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Mass spectrometry

High precision $\delta^{41}K$ using MC-ICP-MS in high resolution and MS/MS mode

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Keywords

MC-ICP-MS, eXtra high resolution (XHR), collision/reaction cell, Pre-cell mass filter, potassium, Neoma

Goal

To demonstrate how the different technologies within the Thermo Scientific™ Neoma™ MC-ICP-MS and Neoma™ MS/MS MC-ICP-MS can cater for a wide variety of potassium isotope applications.

Introduction

Potassium is an important element in both geological and biological science. It is highly enriched in the continental crust and extremely soluble in water, making it one of the most abundant ions in seawater. The water solubility of potassium is a factor in many of its key biological roles, such as the propagation of nerve impulses through cell membranes.

Despite the high importance of potassium in many geological and biological processes, the mass dependent fractionation between its two isotopes, ^{39}K (93.3%) and ^{41}K (6.7%) has not been well characterized until very recently. This is in part due to the difficulty in making high precision $^{41}K/^{39}K$ measurements. One of the largest barriers to measuring the K isotopic composition by MC-ICP-MS is the large $^{40}Ar^{1}H$ interferent on ^{41}K. Different approaches have been trialed to reduce or remove this isobaric interference. These approaches include using 'cold plasma', extra-high resolution to resolve the interferent, or neutralizing $^{40}Ar^{1}H$ using a collision/reaction cell technology.

Here we demonstrate the versatility of the Neoma MC-ICP-MS to measure high precision potassium isotope composition. Neoma MC-ICP-MS is our latest MC-ICP-MS delivering on performance, with market-leading sensitivity, isotope ratio precision and accuracy.

We will share the limits of precision achievable using (i) the eXtra High Resolution (XHR) option, and (ii) the collision/reaction cell (CRC) technology of the Neoma MS/MS MC-ICP-MS. We show that both techniques have their merits and weaknesses and therefore cater for different K isotopes applications.

Methods

Two different experiments were carried out to measure high precision K isotope ratios. In the first experiment, the Neoma MC-ICP-MS was equipped with the XHR option to resolve the $^{40}Ar^{1}H$ interferent on ^{41}K. In the second experiment, the Neoma MC-ICP-MS equipped with a pre-cell mass filter and collision/reaction cell (an upgrade option called Neoma MS/MS MC-ICP-MS). A mixture of H_2 and He in the collision/reaction cell was used to neutralize the $^{40}Ar^{1}H$ interferent.

Sample introduction

In both experiments, the sample introduction system was an ESI® Apex Omega™ Q desolvating nebulizer and ESI microFAST MC™ (Figure 1).

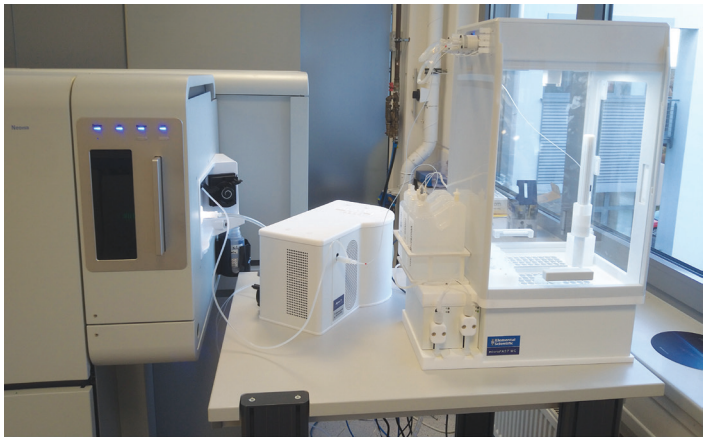

Figure 1. ESI Apex Omega Q and microFAST MC

The autosampler used was the latest microFAST MC. This uses Dual Loop Syringe Loading and Injection technology. The system accurately loads a loop and then smoothly injects the solution into a µFlow concentric nebulizer at defined rates from 5–1,000 µL/min. The valve on the flow injection system selects from two discrete, parallel flow paths. This allows rapid switching between solutions with minimal dead volume between the valve and the nebulizer.

K isotope measurements should benefit greatly from this technology. By minimizing the time between each measurement, bracketing between sample and standard is tighter, improving accuracy. The highly stable flow rate provided by syringe injection also improves precision by acting to minimize signal drift throughout the course of a measurement.

The microFAST MC can be easily controlled via a plugin within the Neoma MC-ICP-MS instrument control software, Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software. All parameters related to the microFAST MC can be set for each sample via the sample list (Figure 2).

Sample List

	Label	Status	Comment	Sample Type	Rack Number	Vial Numbers	Sample Loading Volume	Sample Injection Rate
1	Blank		<Comment>	QC	0	7	650	100
2	Blank		<Comment>	BLK	0	7	650	100
3	SRM3141a		<Comment>	STD	0	4	650	100
4	SRM9996b		<Comment>	SMP	0	3	650	100
5	SRM3141a		<Comment>	STD	0	4	650	100
6	SRM9996b		<Comment>	SMP	0	3	650	100
7	SRM3141a		<Comment>	STD	0	4	650	100
8	SRM9996b		<Comment>	SMP	0	3	650	100
9	SRM3141a		<Comment>	STD	0	4	650	100
10	SRM9996b		<Comment>	SMP	0	3	650	100
11	SRM3141a		<Comment>	STD	0	4	650	100
12	SRM9996b		<Comment>	SMP	0	3	650	100
13	SRM3141a		<Comment>	STD	0	4	650	100

Figure 2. Sample List for K isotopic measurements using the Neoma MC-ICP-MS with the ESI microFAST MC. The desired sample loading volume and sample injection rate (in µL and µL/min respectively) can be simply entered within the sample list.

Neoma MC-ICP-MS and the XHR option

In the first set of experiments, the Neoma MC-ICP-MS was equipped with the high sensitivity Jet Interface and the XHR option. The XHR option improves the existing high resolution (25 µm wide slit) of the Neoma MC-ICP-MS to extra-high resolution by installing an additional intermediate slit after the electrostatic analyzer and reducing the high resolution entrance slit to a 16 µm wide slit. Both the entrance and intermediate slits of the XHR option can be switched in and out of position using pneumatic control. For K isotopes, the XHR slit increases mass resolving power from greater than 9,000 to great than 15,000[1].

Even with the extra-high resolution provided by the XHR option, the $^{40}Ar^{1}H$ needs to be significantly reduced for successful ^{41}K measurements. The $^{40}Ar^{1}H$ can be reduced in a variety of different ways. The most established method is to use 'cold' plasma (≈600 W)[2] to attenuate and reduce the observed $^{40}Ar^{1}H$. However, a method, based on hot plasma (≈1,300 W), using higher N_2 flows to reduce $^{40}Ar^{1}H$ has gained prominence[3]. For our previous generation Thermo Scientific™ Neptune Series™ MC-ICP-MS, it was demonstrated the hot plasma method was superior, due to the higher sensitivities and lower argon hydride formation achieved[1,4].

For this experiment, the following experimental conditions were used (Table 1).

Table 1. Neoma MC-ICP-MS set-up conditions in XHR mode

RF power (W)	1,300
X torch position (mm) **Y torch position (mm)** **Z torch position (mm)**	-3.10 0.55 6.50
Cool Ar gas flow (L/min) **Auxilary Ar gas flow (mL/min)** **Nebulizer Ar gas flow (mL/min)**	14.00 0.80 1.00
Apex Omega N_2 gas flow (mL/min) **Apex Omega Ar gas flow (L/min)**	20 2.00

The N_2 gas flow of the Apex Omega tuned to optimize $^{40}Ar^{1}H$ suppression and the Ar gas flow was tuned for stability. All lenses were tuned for maximum sensitivity and mass resolving power.

Each measurement was 3 minutes (180 s) in duration, made of 45 cycles of 4 s integration. Each sequence was blank corrected, with blank measurements made at the beginning and end of each sequence.

Two K solutions were produced, one consisting of 1.0 µg/g SRM®3141a in 3% HNO_3 and the other 0.5 µg/g SRM 9996b in 3% HNO_3. SRM3141a was used as the reference material: SRM9996b was used as an unknown.

Qtegra ISDS Software for the Neoma MC-ICP-MS allows the mass resolving power to be easily calculated for every cup. The XHR option for the Neoma MC-ICP-MS modifies the entrance slit and adds a software-selectable intermediate slit, located between the electrostatic analyzer and the magnet. This guarantees a mass resolving power greater than 15,000. For K we determined mass resolving powers greater than 20,000 for both ^{39}K and ^{41}K. A clear, flat plateau of ^{41}K free of $^{40}Ar^{1}H$ could easily be set (Figure 3).

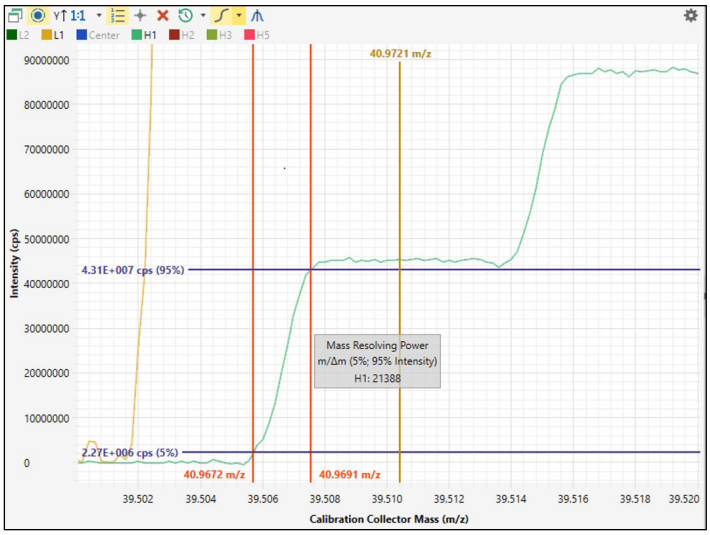

Figure 3. Scan calculating mass resolving power for ^{41}K with the Neoma MC-ICP-MS with XHR Option. Specification >15,000.

Table 2. Cup configuration

Cup	L5	L4	L3	L2	L1	C	H1	H2	H3	H4	H5
			^{38}Ar	^{39}K	^{40}Ca	^{41}K	^{42}Ca	^{43}Ca	^{44}Ca		
Amplifier			10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω		

Neoma MS/MS MC-ICP-MS and the CRC option

In the second set of experiments, the CRC of the Neoma MS/MS MC-ICP-MS was used to measure K isotopes in low resolution mode, using a combination of He and H_2 as a reaction gas to neutralize the ArH interference.

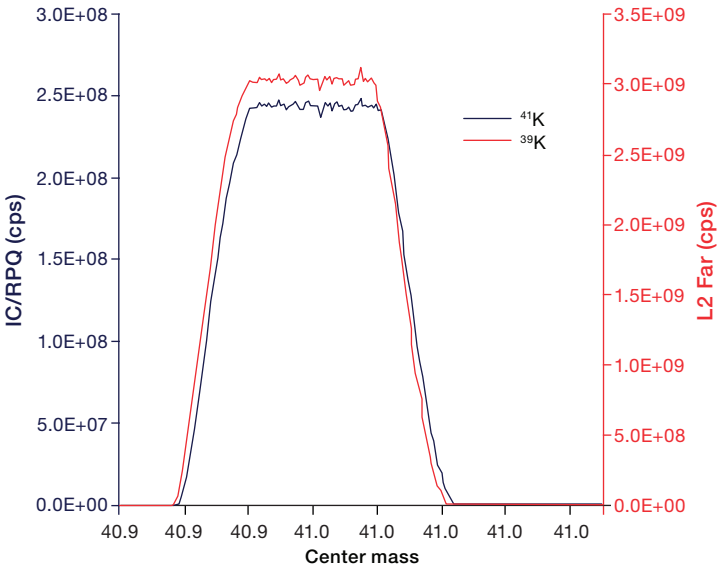

Figure 4. Mass scan across ^{39}K and ^{41}K using 100 ng/g K, flow rate 50 µL/min, 5.0 ml/min H_2 and 1.5 ml/min He. $^{40}ArH^+$ interferent on ^{41}K is eliminated.

Table 3. Neoma MS/MS MC-ICP-MS set-up conditions in CRC mode

RF power (W)	1,300
X torch position (mm) **Y torch position (mm)** **Z torch position (mm)**	-1.54 -1.00 6.00
Cool Ar gas flow (L/min) **Auxilary Ar gas flow (mL/min)** **Nebulizer Ar gas flow (mL/min)**	14.00 0.80 1.00
CRC H_2 gas flow 3.5 (mL/min) **CRC He gas flow 3.5**	5.0 1.5
Apex Omega N_2 gas flow (mL/min) **Apex Omega Ar gas flow (L/min)**	5 4.25

Each measurement was 3 minutes (180 s) in duration, made of 45 cycles of 4 s integration. Each sequence was blank corrected, with blank measurements made at the beginning and end of each sequence.

In these experiments a 100 ppb solution of SRM3141a K was bracketed against itself. The same cup configuration was used as in the XHR experiments (Table 2).

Results

Sensitivity

Sensitivity of the XHR option was 22 V/ppm, whereas with the CRC a sensitivity of >1,250 V/ppm was achieved. This large difference in sensitivity is caused by the difference in transmission between low resolution (CRC method) and XHR resolution. There is therefore a clear advantage to using the CRC of Neoma MS/MS MC-ICP-MS when sample limited.

Effect of signal intensity matching on $^{41}K/^{39}K$ ratio

Irrespective of the method used (i.e. XHR option or CRC), when using the sample-standard bracketing method, signal matching is vital for accurate $\delta^{41}K$. The microFAST MC was used to control the sample injection rate and thus vary the signal intensity of the sample relative to the bracketing standard.

Here, we tested the effect of a mismatch in signal intensity between the sample and its bracketing standard for the XHR option. The results show a decreasing $\delta^{41}K$ value with increasing K concentration mismatch (Figure 4). For the XHR option, each 1% of difference changes $\delta^{41}K$ by 0.01‰. Comparatively, CRC methods would show a stronger dependency on K concentration mismatch because they typically require lower sample concentrations (e.g. 100 ppb K) relative to XHR methods (≤1 ppm K)[5,6].

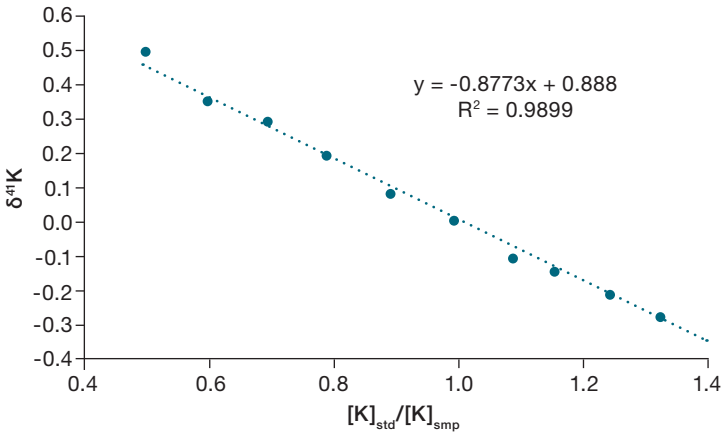

Figure 4. Effect of K concentration mismatch between the sample and standard on the $\delta^{41}K$ value of the sample using XHR option

For both methods, the microFAST MC can be used to easily match sample and standard signal intensities. With Neoma MC-ICP-MS, this can be set within the Qtegra ISDS Software, making the coupling between autosampler and ICP-MS extremely simple.

Precision

To assess the internal precision achievable by both methods, a series of samples were run by SSB. Due to the lower rates of ion transmission with the XHR option, a higher concentration (1 ppm K) standard was used, whereas with the CRC option, it was possible to achieve a higher signal with just 100 ppb of K standard. The results of the two experiments are shown in Figure 5.

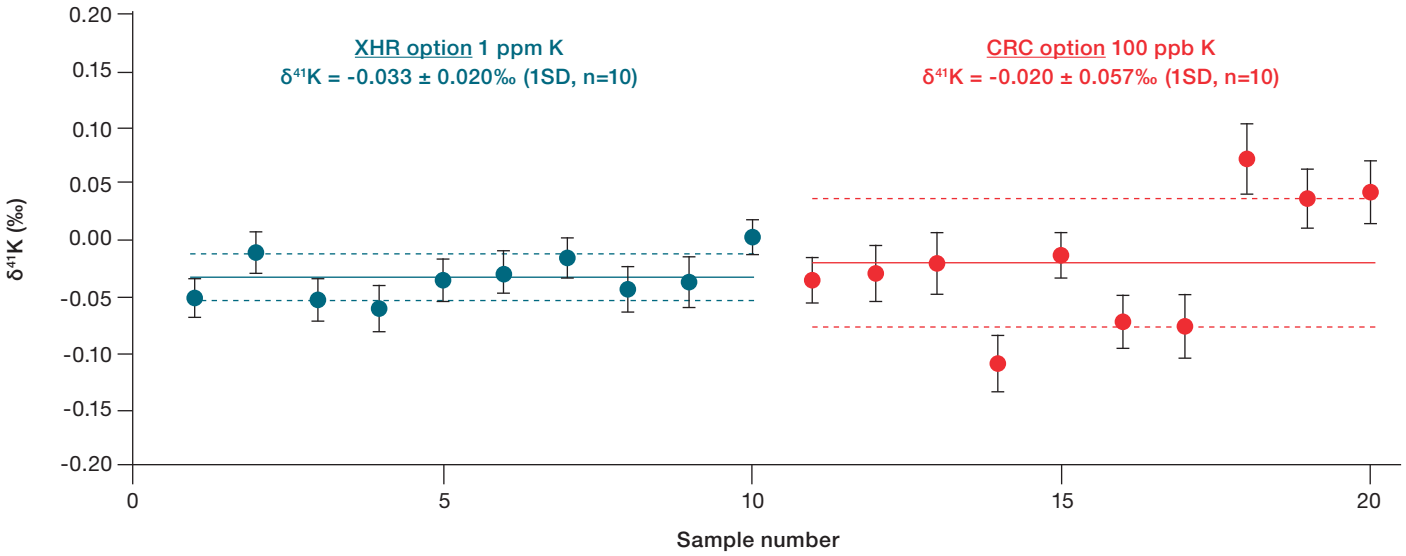

Figure 5. Comparison of internal and external precision achievable on a 3-minute analysis using XHR option (blue) and the CRC option (red). Data is shown in the Appendix.

The results show that it is possible to achieve a better external precision with the XHR option (0.020‰) as opposed to the CRC option (0.057‰), despite the higher signal intensity for the CRC option. This suggests that system stability is typically slightly better with the XHR option. With extra time for stabilization the performance of the CRC option can match what is shown here for the XHR option.

Conclusion

These experiments highlight that each method has its own merits. Where sample size is limited, the CRC option provides almost 100-fold improvement in sensitivity relative to the XHR option. This means that K isotopic analysis can be carried out on very small samples (<100 ppb K). However, smaller sample sizes also come with the trade-off that sample-standard signal and matrix matching is made more difficult, and such matching has been demonstrated to be crucial for accurate $\delta^{41}K$.

Importantly, where sample size is not limited and the same signal can be achieved with both the XHR option and the CRC option, our experiments would suggest that the XHR option provides better system stability. Therefore, where high precision is the priority and sample size unimportant, the XHR option may provide the better solution for K isotope analysis.

Thermo Scientific Neoma MS/MS ICP-MS

Appendix

Table A1. XHR option: ^{39}K, ^{41}K, $^{41}K/^{39}K$ and $\delta^{41}K$ for 10 replicate measurements of 0.5 ng/g K SRM9996b solution, sample standard bracketed against a 1 ng/g solution of K SRM3141a

	^{39}K (cps)	^{41}K (cps)	$^{41}K/^{39}K$	SE	$\delta^{41}K_{SRM3141a}$	SE
1	1.28E+09	9.93E+07	0.0774610	0.0000007	-0.051	0.009
2	1.27E+09	9.85E+07	0.0774652	0.0000007	-0.012	0.009
3	1.27E+09	9.80E+07	0.0774648	0.0000007	-0.051	0.010
4	1.27E+09	9.82E+07	0.0774649	0.0000008	-0.061	0.010
5	1.26E+09	9.80E+07	0.0774678	0.0000007	-0.035	0.009
6	1.26E+09	9.75E+07	0.0774708	0.0000007	-0.029	0.010
7	1.26E+09	9.74E+07	0.0774746	0.0000006	-0.015	0.008
8	1.25E+09	9.72E+07	0.0774757	0.0000008	-0.045	0.010
9	1.25E+09	9.68E+07	0.0774792	0.0000009	-0.035	0.012
10	1.24E+09	9.61E+07	0.0774835	0.0000006	0.003	0.008
Mean	**1.26E+09**	**9.77E+07**	**0.0774708**	**0.0000007**	**-0.033**	**0.009**
SD	**1.17E+07**	**8.95E+05**	**0.0000073**		**0.020**	

Table A2. CRC option: ^{39}K, ^{41}K, $^{41}K/^{39}K$ and $\delta^{41}K$ for 10 replicate measurements of 100 ppb solution of SRM3141a K was bracketed against itself

Delta No.	^{39}K (cps)	^{41}K (cps)	$^{41}K/^{39}K$	SE	$\delta^{41}K$	SE
1	3.60E+09	2.84E+08	0.0789557	0.0000022	-0.035	0.019
2	3.61E+09	2.85E+08	0.0789804	0.0000018	-0.029	0.025
3	3.57E+09	2.82E+08	0.0790141	0.0000017	-0.021	0.027
4	3.54E+09	2.80E+08	0.0790351	0.0000017	-0.109	0.024
5	3.65E+09	2.88E+08	0.0790196	0.0000017	-0.013	0.020
6	3.62E+09	2.86E+08	0.0790048	0.0000019	-0.073	0.023
7	3.67E+09	2.90E+08	0.0790023	0.0000026	-0.076	0.028
8	3.67E+09	2.90E+08	0.0790253	0.0000026	0.071	0.031
9	3.65E+09	2.88E+08	0.0790349	0.0000024	0.036	0.026
10	3.61E+09	2.86E+08	0.0790379	0.0000021	0.043	0.027
Mean	**3.62E+09**	**2.86E+08**	**0.0790110**	**0.0000021**	**-0.020**	**0.025**
SD			**0.0000264**		**0.057**	

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