Multicollector ICP-MS

# Thermo Scientific Neoma MS/MS MC-ICP-MS: Uranium isotopic analysis

S. Dalby, S. Milano, G. Craig, M. Pfeifer, C. Bouman, N. Lloyd; Thermo Fisher Scientific, Bremen, Germany


## Abstract

Accurately constraining lowest abundance Th and U isotopes has become an important tool in geochronology and for nuclear forensics, e.g., in dating geologically young samples or controlling nuclear proliferation. In addition, the large abundance of the main isotopes $^{235}U$ and $^{238}U$ hamper measurements of smallest $^{234}U$ and $^{236}U$ intensities due to tailing effects superimposing on the lower signals.

The Thermo Scientific™ Neoma™ MC-ICP-MS offer several advantages to tackle these challenges. Thermo Scientific™ $10^{13}\Omega$ Amplifier Technology™ extends the dynamic range of the Faraday Cup detectors, giving superior precision compared to $10^{11}\Omega$ amplifiers at signal intensities between several 10kcps to 10s of Mcps, related to their better signal-to-noise ratio[3].
The combination of the game-changing novel pre-cell mass filter and hexapole collision/reaction in a Thermo Scientific™ Neoma™ MS/MS MC-ICP-MS[5] with the RPQ allows an abundance sensitivity of better than 50 ppb at 1 amu for $^{238}U$. This is an order of magnitude improvement when compared to a conventional Neoma MC-ICP-MS with an RPQ.

We present Uranium isotope ratio measurements for the IRMM-183 to IRMM-187 series standard reference materials performed with improved abundance sensitivity on the Neoma MS/MS MC-ICP-MS. An amplifier with $10^{13}\Omega$ resistor was applied for the $^{234}U/^{238}U$ ratio determination and the $^{236}U/^{238}U$ measurements were recorded with a secondary electron multiplier (SEM) applying optimized RPQ settings to reduce the peak tail from $^{238}U$ to single cps.


## Introduction

Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been used to accurately and precisely measure the isotopic composition of uranium for over two decades[1-3]. Due to uranium enrichment, samples often have a wide range of potential isotopic ratios, which is a challenge for analysis. The Neoma MC-ICP-MS is the latest MC-ICP-MS which delivers on performance, with market-leading sensitivity, isotope ratio precision and accuracy. The Neoma MC-ICP-MS can be augmented with a series of proprietary technologies, including the Thermo Scientific™ Jet Interface, RPQ and $10^{13}$ Ohm Amplifier Technology which greatly enhance the capabilities of the platform for determining accurate and precise uranium isotope ratios.

The latest of these technologies is the Neoma MS/MS MC-ICP-MS. This adds a novel pre-cell mass filter and hexapole collision/reaction cell to the Neoma MC-ICP-MS.

ICP-MS/MS, such as the Thermo Scientific™ iCAP™ TQ ICP-MS, have demonstrated the utility of MS/MS technology for measuring the uranium isotopic composition. The prefilter enhances abundance sensitivity, facilitating ultralow $^{236}U/^{238}U$ measurements[4,5]. Helium can be used as collision gas within the collision/reaction cell to remove Pt-based interferences[1], or oxygen can be used as a reaction gas to measure $^{236}U^+$ free of $^{235}UH^+$ interferences[4].

## Method

The Neoma MS/MS MC-ICP-MS used was equipped with three 1013 Ω amplifiers and a single, axial, secondary electron multiplier (SEM). A $10^{13}$ Ω amplifier, which extends the operational range of the Faraday cup detector to lower values compared to the $10^{11}$ Ω amplifier was used to measure $^{234}U$ (Table 1). $^{236}U$ was measured on the central SEM, which was further equipped with an RPQ to lower the observed abundance sensitivity tailing from $^{235}U$ and $^{238}U$.

The Jet interface, combining a high efficiency interface pump with X skimmer and Jet sampler cones, was used to maximize sensitivity. All blanks, standards and samples were aspirated at an uptake rate of approximately 100 µL/min via an ESI® Apex Omega™ Q desolvating nebulizer system. Using a desolvating nebulizer system not only improved sensitivity, but by removing $H_2O$ and $HNO_3$ prior to the ICP-MS, lowered the proportion of $^{235}UH$ interferent on $^{236}U$ by nearly an order of magnitude.

The prefilter of the Neoma MS/MS was tuned to fully transmit all uranium nuclides but exclude all argon-based species, especially the large $^{40}Ar$ ion beam. No gas was added to the collision/reaction cell and all lenses therein were tuned for maximum sensitivity.

The RPQ was tuned for best possible abundance sensitivity, whilst keeping the yield of the SEM at or above 90%.

For the analysis, 20 ng/g U in 3% $HNO_3$ solutions were made for the IRMM™ series of certified reference materials (IRMM-183 to IRMM-187). Ten 3-minute replicate measurements, consisting of 45 repeats of 4 second integration time, were made for IRMM-183, IRMM-184, IRMM-185 and IRMM-187. IRMM-186 was used as the calibration standard, bracketing each analysis of the other four solutions.

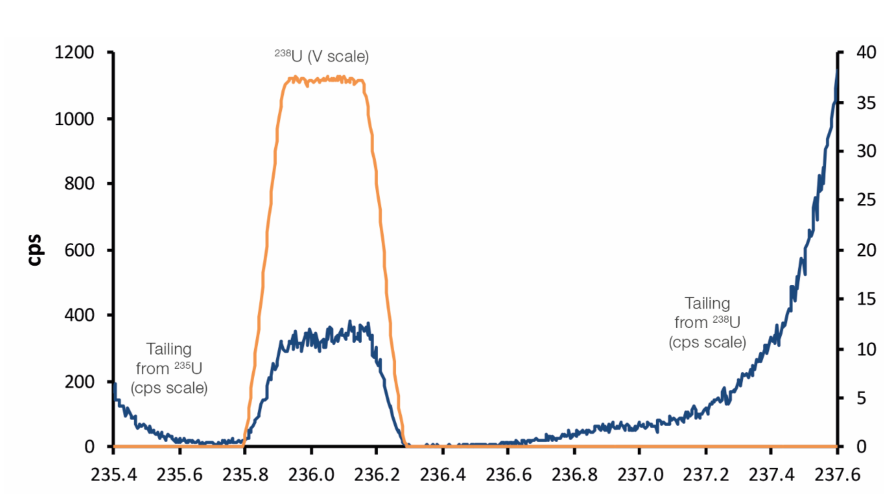
### Abundance sensitivity

The abundance sensitivity of a mass spectrometer is defined as the proportion of ions of a given mass which occur at a neighboring mass. In MC-ICP-MS, this is normally specified by the ratio of $^{238}U$ ions measured at 237.05 m/z, against those measured at 238.05 m/z. As the mass of the $^{238}U$ ions is fixed, the difference is the energy, those occurring at 237.05 m/z have less energy than expected.
By default, the Neoma MC-ICP-MS has a specified abundance sensitivity of 3 ppm at 237.05 m/z. This is more than good enough for most applications, However, $^{236}U$, which is not present in natural uranium, can often be small enough to be significantly interfered by tailing ions from $^{238}U$ and $^{235}U$.
There are ways to reduce the abundance sensitivity. Increasing the resolution is one such way, however moving from low resolution to medium or high resolution also reduces sensitivity, not ideal for measuring a low abundance isotope such as $^{236}U$.
The SEM of the Neoma MC-ICP-MS can be equipped with an RPQ, which acts to reduce tailing on that detector without reducing sensitivity.
The abundance sensitivity specification for the RPQ is 0.5 ppm at 237.05 m/z. The Neoma MS/MS MC-ICP-MS however, improves the abundance specification by a further order of magnitude to 0.05 ppm. by removing argon species, especially $^{40}Ar$, using the prefilter. The abundance tail is generated by space charge effects as the ion beam transits the mass spectrometer. By removing $^{40}Ar$, the major component of the ion beam in ICP-MS, space charge effects are reduced improving abundance sensitivity significantly.

For the 20 ng/g U solutions measured the contribution of the signal at 236.05 m/z was calculated to be just 0.6 cps from $^{238}U$. For IRMM-184, which has the composition closest to natural uranium, the abundance tailing from $^{235}U$ was calculated as 0.3 cps. This corresponded to an abundance sensitivity of 28 ppb at 1 a.m.u and just 0.25 ppb at 2 a.m.u. At less than 1 cps, the correction or abundance sensitivity has almost no impact on the accuracy of $^{236}U/^{238}U$ ratios measured.

Without the prefilter of the Neoma MS/MS MC-ICP-MS this would not necessarily be the case. For a theoretical 50 V $^{238}U$ signal we can estimate the abundance tail would generate 87 cps, 15 cps and 1.5 cps for an abundance sensitivity of 3 ppm, 0.5 ppm and 0.05 ppm (±1 a.m.u) respectively.

**Figure 1. Abundance tailing from $^{238}U$ and $^{235}U$ with the Neoma MS/MS MC-ICP-MS. The tail from $^{238}U$ has been sufficiently reduced that the previously obscured $^{235}UH_2$ peak is visible.**




### Uranium hydride and sensitivity

The major interferent on the minor $^{236}U$ isotope is $^{235}UH$. Using a desolvating nebulizer system, such as the ESI Apex Omega or Teledyne CETAC Aridus3, not only greatly enhances sensitivity in combination with the Jet Interface but greatly reduces the formation of uranium hydride by removing the water from the sample prior to introduction to the ICP.

With the reduction in abundance sensitivity by the prefilter, the uranium hydride is the most significant correction required to measure accurate $^{236}U/^{238}U$. There is a strong correlation between UO/U and UH/U, as hydrogen and oxygen are the constituents of water. During tuning of the sample introduction system, sensitivity was maximized while keeping the UO/U ratio to under 1% (Table 1). This corresponded to a $^{238}UH/^{238}U$ ratio of 1.2 x $10^5$. The uranium hydride interference may have been reduced further by the addition of either hydrogen or oxygen to the collision/reaction cell but was not implemented here. The sensitivity achieved for U was 1.16 x $10^{11}$ cps, or 1866 V/ppm. For an uptake rate of 100µL/min this gave a sample ion yield of 2.76%, or for every 10000 atoms of uranium added 276 atoms were detected.

**Table 1. Mean measured signal for each uranium isotope and uranium oxide. Uranium oxide is correlated with uranium hydride.**

| | $^{234}U$ (cps) | $^{235}U$ (cps) | $^{236}U$ (cps) | $^{238}U$ (cps) | $^{238}U$ (cps) | UO/U (%) |
|---|---|---|---|---|---|---|
| IRMM-183 | 4.10E+04 | 6.64E+06 | 2.75E+05 | 2.09E+09 | 2.57E+07 | 1.2 |
| IRMM-184 | 1.34E+05 | 1.83E+07 | 2.66E+02 | 2.55E+09 | 2.24E+07 | 0.9 |
| IRMM-185 | 3.79E+05 | 4.25E+07 | 5.47E+03 | 2.14E+09 | 2.02E+07 | 0.9 |
| IRMM-186 | 6.57E+05 | 6.90E+07 | 6.71E+04 | 2.27E+09 | 2.29E+07 | 1.0 |
| IRMM-187 | 8.58E+05 | 1.05E+08 | 1.43E+05 | 2.25E+09 | 2.09E+07 | 0.9 |

## Results

For all four sample materials the measured precision for $^{235}U/^{238}U$ was better than 0.01% RSD. The greater the $^{235}U$ enrichment, the more precise the $^{235}U/^{238}U$ ratio measurement, inline with expected performance from counting statistics. The relative difference (RD) of the measured $^{235}U/^{238}U$ ratios to the certified values,6 were all less than 0.020% (IRMM-183 0.007%, IRMM-184 0.018%, IRMM-185 0.000%, IRMM-187 -0.001%), see Table 2.

The first minor ratio, $^{234}U/^{238}U$, with $^{234}U$ measured using $10^{13}$ Ω amplifier technology, precision also improved across the IRMM series, as the $^{234}U$ signal intensity increased in tandem with the $^{235}U$ signal intensity. The RD to the certified values was also correlated to higher signal intensity, the RD measured for IRMM-183, 0.59% was much greater than the 0.03% achieved for IRMM-187 (Table 2).

The smallest $^{234}U$ signal intensity measured, for IRMM-183, was significantly smaller than the measured $^{236}U$ signal intensity for IRMM-183 and IRMM-187. This overlap in signal intensity allows some comparisons to be made between SEM/RPQ and $10^{13}$ Ω amplifier technology. Theoretically, the isotope ratio precision which can be achieved with SEM/RPQ and $10^{13}$ Ω amplifiers should overlap at a single intensity of approximately 1,000,000 cps, a signal intensity greater than any achieved here for either $^{234}U$ or $^{236}U$. However, experimentally, our results demonstrate an overlap in isotope ratio precision at a much lower signal intensity, somewhere between 1 – 2 mV (62,414 – 124,818 cps). Signal intensities less than 1 mV can still be measured to high isotope ratio precision with $10^{13}$ Ω amplifier technology, the $^{234}U$ signal intensity was just 42,000 cps, and could be even less[3].

However, as the signal level approaches 0, such as the less than 300 cps $^{236}U$ measured for IRMM-184, the SEM/RPQ is the far superior choice of detector, not only for isotope ratio precision, but also accuracy.

The second minor ratio, $^{236}U/^{238}U$, with $^{236}U$ measured on the SEM/RPQ, had the lowest abundance measured. IRMM-184 was the most challenging, with a certified $^{236}U/^{238}U$ ratio of 1.24 x $10^{-7}$. After correcting for 235UH⁺ the measured $^{236}U/^{238}U$ was 1.18 x $10^{-7}$, a RD of -4.92% to the certified value (Table 2). The isotope ratio precision was better than 1%. The RD for $^{236}U/^{238}U$ decreased as signal intensity increased (IRMM-183 0.05%, IRMM-185 -0.83%, IRMM-187 -0.05%), see Table 2.

**Table 2. Measured and certified $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236/238}U$ ratios in IRMM-183, IRMM-184, IRMM-185, IRMM-187, including the achieved accuracy**

| | Measured | | | Certified[6] | | | Accuracy (Relative Difference, RD) | | |
|---|---|---|---|---|---|---|---|---|---|
| | $^{234}U/^{238}U$ | $^{235}U/^{238}U$ | $^{236}U/^{238}U$ | $^{234}U/^{238}U$ | $^{235}U/^{238}U$ | $^{236}U/^{238}U$ | $^{234}U/^{238}U$ | $^{235}U/^{238}U$ | $^{236}U/^{238}U$ |
| IRMM-183 | 0.00001993 | 0.0032185 | 0.000148500 | 0.000019814 | 0.00321826 | 0.000148492 | 0.59% | 0.007% | 0.005% |
| IRMM-184 | 0.00005334 | 0.0072644 | 0.000000118 | 0.000053196 | 0.00726310 | 1.24100E-07 | 0.27% | 0.018% | -4.915% |
| IRMM-185 | 0.00017980 | 0.0200659 | 0.000002883 | 0.000179659 | 0.02006590 | 0.000002907 | 0.08% | 0.000% | -0.826% |
| IRMM-187 | 0.00038740 | 0.0473425 | 0.000072010 | 0.000387298 | 0.04734300 | 0.000072049 | 0.03% | -0.001% | -0.054% |

**Figure 2. Uranium isotope rations for IRMM-184. Solid line = mean, dotted line = SD. A) $^{234}U/^{238}U$, B) $^{235}U/^{238}U$, C) $^{236}U/^{238}U$. $^{234}U$ = $10^{13}$ Ω, $^{235}U$ = $10^{11}$ Ω, $^{236}U$ = IC/RPQ.**

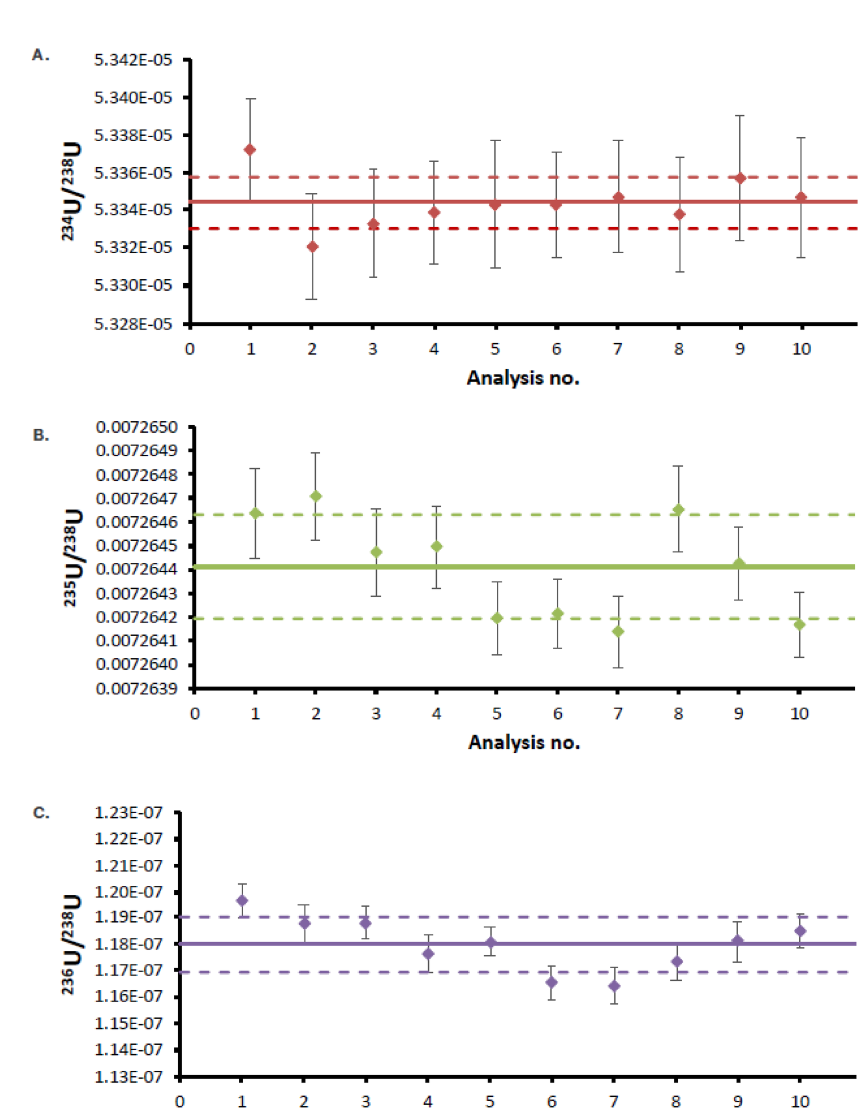
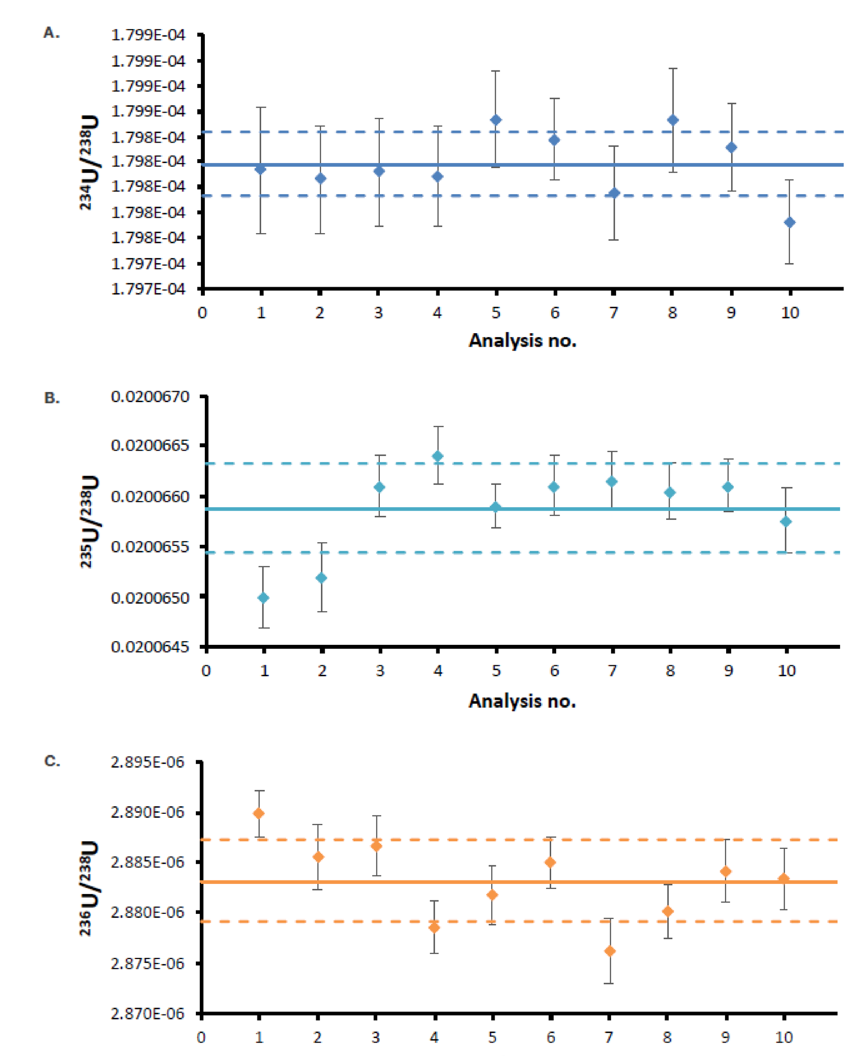
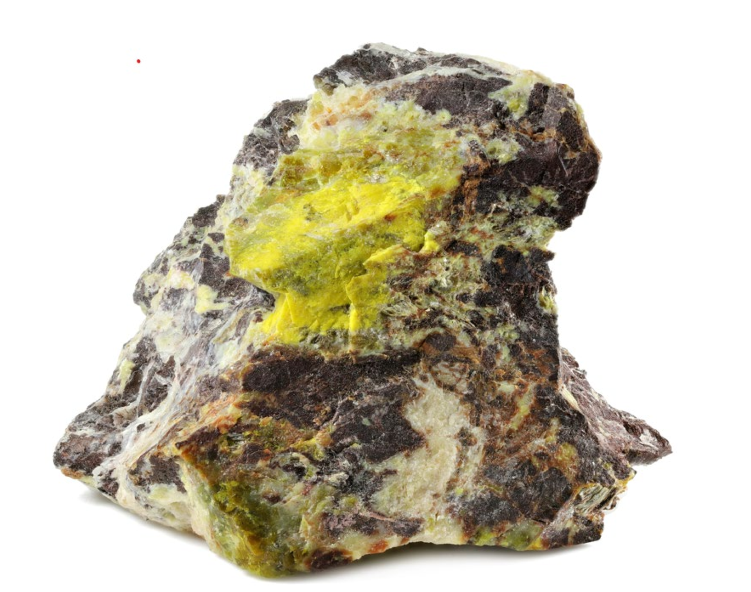



**Figure 3. Uranium isotope rations for IRMM-185. Solid line = mean, dotted line = SD. A) $^{234}U/^{238}U$, B) $^{235}U/^{238}U$, C) $^{236}U/^{238}U$. $^{234}U$ = $10^{13}$ Ω, $^{235}U$ = $10^{11}$ Ω, $^{236}U$ = IC/RPQ.**




## Conclusions

The Neoma and Neoma MS/MS MC-ICP-MS have unique features, such as enhanced abundance sensitivity, low hydride formation, as well as low noise amplifiers that enable precise and accurate analysis of major and minor isotopes in the IRMM-183-187 series.




## References

1. K. Yamamoto, O. Takeshi, G. Kitamura, H. Takahashi, and T.Hirata, Environmental Technology & Innovation., 2024,36, 103761–103769.
2. S. F. Boulyga, A. Koepf, S. Konegger-Kappel, Z. Macsik and G. Stadelmann, J. Anal. At. Spectrom., 2016, 31,2272-2284.
3. N. A. Zirakparvar, B. Manard, C. Hexel, D. Dunlap, S.Metzger, D. Bostick, V. Bradley, B. Ticknor, International Journal of Mass Spectrometry, 2023, 492, 117114-117123.
4. M. Tanimizu, N. Sugiyama, E. Ponzevera and G. Bayon, J.Anal. At. Spectrom., 2013, 28, 1372–1376.
5. G. Craig, H. Wehrs, D. G. Bevan, M. Pfeifer, J. Lewis, C. D. Coath, T. Elliott., C. Huang, N. S. Lloyd and J. B.Schwieters, Anal. Chem., 2021, 93, 10519-10527.



## Trademarks/licensing

© 2025 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified. ESI and Apex Omega are trademarks of Elemental Scientific Inc. IRMM is a trademark of The European Union, represented by the European Commission. Teledyne Cetac and Aridus3 are trademarks of Teledyne Instruments, Inc. This information is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others. **PO-003519 EN 0125**


**Science at a scan**
Scan the QR code on the right with your mobile device to find out more about MC-ICP-MS.

Learn more at thermofisher.com/msms