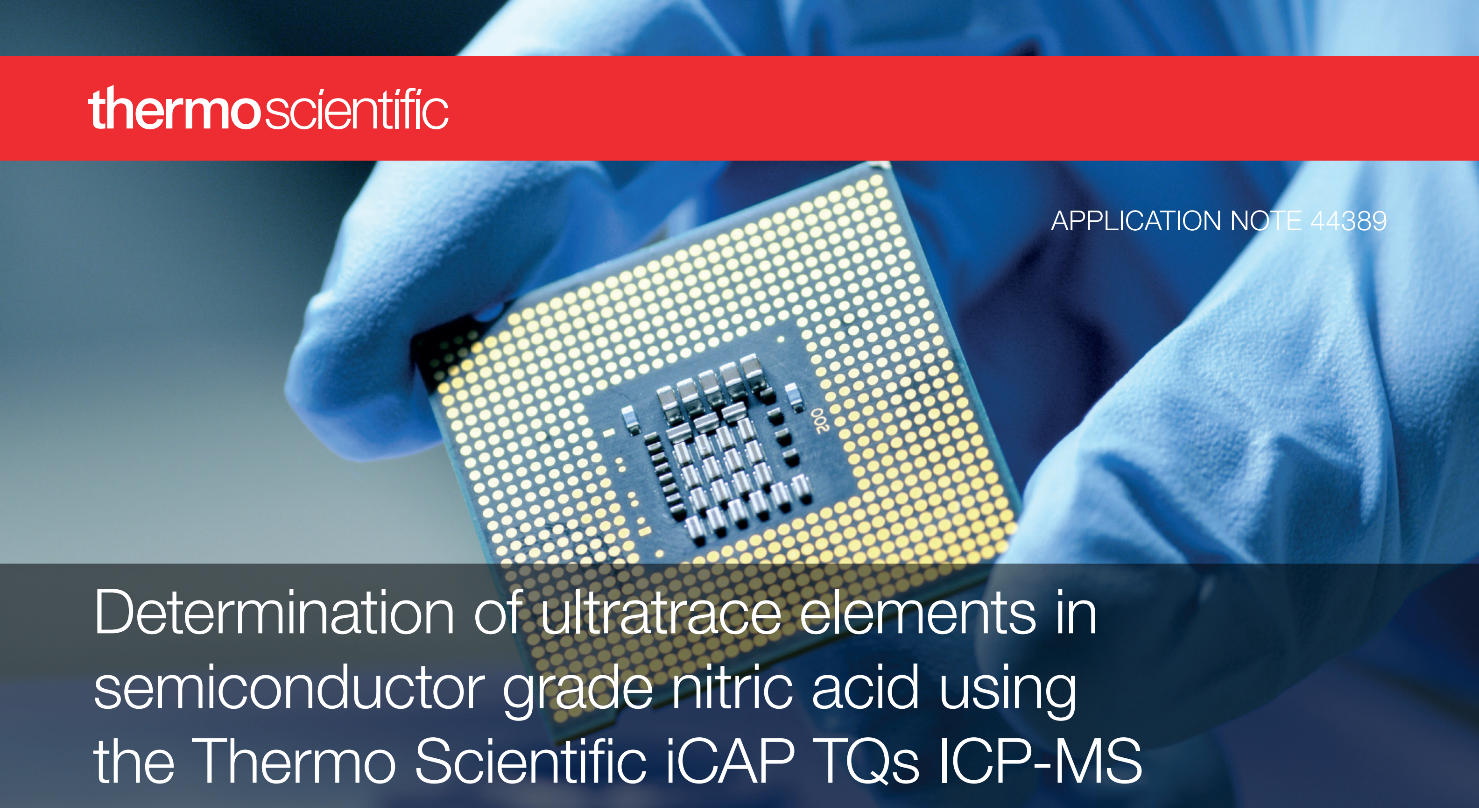

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APPLICATION NOTE 44389

Determination of ultratrace elements in semiconductor grade nitric acid using the Thermo Scientific iCAP TQs ICP-MS

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iCAP TQs, Semiconductor,
Triple quadrupole, Ultratrace

Goal

To demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS for performing reproducible ultratrace ng·L^{-1} (ppt) measurements of semiconductor relevant elements in nitric acid with reliable switching between multiple analysis modes (hot/cold plasma, single/triple quadrupole) within a single measurement.

Introduction

The continually growing demand for advanced electronic devices is driving the need to improve production efficiencies and increase yield in the semiconductor wafer manufacturing industry. Control of the wafer fabrication process, manufacturing environment, chemical reagent purity and level of wafer surface contamination are of the utmost importance for improving yield. Elemental impurities in the often complex and aggressive chemicals used in semiconductor manufacturing are generally below 10 ng·L^{-1} and demand for sensitive, accurate quality control is growing.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is a powerful technique for the analysis of ultratrace elements in semiconductor manufacturing support or high purity chemical production applications (for example, incoming supplier or process control). The iCAP TQs ICP-MS is equipped with a high transmission interface and an inert sample introduction system to achieve the high intensity signals and low backgrounds required for sub ng·L^{-1} concentration determinations in complex matrix samples. The iCAP TQs ICP-MS leverages powerful triple quadrupole technology for improved interference removal, robust in-sample switching between hot and cold plasma conditions, in a small, compact package which, with a dry fore-vacuum pump, is ideally suited for operation in clean room environments.

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The iCAP TQs ICP-MS, as part of the Thermo Scientific iCAP Qnova Series, is controlled by the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software that includes a unique method development tool, Reaction Finder, which automatically selects the appropriate analysis mode for each target analyte. In this application note, cold plasma, kinetic energy discrimination and triple quadrupole ICP-MS technologies are combined within a single analytical method for the ultratrace elemental analysis of semiconductor grade HNO_3. Through the use of cold plasma, the ICP ion source is run at a significantly lower RF power leading to a decrease in ionization efficiency that limits the formation of background argon and some sample matrix based interferences. For analytes that are more sensitive under hot plasma conditions, the QCell collision reaction cell was either filled with He for kinetic energy discrimination (He KED) or with a reactive gas (H_2, NH_3 or O_2) for a triple quadrupole based analysis.

Instrumentation

An iCAP TQs ICP-MS was used for all measurements. The sample introduction system used consisted of a quartz glass cyclonic spraychamber, a PFA 100 μL·min^{-1} self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) and a quartz torch with a 2.0 mm i.d. removable sapphire injector. Platinum tipped sampler and skimmer cones with a cold plasma extraction lens were used. The iCAP TQs ICP-MS was equipped with a dry fore-vacuum pump for compatibility with clean room environments. The iCAP TQs ICP-MS used in this study was not installed in a cleanroom.

The instrument was operated in three single quadrupole (SQ) ICP-MS modes:

- CH-SQ-N/A: hot plasma
- CL-SQ-N/A: cold plasma
- CH-SQ-KED: hot plasma with He KED

And three triple quadrupole (TQ) modes:

- CL-TQ-H_2: cold plasma, on mass with H_2/He
- CL-TQ-NH_3: cold plasma, on mass with NH_3
- CH-TQ-O_2: hot plasma, mass shift or on mass with O_2

Table 1 summarizes the instrument configuration and operating parameters used. Measurement modes were optimized using the default autotune procedures in the Qtegra ISDS Software.

Table 1. Instrument configuration and operating parameters.

Parameter	Value					
Nebulizer	PFA concentric, 100 μL·min^{-1} (self-aspirating)					
Spraychamber	Quartz, cyclonic, peltier cooled at 2.7 °C					
Injector	2.0 mm i.d., sapphire					
Interface	Pt sampler and Pt skimmer high sensitivity type					
Extraction lens	Cold plasma					
Measurement mode	Single quadrupole mode			Triple quadrupole mode		
	CH-SQ-N/A	CL-SQ-N/A	CH-SQ-KED	CL-TQ-H_2	CL-TQ-NH_3	CH-TQ-O_2
Forward power	1550 W	580 W	1550 W	580 W	580 W	1550 W
Nebulizer gas	1.01 L·min^{-1}	0.98 L·min^{-1}	1.01 L·min^{-1}	0.98 L·min^{-1}	0.98 L·min^{-1}	1.01 L·min^{-1}
CRC gas	-	-	Pure He, 4.2 mL·min^{-1}	10% H_2 in He, 7.0 mL·min^{-1}	Pure NH_3, 0.2 mL·min^{-1}	Pure O_2, 0.4 mL·min^{-1}
Dwell time	100 to 300 ms per analyte, 5 sweeps					

Sample preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ cm) and left to dry in a laminar flow clean hood before use. Samples of 2% (v/v) HNO_3 were prepared from semiconductor grade nitric acid (Fisher Scientific Optima™). Standards at concentrations of 10, 25, 50 and 100 $ng \cdot L^{-1}$ were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (SPEX CertiPrep™) directly to aliquots of the 2% HNO_3 samples. Semiconductor grade nitric acid was used for the rinse and blank solutions.

Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system (Figure 1) is a powerful analytical tool for multi-element analysis in semiconductor (or any other high purity chemical) samples. By providing the analyst with unlimited flexibility of ICP-MS technologies (cold plasma, kinetic energy discrimination or triple quadrupole), the ultimate performance can be achieved, specifically tailored for each application.

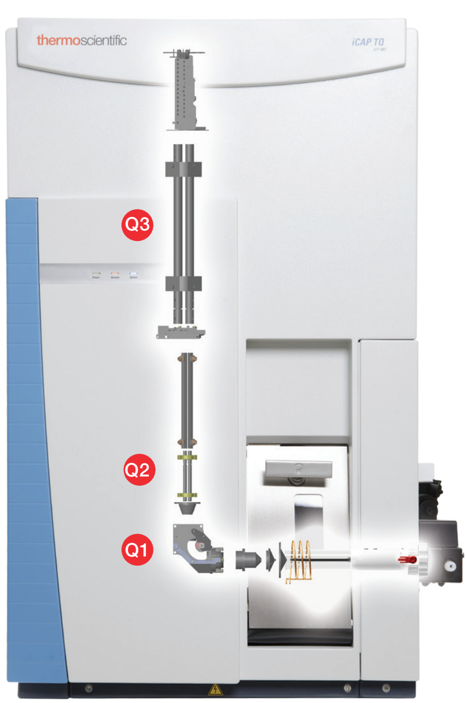


Figure 1. Thermo Scientific iCAP TQs ICP-MS.

For example, using the CH-TQ-O_2 mass shift mode (schematically shown in Figure 2), the first quadrupole (Q1) uses intelligent mass selection (iMS) to reject unwanted ions. The second quadrupole (Q2) selectively shifts the V^+ target analyte to the $[VO]^+$ product ion using O_2 as the reaction gas, while the ClO^+ interference ions do not react with O_2. The third quadrupole (Q3) isolates the $[VO]^+$ product ions and removes any remaining interferences through a second stage of mass filtration to achieve a completely interference free analysis. The advantage of the CH-TQ-O_2 mass shift mode over the use of CH-SQ-KED (He KED as used in single quadrupole ICP-MS) for the analysis of ^{51}V can be seen in Figure 3 where the use of CH-TQ-O_2 mode on the Thermo Scientific iCAP TQs ICP-MS enables significantly lower background equivalent concentration (BEC) and detection limits (LOD).

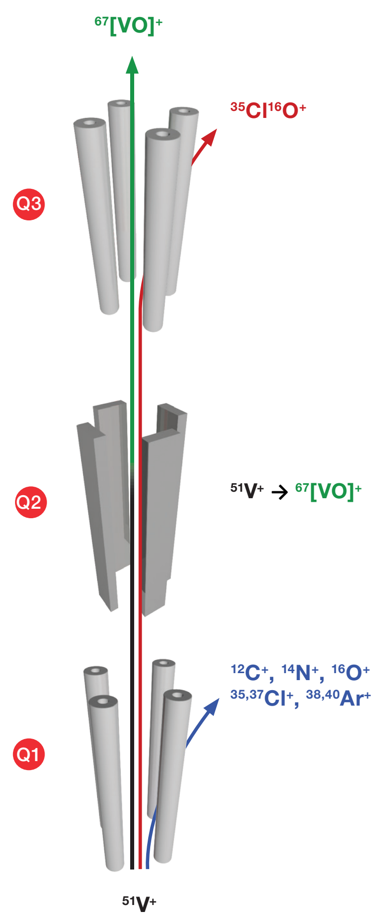
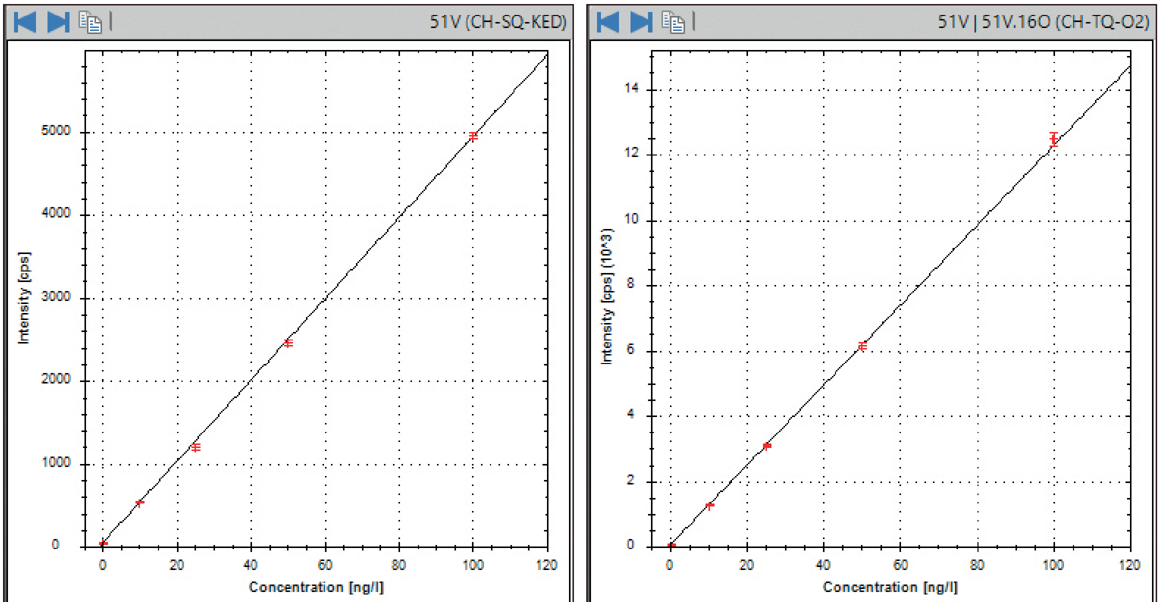


Figure 2. Schematic showing CH-TQ-O_2 mass shift analysis of ^{51}V.



f(x) = b*x + a (51V, CH-SQ-KED)

Parameter	Value	Confidence Delta a	StdErr	Rel. StdErr [
b	49.0	N/A	N/A	N/A
a	43.8	N/A	N/A	N/A
R²	0.99961			
BEC	0.894 ng/l			
IDL(LOD)	0.534 ng/l			
RSE	3.9 %			

f(x) = b*x + a (51V | 51V.16O, CH-TQ-O2)

Parameter	Value	Confidence Delta a	StdErr	Rel. StdErr [
b	122.0	N/A	N/A	N/A
a	54.1	N/A	N/A	N/A
R²	0.99952			
BEC	0.444 ng/l			
IDL(LOD)	0.016 ng/l			
RSE	1.7 %			

Figure 3. Comparison of calibration curves for ^{51}V in CH-SQ-KED and CH-TQ-O_2 mass shift modes. Through the use of CH-TQ-O_2 mass shift mode based analysis, instrumental sensitivity increases and BEC and LODs are significantly decreased.

In this second example, calcium (^{40}Ca) is analyzed in cold plasma using CL-TQ-H_2 mode on mass analysis (shown schematically in Figure 4). At the low RF powers used in cold plasma the overall ionization efficiency of the ICP is decreased, limiting the formation of ^{40}Ar that would otherwise interfere with ^{40}Ca. Any remaining ^{40}Ar is removed in the second quadrupole (Q2) through reaction with H_2 that also removes any Na or water cluster based polyatomic interferences. The third quadrupole (Q3) finally isolates the ^{40}Ca target ion free from interference. The advantage of a CL-TQ-H_2 mode on mass analysis over the use of CL-SQ-NH_3 (cold plasma / NH_3 reaction mode as used in single quadrupole ICP-MS) for the analysis of ^{40}Ca can be seen in Figure 5 where the use of CL-TQ-H_2 mode on the Thermo Scientific iCAP TQs ICP-MS enables significantly lower BEC and LOD.

BEC and LOD, based on three times the standard deviation of ten replicate measurements of the calibration blank, were determined for 44 elements in 2% HNO_3 (Table 2). Sub ng·L^{-1} detection limits were obtained for all 44 elements.

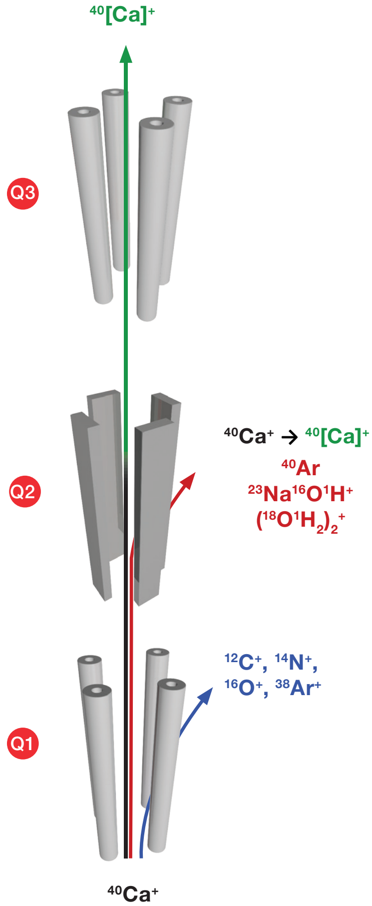
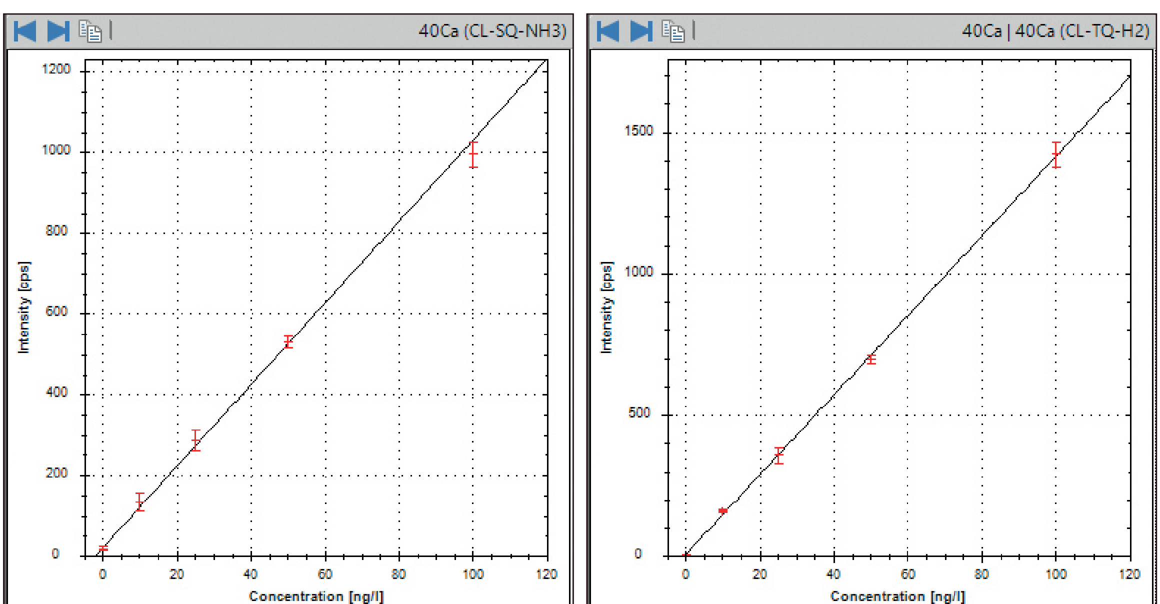


Figure 4. Schematic showing CH-TQ-H_2 on mass analysis of ^{40}Ca.



f(x) = b*x + a

Parameter	Value	Confidence Delta a	StdErr	Rel. StdErr [
b	10.1	N/A	N/A	N/A
a	18.8	N/A	N/A	N/A
R²	0.99727			
BEC	1.861 ng/l			
IDL(LOD)	1.775 ng/l			
RSE	10.4 %			

f(x) = b*x + a

Parameter	Value	Confidence Delta a	StdErr	Rel. StdErr [
b	14.1	N/A	N/A	N/A
a	4.6	N/A	N/A	N/A
R²	0.99969			
BEC	0.328 ng/l			
IDL(LOD)	0.084 ng/l			
RSE	7.3 %			

Figure 5. Comparison of calibration curves for ^{40}Ca in CL-SQ-NH_3 and CL-TQ-H_2 on mass modes. Through the use of CL-TQ-H_2 on mass mode based analysis, instrumental sensitivity increases and BEC and LODs are significantly decreased.

Table 2. LOD and BEC data for the analysis of 44 elements in 2% semiconductor grade HNO_3. Please note that BEC and LOD values are dependent on the sample measured.

Analyte	Analysis mode	LOD ($ng \cdot L^{-1}$)	BEC ($ng \cdot L^{-1}$)
^{7}Li at 7 *m/z*	CL-TQ-H_2	0.01	0.01
^{9}Be	CH-SQ-N/A	0.04	0.18
^{11}B	CH-SQ-N/A	0.63	4.98
^{23}Na at 23 *m/z*	CL-TQ-H_2	0.05	0.24
^{24}Mg at 24 *m/z*	CL-TQ-H_2	0.06	0.07
^{27}Al at 27 *m/z*	CL-TQ-H_2	0.03	0.93
^{39}K at 39 *m/z*	CL-TQ-H_2	0.20	0.74
^{40}Ca at 40 *m/z*	CL-TQ-H_2	0.08	0.33
^{45}ScO at 61 *m/z*	CH-TQ-O_2	0.16	0.48
^{48}Ti at 64 *m/z*	CH-TQ-O_2	0.04	0.90
^{51}VO at 67 *m/z*	CH-TQ-O_2	0.02	0.44
^{52}Cr	CL-SQ-N/A	0.59	0.17
^{56}Fe at 56 *m/z*	CL-TQ-NH_3	0.63	0.55
^{59}Co at 59 *m/z*	CL-TQ-H_2	0.02	0.02
^{60}Ni at 60 *m/z*	CL-TQ-H_2	0.21	0.32
^{63}Cu at 63 *m/z*	CL-TQ-H_2	0.09	0.20
^{66}Zn	CL-SQ-N/A	0.66	0.39
^{71}Ga at 71 *m/z*	CL-TQ-H_2	0.01	0.01
^{74}Ge at 74 *m/z*	CH-TQ-O_2	0.39	0.34
^{75}As at 91 *m/z*	CH-TQ-O_2	0.15	0.60
^{80}Se at 96 *m/z*	CH-TQ-O_2	0.11	0.21
^{85}Rb at 85 *m/z*	CL-TQ-H_2	0.02	0.01
^{88}Sr	CH-SQ-KED	0.36	0.22
^{89}Y at 105 *m/z*	CH-TQ-O_2	0.02	0.01
^{90}Zr	CH-SQ-KED	0.04	0.01
^{93}Nb	CH-SQ-KED	0.05	0.02
^{98}Mo at 114 *m/z*	CH-TQ-O_2	0.76	0.57
^{101}Ru	CH-SQ-KED	0.13	0.03
^{103}Rh	CH-SQ-KED	0.08	0.19
^{107}Ag	CH-SQ-KED	0.17	0.36
^{111}Cd	CH-SQ-KED	0.83	0.45
^{115}In at 115 *m/z*	CL-TQ-NH_3	0.06	0.28
^{121}Sb	CH-SQ-KED	0.13	0.02
^{138}Ba	CH-SQ-KED	0.13	0.14
^{178}Hf	CH-SQ-KED	0.03	0.01
^{181}Ta	CH-SQ-KED	0.01	0.01
^{184}W	CH-SQ-KED	0.08	0.05
^{195}P at 195 *m/z*	CH-TQ-O_2	0.19	0.30
^{197}Au	CH-SQ-KED	0.08	0.03
^{202}Hg	CH-SQ-N/A	0.20	0.27
^{205}Tl	CH-SQ-KED	0.10	0.14
^{208}Pb	CH-SQ-KED	0.15	0.31
^{209}Bi	CH-SQ-KED	0.04	0.03
^{238}U	CH-SQ-KED	0.003	0.004

Conclusion

The iCAP TQs ICP-MS has been shown to provide sensitive and accurate multielemental analysis of semiconductor grade HNO_3 at ultratrace ($ng \cdot L^{-1}$) concentration levels. The combination of single and triple quadrupole technologies with or without cold plasma provides the flexibility to deliver optimum conditions for all analytes to reduce background equivalent concentrations and achieve excellent detection limits.

The reliable switching of the iCAP TQs ICP-MS between multiple analysis modes enables smooth transition between hot and cold plasma modes and single or triple quadrupole modes within a single measurement, improving ease of use and productivity.

Find out more at **thermofisher.com/TQ-ICP-MS**

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