130 μA of trap current with the source slit being 0.1 mm wide. The data show that the variation of $^{40}Ar/^{36}Ar$ ratio is 0.65% over the range. We also found that the repeller voltage had strong influence to the linearity of the isotope ratios. A repeller voltage of –2.3 V and an electron voltage of 80 eV were found to be optimal.

Mass Discrimination

In order to precisely determine isotope ratios of noble gases from geological samples, mass discrimination of the noble gas mass spectrometer used must be determined. The mass discrimination is characterized by a mass discrimination factor (D), which is defined as

$$D = (\text{isotope ratio})_{\text{true}} \Big/ (\text{isotope ratio})_{\text{measured}}.$$

For Ar isotopes in air, the true $^{38}Ar/^{36}Ar$ ratio is 0.1885 [6]. For the air Ar data in Figure 4, which were taken by the Helix MC *Plus*, the measured $^{38}Ar/^{36}Ar$ ratio is 0.1937. A discrimination factor of 0.9732 was obtained. This discrimination factor is important to correct mass discrimination for Ar isotope measurements when unknown geological samples are measured by the Helix MC *Plus*. Similarly, discrimination factors for other noble gas elements can be obtained by measuring standard samples of other noble gases.

Conclusion

These results from the Helix MC *Plus* mass spectrometer at ANU demonstrate the capability of higher mass resolution and sensitivity than conventional noble gas mass spectrometers, while precision is equivalent or slightly better. It is possible to sequentially measure a full suite of noble gases from He to Xe in multi-collector modes by adjusting collector positions for each noble gas. The linearity in sensitivity and mass discrimination of the mass spectrometer has been examined using different aliquots of noble gases, and ensures reliable determinations of isotope ratios for unknown amount of noble gases released from geological samples. The software platform Qtegra used by the Helix MC *Plus* is capable of automatically switching the measurements between the various noble gases. Our commissioning work indicates that by integrating the software drivers of the devices on the noble gas extraction line into Qtegra, full automation of both sample preparation and measurements can be achieved by using one computer program.

The unique capabilities of the Helix MC *Plus* provide the opportunity to revolutionize noble gas research in cosmo-geochemistry. For example, the high mass resolution of Helix MC *Plus* makes it possible to measure virtually isobaric (atomic and molecular) interference-free ^{36}Ar and ^{21}Ne with important applications in both Ar-Ar dating and ^{21}Ne cosmogenic surface exposure dating of young samples.

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