



# Thermo Scientific iCAP TQ ICP-MS: Typical limits of detection

## Authors

Tomoko Vincent

## Keywords

BEC, LOD, SQ-KED, TQ mass shift,  
TQ on mass, typical performance

## Introduction

Inductively Coupled Plasma – Mass Spectrometry is a powerful technique for the analysis of trace elements in many application areas such as environmental analysis, food safety testing and clinical research. The main reasons to choose ICP-MS are its low limits of detection combined with an extended linear dynamic range and the ability to analyze varying sample matrices without suffering from extensive matrix effects. The Thermo Scientific™ iCAP™ TQ ICP-MS has been designed to deliver these characteristics while also offering the greatest ease of use and the simplest method development.

Detection limits are a set of key performance indicators demonstrating an instrument's capabilities and are useful as an aid in determining that instrument's suitability for a specific analysis. They demonstrate the lowest level of analyte distinguishable from the background noise under optimal conditions and are typically determined several times for statistical accuracy.

The iCAP TQ ICP-MS has expanded capabilities when compared to single quadrupole (SQ) ICP-MS systems. This is based on more selective isolation of the analyte and controlled reaction chemistries in the collision/reaction cell (CRC). The iCAP TQ ICP-MS also has the ability to operate in SQ mode when advanced interference removal is not required. For many analytes in routine analysis, measurement with a CRC and Kinetic Energy Discrimination (KED) mode is sufficient.

This technical note demonstrates typical performance and limits of detection (LODs) using SQ modes and triple quadrupole (TQ) modes for more challenging interferences using the iCAP TQ ICP-MS.

## Limits of Detection

Detection limits can be defined as either the Instrument Detection Limit (IDL) or the Method Detection Limit (MDL), and are accompanied by the Background Equivalent Concentration (BEC). The IDL defines the lowest concentration of an analyte that can be detected under ideal conditions by the instrument, and is normally measured on a single element basis using a clean sample (e.g. using ultrapure 2% nitric acid matrix).

The MDL, in comparison, determines the lowest level of analyte that can be detected in a sample matrix using the proposed method of analysis and takes into account sample preparation steps. This is usually determined on a multi-element basis by diluting standard solutions to concentration levels that can no longer be accurately read, or by adding a low concentration spike into a real sample. There are numerous procedures for determining and calculating the MDL, but most methods require numerous analytical runs, over several days, to ensure a realistic determination of instrument performance.

In this document, detection limits were calculated using the raw intensity data from the standard and the blank as per the following equation:

$$IDL = 3SD_{blk} \times \frac{STD_{conc}}{STD_x - BLK_x}$$

Where:

IDL is the instrument detection limit

$SD_{blk}$  is the standard deviation of the intensities of the multiple blank measurements

$STD_x$  is the mean signal for the standard

$BLK_x$  is the mean signal for the blank

$STD_{conc}$  is the concentration of the standard

## Sample preparation

All solutions were prepared in freshly rinsed vials. To determine typical IDLs in SQ (SQ-STD and SQ-KED) mode, standards at concentrations of 0 (blank), 0.2, 5 and 10  $\mu\text{g}\cdot\text{L}^{-1}$  were prepared gravimetrically by adding the appropriate quantity of a multi-elemental stock solution (SPEX CertiPrep) directly to 2% m/m  $\text{HNO}_3$  (65%  $\text{HNO}_3$  Optima™ grade, Fisher Chemicals) and 0.5% m/m HCl (32-35% HCl Optima™ grade, Fisher Chemical).

## Instrumentation

An iCAP TQ ICP-MS was used for all measurements (N.B. the instrument was not installed in a clean room). The sample introduction system used consisted of a Peltier cooled (2.7 °C), baffled cyclonic quartz spraychamber, a concentric nebulizer and quartz torch with a 2.5 mm i.d. removable quartz injector. A Ni sampler and Ni skimmer with a default 2.8 mm insert was used.

The instrument was operated in SQ-KED with pure He gas mode and three different TQ modes using pure  $\text{NH}_3$  (TQ- $\text{NH}_3$ ), pure  $\text{H}_2$  (TQ- $\text{H}_2$ ) and pure  $\text{O}_2$  (TQ- $\text{O}_2$ ). All samples were presented for analysis using a Teledyne CETAC™ ASX-560 Autosampler.

Table 1 summarizes the configuration and operating parameters. Measurement modes were optimized using the default autotune procedures in Thermo Scientific™ Qtegra™ Intelligent Scientific Data System™ (ISDS) Software.

**Table 1. Instruments configuration and operating parameters.**

Parameter	Value				
Nebulizer	MicroMist Borosilicate Concentric nebulizer 0.4 mL·min <sup>-1</sup> , pumped at 40 rpm				
Spraychamber	Quartz cyclonic spraychamber cooled at 2.7 °C				
Injector	2.5 mm id, Quartz				
Interface	High Sensitivity (2.8 mm), Ni cones				
RF Power	1550 W				
Nebulizer Gas Flow	0.9998 mL·min <sup>-1</sup>				
	SQ-STD	SQ-KED	TQ-NH <sub>3</sub>	TQ-O <sub>2</sub>	TQ-H <sub>2</sub>
Gas Flow	-	4.5 mL·min <sup>-1</sup>	0.29 mL·min <sup>-1</sup>	1.2 mL·min <sup>-1</sup>	10.5 mL·min <sup>-1</sup>
CR Bias	-2	-21 V		-7.9 V	
Q3 Bias	-1	-18 V		-11 V	
Scan Settings	0.3 s dwell time per analyte, 5 sweeps				

## Results

### SQ Measurement Modes

The typical performance of the iCAP TQ ICP-MS using SQ-STD and SQ-KED mode are shown in Table 2.

Table 2. Typical BEC and IDL in SQ-STD and SQ-KED mode. All results are reported in ng·L<sup>-1</sup>.

	SQ-STD		SQ-KED	
	IDL	BEC	IDL	BEC
<sup>9</sup> Be	0.05	<0.01	0.10	<0.01
<sup>39</sup> K	822	34552	421	7680
<sup>44</sup> Ca	1698	62536	60	190
<sup>48</sup> Ti	1.3	14	1.4	0.7
<sup>51</sup> V	721	6459	2.3	35
<sup>52</sup> Cr	24	580	2.5	18
<sup>55</sup> Mn	4.2	86	1.1	1.8
<sup>56</sup> Fe	4641	60838	7	37
<sup>59</sup> Co	0.7	3.6	0.3	0.3
<sup>65</sup> Cu	4.1	27	1.5	3.9
<sup>66</sup> Zn	8.0	91	5.2	9.6
<sup>75</sup> As	85	2328	2.2	2.3
<sup>78</sup> Se	83	2564	20	12
<sup>89</sup> Y	0.06	0.19	0.06	0.01
<sup>111</sup> Cd	0.9	3.3	0.13	0.02
<sup>115</sup> In	0.08	0.49	0.09	0.52
<sup>139</sup> La	0.03	0.02	0.02	0.02
<sup>140</sup> Ce	0.03	0.05	0.05	0.06
<sup>141</sup> Pr	0.02	0.01	0.02	<0.01
<sup>144</sup> Nd	0.03	0.03	0.06	0.02
<sup>149</sup> Sm	0.06	0.01	0.04	<0.01
<sup>153</sup> Eu	0.01	<0.01	<0.01	<0.01
<sup>157</sup> Gd	0.10	0.03	0.08	0.03
<sup>159</sup> Tb	0.01	<0.01	<0.01	<0.01
<sup>163</sup> Dy	0.01	<0.01	0.02	<0.01
<sup>165</sup> Ho	<0.01	<0.01	<0.01	<0.01
<sup>166</sup> Er	0.01	<0.01	0.01	<0.01
<sup>169</sup> Tm	<0.01	<0.01	<0.01	<0.01
<sup>172</sup> Yb	0.01	<0.01	<0.01	<0.01
<sup>175</sup> Lu	<0.01	<0.01	0.01	<0.01
<sup>209</sup> Bi	0.04	0.04	0.05	0.02
<sup>232</sup> Th	0.03	0.02	0.04	0.04
<sup>238</sup> U	0.02	0.01	0.01	<0.01

## TQ Measurement Modes

The iCAP TQ ICP-MS consists of three quadrupoles to improve interference removal when compared to single quadrupole (SQ) ICP-MS. The first quadrupole (Q1) rejects all unwanted ions (such as precursor species that may recombine in the CRC and subsequently interfere with the target analyte).

The second quadrupole (Q2) is used to selectively shift the interference or target analyte with an appropriate (CRC) gas.

The third quadrupole (Q3) isolates the product ion and removes any remaining interferences through a second stage of mass filtration allowing for interference free analysis of the analyte. (Figure 1)

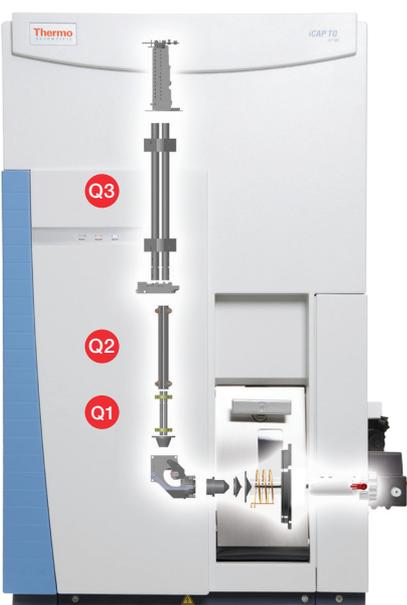


Figure 1. iCAP TQ ICP-MS.

The standard gases that are compatible with the iCAP TQ ICP-MS are He (collision gas) and  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{H}_2$  (reaction gases). As all of these gases can be used in a single method, the best limits of detection can be achieved for all analytes in one analytical run.

### TQ- $\text{O}_2$ mode

Oxygen reaction mode can be used in mass shift or on mass mode for analytes or interferences respectively that preferentially oxidize.

In the first example, arsenic in cobalt matrix is analyzed in TQ- $\text{O}_2$  mass shift mode. Arsenic undergoes reaction with  $\text{O}_2$  in the Q2 CRC and the  $\text{AsO}^+$  product ion formed at  $m/z$  91 is isolated from  $\text{CoO}^+$  in Q3 for measurement. The limitation of SQ-ICP-MS, due to the  $\text{CoO}^+$  interference on  $m/z$  75 can be seen in Table 3. Although SQ-KED can be used effectively for some polyatomic interferences, energy discrimination is not sufficient to completely remove the  $\text{CoO}^+$ , resulting in a BEC of over  $7.9 \mu\text{g}\cdot\text{L}^{-1}$ . In TQ- $\text{O}_2$  mode, the interference removal was improved such that a BEC of  $18 \text{ ng}\cdot\text{L}^{-1}$  and the successful calibration of  $0.2$ ,  $5$  and  $10 \mu\text{g}\cdot\text{L}^{-1}$  As as  $\text{AsO}^+$  was achieved (Figure 2).

Table 3. Comparison of arsenic results in the  $10 \text{ mg}\cdot\text{L}^{-1}$  Co matrix with different measurement modes.

Matrix	Polyatomic interference	SQ-KED		TQ- $\text{O}_2$	
		BEC	IDL	BEC	IDL
Co $10 \text{ mg}\cdot\text{L}^{-1}$	CoO	$7.963 \mu\text{g}\cdot\text{L}^{-1}$	$0.330 \mu\text{g}\cdot\text{L}^{-1}$	$18 \text{ ng}\cdot\text{L}^{-1}$	$8.0 \text{ ng}\cdot\text{L}^{-1}$

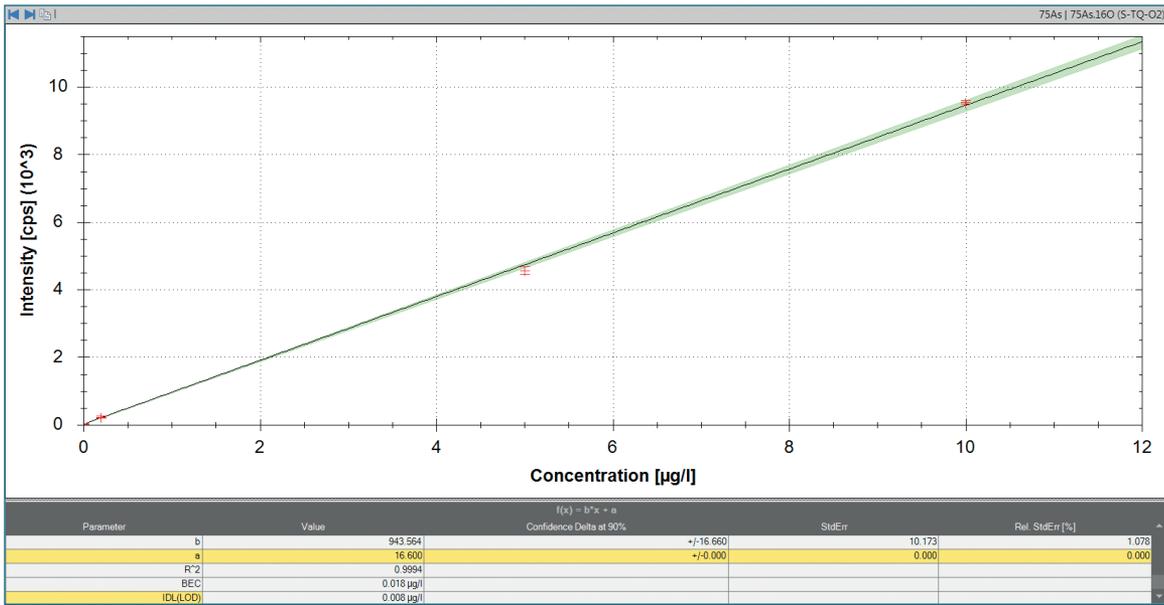


Figure 2. Calibration curve of  $^{75}\text{As}^{16}\text{O}^+$  in  $10 \text{ mg}\cdot\text{L}^{-1}$  Co with TQ- $\text{O}_2$  mode.

In the second example, cadmium in a molybdenum matrix is analyzed in TQ- $\text{O}_2$  on mass mode. Mo is preferentially oxidized in the Q2 CRC to higher oxides, whilst the cadmium is not oxidized and is therefore isolated in Q3 at the original isotope  $m/z$ . Figure 3 shows the standard calibration curve for Cd in  $10 \text{ mg}\cdot\text{L}^{-1}$  Mo matrix samples and Table 4 demonstrates the improvement in interference removal compared to the SQ-KED mode. In SQ-KED, the limitation of interference removal for this challenging sample is again demonstrated with the BEC of nearly  $4 \text{ µg}\cdot\text{L}^{-1}$ , whilst in TQ- $\text{O}_2$  mode, the BEC was less than  $2 \text{ ng}\cdot\text{L}^{-1}$ .

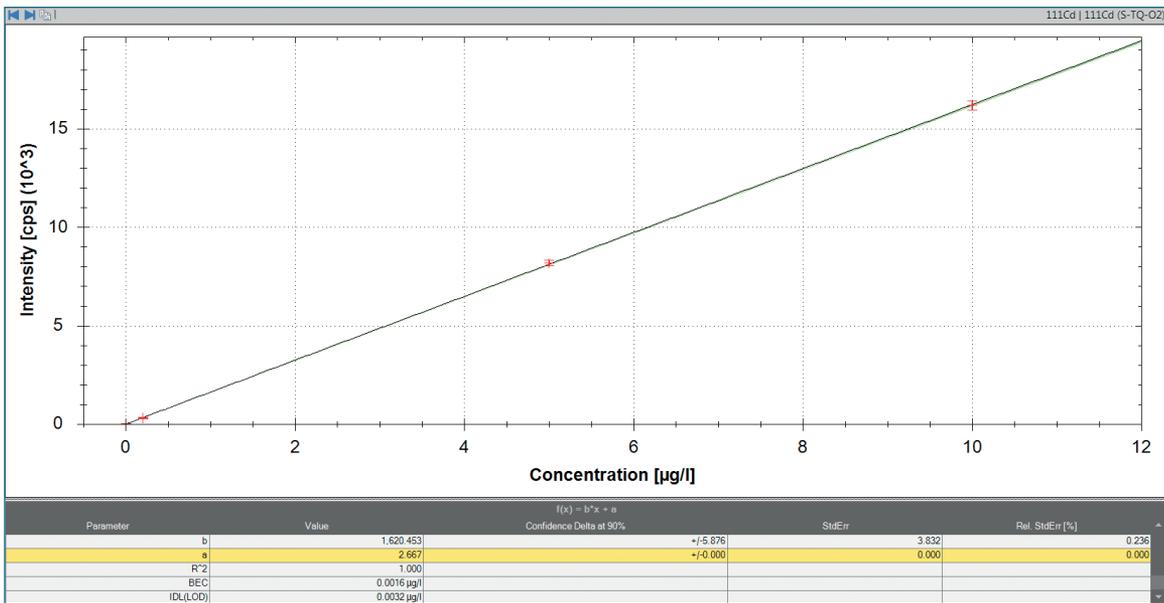


Figure 3. Calibration curve of  $^{111}\text{Cd}^+$  in  $10 \text{ mg}\cdot\text{L}^{-1}$  Mo with TQ- $\text{O}_2$  mode.

Table 4. Comparison of cadmium results in the 10 mg·L<sup>-1</sup> Mo matrix with different measurement modes.

Matrix	Polyatomic interference	SQ-KED		TQ-O <sub>2</sub>	
		BEC	IDL	BEC	IDL
Mo 10 mg·L <sup>-1</sup>	MoO	3.907 µg·L <sup>-1</sup>	0.258 µg·L <sup>-1</sup>	1.6 ng·L <sup>-1</sup>	3.2 ng·L <sup>-1</sup>

**TQ-NH<sub>3</sub> mode**

Ammonia gas is used to form clusters with certain elements, again providing a mass shift of the interference or the analyte.

The use of NH<sub>3</sub> is a typical approach for the analysis of titanium. Ti creates a series of clusters with NH<sub>3</sub>, of which clusters that experience a mass shift away from any interferences can be selected for analysis. The cluster at m/z 114 (<sup>48</sup>Ti(NH<sub>3</sub>)<sub>3</sub>NH) is often interference free and is one of the most abundant clusters formed, giving a good sensitivity for the signal.

Figure 4 shows the standard calibration curve result with 1% m/m H<sub>2</sub>SO<sub>4</sub> matrix samples and Table 5 shows the comparison with SQ-KED mode for this matrix.

TQ-NH<sub>3</sub> mode exceeded the SQ-ICP-MS performance and produced accurate results.

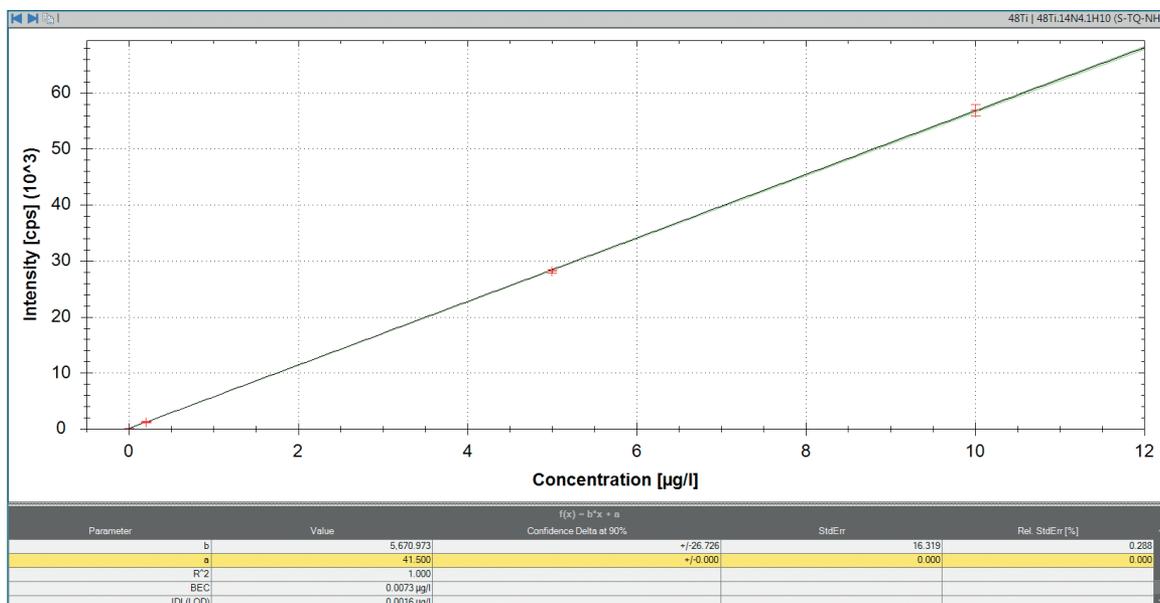


Figure 4. Calibration curve of <sup>114</sup>(Ti(NH<sub>3</sub>)<sub>3</sub>NH)\* in 1% m/m H<sub>2</sub>SO<sub>4</sub> with TQ-NH<sub>3</sub> mode.

Table 5. Comparison of titanium results in the 1% H<sub>2</sub>SO<sub>4</sub> matrix with different measurement modes.

Matrix	Polyatomic interference	SQ-KED		TQ-NH <sub>3</sub>	
		BEC	IDL	BEC	IDL
1% H <sub>2</sub> SO <sub>4</sub>	SO	62.3 µg·L <sup>-1</sup>	1.994 µg·L <sup>-1</sup>	7.3 ng·L <sup>-1</sup>	1.6 ng·L <sup>-1</sup>

## TQ-H<sub>2</sub> mode

Hydrogen gas is an effective way to eliminate argon based polyatomic interferences in TQ on mass mode, but it can also be used for mass shifts of the analyte.

A typical on mass mode example is the elimination of argon based interferences on selenium isotopes for ultralow detection of selenium. The TQ-H<sub>2</sub> on mass mode maintains high sensitivity for selenium isotopes for

example and as such can provide excellent performance. The calibration of selenium in 0.5% HCl / 2% HNO<sub>3</sub> using TQ-H<sub>2</sub> mode (Figure 5) shows a sensitivity of 4909 cps/μg·L<sup>-1</sup> and excellent linearity with an R<sup>2</sup> value of 0.9999. Table 6 compares the IDL achieved in SQ-KED mode (< 20 ng·L<sup>-1</sup>) and TQ-H<sub>2</sub> mode (< 0.5 ng·L<sup>-1</sup>) in 2% HNO<sub>3</sub>.

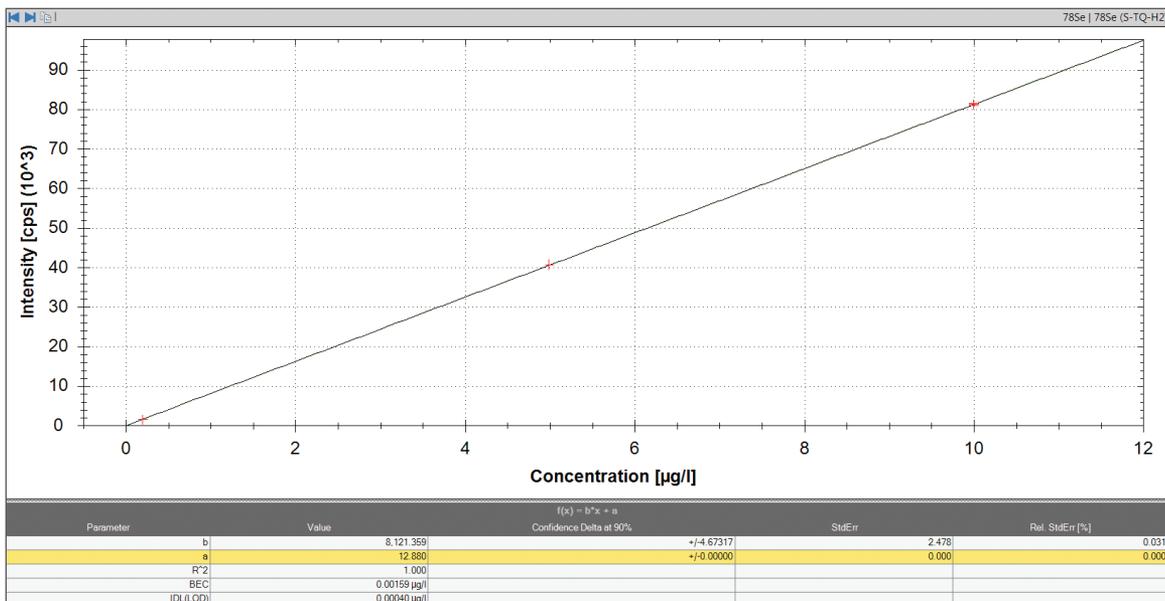


Figure 5. Calibration curve of <sup>78</sup>Se in 2% HNO<sub>3</sub> with TQ-H<sub>2</sub> mode.

Table 6. Comparison of Selenium results in 2% HNO<sub>3</sub> matrix with different measurement modes.

Matrix	Polyatomic interference	SQ-KED		TQ-H <sub>2</sub>	
		BEC	IDL	BEC	IDL
2% HNO <sub>3</sub>	ArAr	12 ng·L <sup>-1</sup>	19.7 ng·L <sup>-1</sup>	1.59 ng·L <sup>-1</sup>	0.40 ng·L <sup>-1</sup>

## Conclusion

The Thermo Scientific iCAP TQ ICP-MS demonstrated excellent performance to provide a significant improvement to analytical laboratory capabilities through improved interference removal and lower limits

of detection. The flexible configuration and suite of measurement modes delivers a complete solution for a wide range of trace elemental analysis in both research and routine applications.

Find out more at [thermofisher.com/TQ-ICP-MS](https://thermofisher.com/TQ-ICP-MS)

**For Research Use Only. Not for use in diagnostic procedures.** ©2017 Thermo Fisher Scientific Inc. All rights reserved. CETAC is a trademarks of Teledyne Instruments Inc. and ASX 560 is used in trade by Teledyne CETAC Technologies. All other trademarks are the property of Thermo Fisher Scientific. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details. **TN43287-EN 0117**

**ThermoFisher**  
SCIENTIFIC