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Measurement of Stable Isotope $^{41}K/^{39}K$ Ratios by MC-ICP-MS

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Abstract

The measurement of the stable isotope ratio $^{41}K/^{39}K$ by conventional MC-ICP-MS is challenging due to scattered ions from $^{40}Ar^+$ and interference by $^{40}Ar^1H^+$. TIMS and SIMS are not sufficiently precise to resolve the small spread of isotopic variation. The first measurements showing variation in this isotopic system were only recently made, using a Thermo Scientific™ NEPTUNE Plus™ MC-ICP-MS, operating in high-resolution mode and using cold wet plasma conditions and sample standard bracketing [1-4]. The typical repeatability of measurements is 0.08 – 0.12 ‰ (2σ). An alternative approach has been to use collision cell MC-ICP-MS [5-8].

The potassium isotopic system has applications in terrestrial geochemistry, planetary science, and potentially for biomedical and agricultural research.

Two areas are explored to improve the precision using conventional MC-ICP-MS. The first is to enhance the resolving power of the mass spectrometer, since the mass difference between $^{41}K^+$ and $^{40}Ar^1H^+$ is small (ca. 3 mu). The second is to improve the efficiency and the stability of the sample introduction. Experiments were conducted using a NEPTUNE Plus modified for higher mass resolution. This was coupled to an Elemental Scientific™ apex Ω™ desolvating nebulizer system and an Elemental Scientific™ micro*FAST* MC™ syringe driven flow injection system. Data are reported for $\delta^{41}K$ precision using this setup.

Introduction

$^{41}K/^{39}K$ measurements are routinely made at Princeton University™ with a standard Thermo Scientific NEPTUNE Plus MC-ICP-MS instrument operated in cold plasma (RF <600 W) at high resolution (ca. 10,000 RP). This configuration both minimizes $^{40}Ar^+$ and $^{40}Ar^1H^+$, and separates $^{41}K^+$ from $^{40}Ar^1H^+$. $\delta^{41}K$ values are obtained by sample standard bracketing with 0.17 ‰ (2σ) reproducibility (including sample chemistry).

In this poster note we explore ways to improve precision through:

- Enhancing the resolution of the mass spectrometer.
- $^{40}Ar^+$ and $^{40}Ar^1H^+$ suppression.
- Using standard hot dry plasma conditions.
- Rapid sample standard bracketing.

Table 1. Summary of operating parameters.

Nebulizer Uptake Rate	80 – 100 µL/min
ICP RF Power	1200 W
Cones	Ni (standard, 0.8H)
Entrance Slit	16 µm
Intermediate Slit	standard / high-resolution
Data Acquisition	180 s
Uptake/Wash Time (s)	free aspiration: 60 / 180 micro*FAST* MC: 15 / 45

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Materials and Methods

A Thermo Scientific NEPTUNE Plus MC-ICP-MS was fitted with a 16 µm entrance slit and a switchable intermediate aperture to provide 18,000 resolving power (5, 95% edge definition) at 1.5% transmission.

The Elemental Scientific apex Ω high-sensitivity sample introduction system is used to maximize analyte sensitivity and minimize ArH^+ interferences. At typical N_2 flowrates (3 -7 mL/min) oxides and hydrides are reduced by two orders of magnitude. We investigate higher N_2 flow rates to further reduce $^{40}Ar^1H^+$ through reduction of Ar^+ in the beam.

Solutions are introduced to the apex Ω using either a self-aspirating nebulizer (Elemental Scientific PFA-100 µFlow) or a dual-loop syringe driven injection system (Elemental Scientific micro*FAST* MC). At identical flowrates the micro*FAST* MC delivers a 20 – 30% sensitivity enhancement and very stable signal profiles, ideal for high-precision isotope ratios. Furthermore, dual alternating loop injections reduce the time between sample and standard measurements by 3 minutes (Table 1, Figure 2)

Potassium was purified using a Thermo Scientific™ Dionex™ ICS-5000+ Capillary HPIC™ system at Princeton University. Two materials were processed: NIST SRM 70b Potassium Feldspar and Bermuda seawater (BSW). The purified solutions were diluted to 1 – 2 µg/g concentration in 3 wt.% HNO_3 acid (Thermo Scientific™ Optima™ Nitric Acid with Thermo Scientific™ Barnstead™ DI water).

Table 2. Signal intensity, interference intensity and signal to interference ratio are tabulated as a function of increasing N_2 gas addition to the apex Ω on the NEPTUNE Plus. A flow rate of 25 ml/min N_2 provides the optimal balance between ^{41}K, $^{41}K/^{40}Ar^1H$ ratio and minimized tailing of $^{40}Ar^1H$ onto ^{41}K (K = 1 µg/g). The K signal and $^{41}K/^{40}Ar^1H$ ratio is comparable to that obtained under cold wet cold plasma conditions.

$N_{2\,(g)}$ (ml/min)	$^{40}Ar^1H$ (V)	^{41}K (V)	Ratio
10	1.73	1.33	0.77
20	0.49	0.57	1.16
30	0.07	0.31	4.43
40	0.038	0.22	5.79
50	0.039	0.194	4.97
60	0.034	0.174	5.12

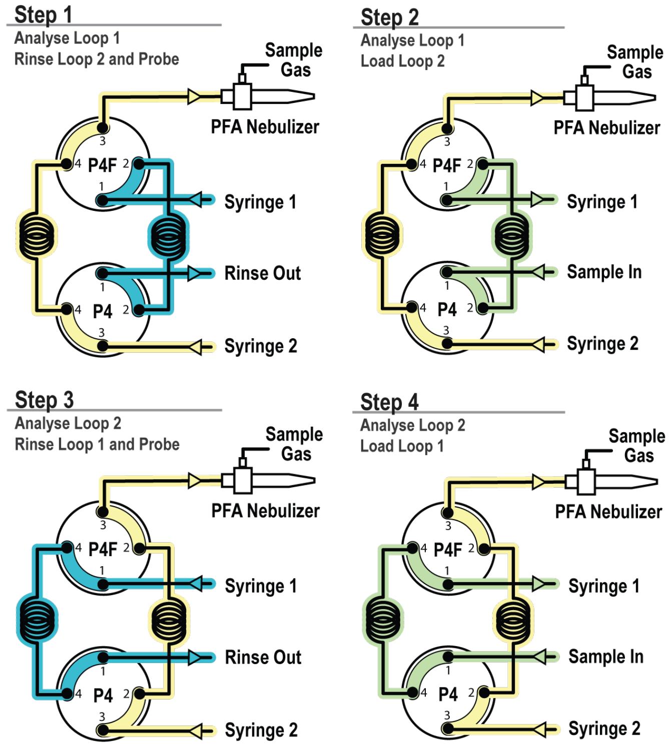

Figure 1. Flow paths illustrating the micro*FAST* MC patented dual loop injection for rapid sample standard bracketing.

Results

Initial optimization of the apex Ω for the reduction of the $^{40}Ar^1H^+$ interferences on the K isotopes was performed in using the Thermo Scientific™ ELEMENT 2™ HR-ICP-MS. Two effects are apparent when increasing the N_2 gas addition: 1) hydride formation is reduced through the removal water at N_2 flow rates below 10 mL/min, 2) at higher N_2 flow rates (up to 60 mL/min) the Ar^+ decreases as well as the ArH^+ (Figure 3b). Similar experiments on the NEPTUNE Plus find optimal ^{41}K and $^{41}K/^{40}Ar^1H$ ratios at N_2 flow rates above 20 mL/min (Table 2).

Interference reduction combined with high mass resolution (18,000 RP) provides broad interference-free plateaus for data collection (Figure 4 and 5). The optimized configuration results in 0.06 ‰ SD (2σ) external precision (Figure 6). Comparable precision, but higher throughput, is obtained for half the concentration (1 µg/g) when using the syringe injection and a resolution of 12,000 (Table 3).

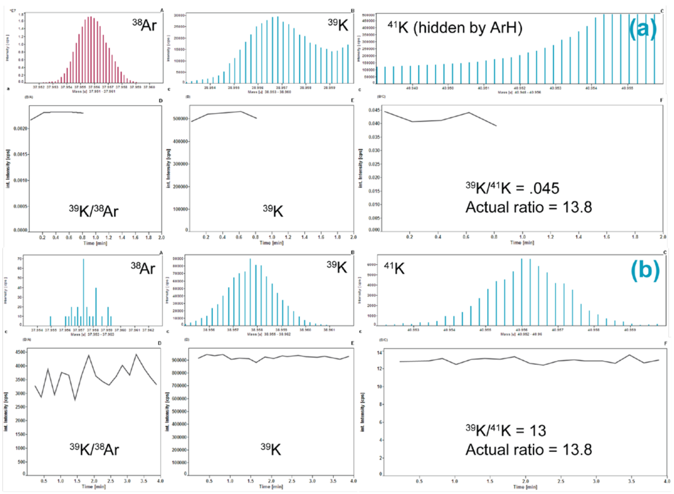

Figure 2. High-resolution scans from the ELEMENT 2 of a 10 ng/g K solution illustrating relative intensity of K, Ar and ArH signal intensities with (a) wet plasma and (b) dry plasma apex Ω with excess N_2 addition (60 mL/min).

Table 3. Two different setups provide comparable external precision for 0.8 and 0.4 µg sample amounts.

[K] µg/g	Nebulizer	Resolution	External Precision (SD, 2σ) $\delta^{41}K_{BSW}$
2	Self-aspirating	18,000	0.06
1	Syringe-driven	12,000	0.07

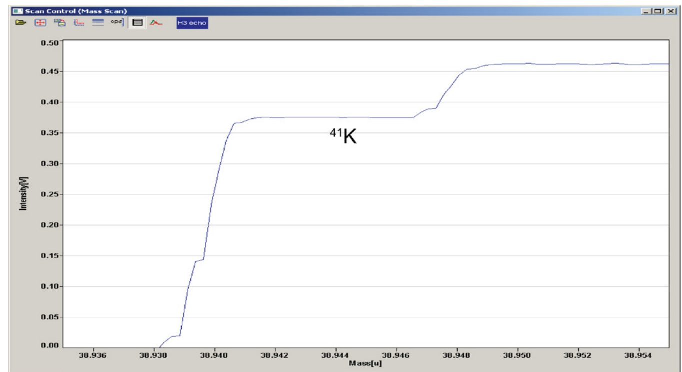

Figure 3. Mass scan showing the separation of ^{41}K from $^{40}Ar^1H$ at a mass resolving power of 18,000 (5, 95% edge definition).

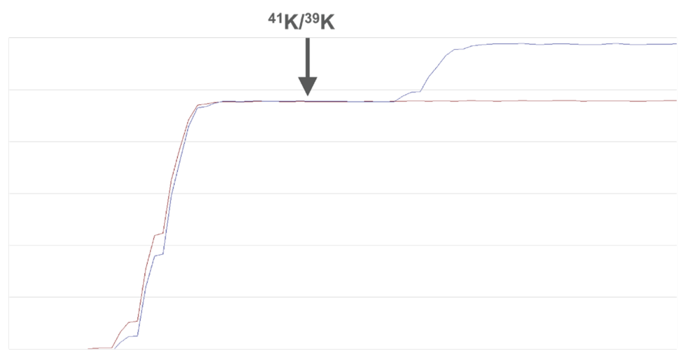

Figure 4. Mass scan showing the precise alignment of ^{41}K and ^{39}K (normalized to ^{39}K signal intensity).

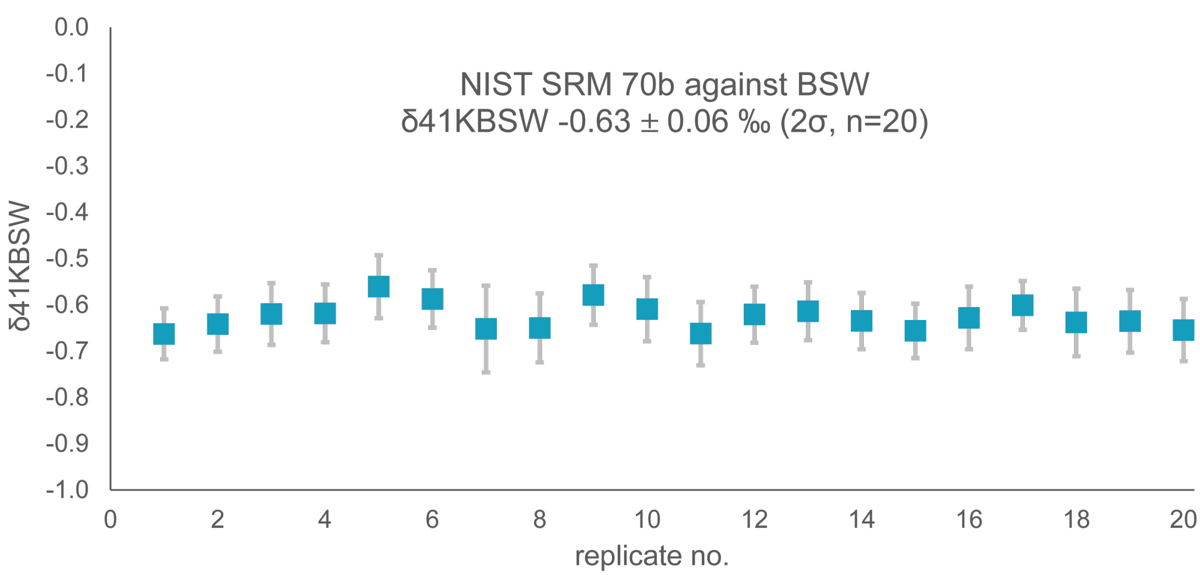

Figure 5. External precision (2SD) for $\delta^{41}K$ from 0.8 µg sample amounts, measured by sample standard bracketing.

Discussion

The potassium isotopic system is relatively unexplored for stable isotopic fractionation, with resolvable variation only recently demonstrated [1]. The isotopic system is attractive for both geochemistry and biochemistry applications.

The first measurements were made using a NEPTUNE Plus operating in high-resolution and using cold wet plasma.

Subsequent studies by Wang & Jacobsen [5,6] and by Li et al [7,8] used $^{1}H_2$ or $^{2}H_2$ gas in a collision cell MC-ICP-MS to suppress the ^{40}Ar and $^{40}Ar^{1}H$. $\delta^{41}K$ isotope ratio precision using sample standard bracketing for the Isoprobe-P instrument is 0.2 – 0.3 ‰ SD (2σ). Reported uncertainty can be reduced by taking the standard error of the mean of 8 or more replicate measurements (up to n=115) [5,6], assuming Poisson distributed variability between standards measurements.

We show data with an external precision for sample standard bracketing measurements of 0.06 ‰ SD (2σ, individual SSB measurements), using 0.4 – 0.8 μg per measurement. The standard error of the mean for a quintuplicate analysis is 0.03 ‰ (n=5, 2σ).

Accuracy of the measurements is within close agreement to values obtained by coauthors at Princeton University using the cold wet plasma technique (-0.68 ±0.17 ‰, n=33 with separate column chemistries). It should be noted that the sample purification chemistry contributes non-trivial uncertainty and limits the external reproducibility.

The high-resolution mode of the standard NEPTUNE Plus instrument is sufficient for the separation of $^{41}K^{+}$ from $^{40}Ar^{1}H^{+}$, and can be used to determine precise and accurate $\delta^{41}K$ values using cold wet plasma tuning. Critical to the measurements is the excellent stability of the NEPTUNE Plus with respect to peak-position and mass bias.

The setup explored in this poster offers:

- Enhanced mass resolution to broaden the interference-free plateau and minimize tailing onto $^{41}K^{+}$.
- $^{40}Ar^{+}$ and $^{40}Ar^{1}H^{+}$ suppression in hot plasma conditions.
- Efficient sample introduction to compensate for the loss of transmission from the enhanced mass resolution.
- Dual-loop loading to reduce the spacing of SSB measurements and increase sample throughput.
- Precise & accurate $\delta^{41}K$ determination.

Conclusions

- Stable isotope ratio $^{41}K/^{39}K$ can be precisely measured using conventional high-resolution MC-ICP-MS.
- The apex Ω provides sensitivity with interference suppression, enabling precise $^{41}K/^{39}K$ measurements in hot plasma conditions.
- Rapid sample standard bracketing with the micro*FAST* MC and apex Ω achieves optimal mass bias stability.
- 0.06 ‰ external repeatability (2σ) for $\delta^{41}K$ can be achieved for 0.8 μg sample amounts.
- The Thermo Scientific NEPTUNE Plus is ideal for investigating isotopic fractionation processes of potassium and for application of stable potassium isotope ratio data in the field of geochemistry and biochemistry.

References

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