

Trace elemental analysis

Thermo Scientific iCAP MTX ICP-MS: Typical limits of detection

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Introduction

Since its commercial introduction in the 1980s, ICP-MS has revolutionized trace elemental analysis by providing fast, multielement detection for a wide range of applications. After continuous improvement in interference removal using collision/reaction cell technology in single quadrupole ICP-MS, the last decade has seen accelerated development of ICP-MS using triple quadrupole technology. These systems allow for consistent interference removal regardless of the sample matrix.

The Thermo Scientific™ iCAP™ MTX ICP-MS has been designed to deliver superior interference removal, accomplished using mass filtration before and after the QCell collision reaction cell (CRC), so that any interference can be confidently removed using different gases. This enables the highest confidence in data quality to be achieved as well as superior detection limits obtained in the most challenging sample types. At the same time, it allows all laboratories to benefit from these characteristics through its ease of use and simplest method development.

Instrumental detection limits are a set of key performance indicators detailing an instrument's capabilities and are useful as an aid in determining that instrument's suitability to a chosen task. They demonstrate the lowest level of analyte distinguishable from the background noise under optimal conditions and are typically determined several times for statistical accuracy. Method detection limits (MDL), in comparison, determine the lowest level of analyte that can be detected in a sample matrix using the proposed method of analysis and consider 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.

The instrumental detection limit typically depends on two factors: sensitivity observed for the analyte of choice, as well as low fluctuation of the background signal. To accomplish both, the Thermo Scientific™ iCAP™ MX Series ICP-MS instruments feature a series of innovations. To improve sensitivity, the ion optics of the system can be optimized during the measurement to yield optimum transmission for every m/z ratio.* Backgrounds can be effectively controlled due to the novel interface design in conjunction with the proven performance of the RAPID lens. Both features allow for an additional filtering of the ion beam prior to the mass filtration.

To accurately detect and quantify an element of interest, it must be ensured that the measured isotope can be detected free from spectral interferences. While isobaric interferences can be avoided by adequate selection of the isotope to be measured for a given analyte, other types of interferences can be of more concern.

For effective interference removal, collision/reaction cells (CRCs) are used. CRCs may be operated in different ways depending on the nature of the interference to be eliminated. Interference removal based on triple quadrupole technology (also referred to as MS/MS) includes a mass filtration step before the collision/reaction cell, removing all ions of lower and higher mass than the analyte and its interferences with identical mass-to-charge ratio. This initial mass filtration allows reactive gases to be used for interference removal, which can induce highly selective ion-molecule reactions between either the analyte or the interfering ions with the gas. Commonly, triple quadrupole ICP-MS systems are operated in the following modes:

- The so-called standard mode, where the CRC is bypassed, often provides the highest sensitivity. For analytes in the low mass range (i.e., lithium, beryllium) as well as in the high mass range, this mode of operation allows the lowest limits of detection to be achieved, if spectral interferences can be excluded.
- In the kinetic energy discrimination (KED) mode, unwanted polyatomic interferences are filtered out using an inert collision gas (often helium) based on the difference in collision cross-section sizes of the analyte and polyatomic interferences. The proprietary design of the Thermo Scientific™ QCell™ CRC adds an automatically configured low mass cut-off to the interference removal toolbox. The combination of KED with a low mass cut-off allows unwanted precursor ions to be filtered in the CRC, which are therefore unable to recombine further downstream in the mass spectrometer. This leads to a further reduction of backgrounds and improved detection limits.

- In the TQ-O₂ mode, oxygen induces a variety of effective chemical reactions with different elements. For most cases, an oxidation reaction will occur, leading to a mass shift of the analyte (e.g., ⁷⁵As⁺ will be converted into ⁷⁵As¹⁶O⁺). In some cases, elimination of the interference is also based on a chemical reaction of the interference (i.e., removal of ⁹⁵Mo¹⁶O⁺ interfering with ¹¹¹Cd⁺). This allows for effective suppression of polyatomic as well as doubly charged ions.
- In the TQ-NH₃ mode, ammonia (NH₃) can react in different ways. Whereas with some elements, such as titanium, it forms a wide variety of reaction products (for example TiNH(NH₃)_x), it can also effectively eliminate polyatomic (especially chlorine based) polyatomics. The removal of isobaric overlaps is possible as well, for example, the elimination of ²⁰⁴Hg from ²⁰⁴Pb. Ammonia usually forms different product ions with a specific analyte, so that absolute sensitivity may be lower compared to other modes; however, the higher selectivity allows more efficient interference removal in demanding sample matrices.

Detection limits themselves 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).

Method

Sample preparation

Blank solutions and calibration standards at 1, 5, and 10 µg·L⁻¹ were prepared gravimetrically by adding the appropriate quantity of a multi-elemental stock solution (SPEX™ CertiPrep) directly to a solution containing 2% m/m HNO₃ (65% HNO₃, Optima™ grade, Fisher Chemical™) for measurements in standard mode and 2% m/m HNO₃ and 0.5% m/m HCl (32–35% HCl, Optima™ grade, Fisher Chemical™) for measurements in KED mode. All solutions were prepared in freshly rinsed vials. This acid matrix was selected to reflect a sample preparation procedure that is broadly appropriate to a wide variety of industries and applications.

The instrument's performance using selected reactive gases (O₂ and NH₃) was also tested using the same solutions as previously described for KED mode.

*Patent pending

Instrument configuration

An iCAP MTX ICP-MS with a Thermo Scientific™ iSC-65 Autosampler was used for all tests. The instrument was equipped with the iCAP MX Series PFA nebulizer, glass spray chamber (Peltier cooled to operate at 2.7 °C), a 2.5 mm i.d. quartz injector, and a demountable quartz torch, as well as nickel-based sample and skimmer cones. The full system configuration as well as typically applied parameters are summarized in Table 1. The detection limits were determined in the high sensitivity mode.

To test the performance of the KED interference correction, a relatively high concentration of HCl in the acid matrix was used in this study (0.5% m/m), which subsequently leads to a high number of complex Cl-based polyatomic interferences to be observed.

Table 1. Instrument configuration and operating parameters

Parameter	Value
Spray chamber	Glass cyclonic spray chamber, cooled at 2.7 °C
Nebulizer	iCAP MX Series PFA nebulizer
Pump tubing	40 rpm, 0.581 mm i.d., PVC orange-yellow pump tubing
Torch	Quartz torch
Injector	2.5 mm i.d., quartz injector
Interface	Nickel sampler and nickel skimmer
Plasma power	1,550 W
Nebulizer gas flow	1.00 L·min ⁻¹
CRC gas flow	He, 4.2 mL·min ⁻¹ O ₂ , 0.35 mL·min ⁻¹ NH ₃ , 0.29 mL·min ⁻¹
KED	3 V
Scan setting	0.1 s dwell time, 5 sweeps, 3 main runs

Results

The typical performance of the iCAP MTX ICP-MS using STD and He KED mode is shown in Table 2, where detection limits were calculated using the raw intensity data from the standard and the blank, as per 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

The Thermo Scientific™ iCAP™ MX Series offers two principal modes of operation, Sensitivity and Matrix, intended to balance the fundamental requirement of sensitivity with the ability to effectively handle potential matrix load from the samples. While the Sensitivity mode delivers the highest signals, the Matrix mode is typically used for the analysis with higher matrix load. The data summarized in Table 2 refers to the Sensitivity mode, typically offering a 30% increase in sensitivity. However, the achievable detection limits in Matrix mode will often be highly comparable.

Table 2 (part 1). Typical LODs achieved with the iCAP MTX ICP-MS in STD and He KED mode, as well as TQ-O₂ and TQ-NH₃ modes. All results are reported in ng·L⁻¹.

	Standard mode	KED mode	TQ-O ₂ mode	TQ-NH ₃ mode
	2% HNO ₃		2% HNO ₃ , 0.5% HCl	
⁷ Li	0.6	6.0	9.1 [⁷ Li]	–
⁹ Be	0.27	12	2.8 [⁹ Be]	–
¹¹ B	9.3	48	21 [¹¹ B]	–
²³ Na	35	45	21.1 [²³ Na]	41 [²³ Na]
²⁴ Mg	3.1	12.2	2.9 [²⁴ Mg]	30 [²⁴ Mg]
²⁷ Al	2.7	81	15.2 [²⁷ Al]	42 [²⁷ Al]
³⁹ K	–	214	–	–
⁴⁴ Ca	18.3	12.3	–	–
⁴⁵ Sc	1.0	0.9	0.42 [⁴⁵ Sc ¹⁶ O] ⁺	1.1 [⁴⁵ Sc]
⁴⁸ Ti	0.7	1.2	0.5 [⁴⁸ Ti ¹⁶ O] ⁺	5.5 [⁴⁸ Ti ¹⁴ N(¹⁴ N ¹ H ₃) ₃] ⁺
⁵¹ V	0.3	0.2	0.1 [⁵¹ V ¹⁶ O] ⁺	0.9 [⁵¹ V]
⁵² Cr	12.1	1.6	1.5 [⁵² Cr ¹⁶ O] ⁺	1.9 [⁵² Cr]
⁵⁵ Mn	0.7	0.6	0.5 [⁵⁵ Mn]	0.6 [⁵⁵ Mn]
⁵⁶ Fe	–	6.7	–	–
⁵⁷ Fe	547	–	7.7 [⁵⁷ Fe]	–
⁵⁹ Co	0.1	0.3	0.1 [⁵⁹ Co]	0.7 [⁵⁹ Co]
⁶⁰ Ni	1.0	1.0	1.2 [⁶⁰ Ni]	–
⁶³ Cu	0.6	0.9	0.6 [⁶³ Cu]	–
⁶⁶ Zn	1.6	4.8	2.7 [⁶⁶ Zn]	–
⁷¹ Ga	0.4	0.1	0.09 [⁷¹ Ga]	–
⁷² Ge	0.8	0.4	0.3 [⁷² Ge]	0.3 [⁷² Ge ¹⁴ N ¹ H ₂]
⁷⁵ As	0.7	0.3	0.2 [⁷⁵ As ¹⁶ O] ⁺	1.4 [⁷⁵ As]
⁷⁷ Se	14.5	4.8	–	3.7 [⁷⁷ Se]
⁷⁸ Se	–	–	1.0 [⁷⁸ Se ¹⁶ O] ⁺	–
⁸⁵ Rb	0.1	0.3	0.1 [⁸⁵ Rb]	0.1 [⁸⁵ Rb]
⁸⁸ Sr	0.2	1.1	0.6 [⁸⁸ Sr ¹⁶ O] ⁺	7.0 [⁸⁸ Sr]
⁸⁹ Y	0.02	0.03	0.03 [⁸⁹ Y ¹⁶ O] ⁺	0.2 [⁸⁹ Y]
⁹⁰ Zr	0.04	0.2	0.2 [⁹⁰ Zr ¹⁶ O] ⁺	0.7 [⁹⁰ Zr]
⁹³ Nb	0.04	0.1	0.4 [⁹³ Nb ¹⁶ O] ⁺	0.4 [⁹³ Nb]
⁹⁵ Mo	0.5	0.4	1.5 [⁹⁵ Mo ¹⁶ O] ⁺	1.9 [⁹⁵ Mo]
¹⁰¹ Ru	0.6	0.1	2.2 [¹⁰¹ Ru]	0.6 [¹⁰¹ Ru]
¹⁰³ Rh	0.07	0.09	0.06 [¹⁰³ Rh]	0.2 [¹⁰³ Rh]
¹⁰⁵ Pd	0.3	0.2	0.4 [¹⁰⁵ Pd]	0.3 [¹⁰⁵ Pd]
¹⁰⁷ Ag	0.1	0.05	0.05 [¹⁰⁷ Ag]	0.3 [¹⁰⁷ Ag]
¹¹¹ Cd	0.26	0.08	0.08 [¹¹¹ Cd]	0.07 [¹¹¹ Cd]
¹¹⁵ In	0.01	0.03	0.01 [¹¹⁵ In]	0.4 [¹¹⁵ In]
¹¹⁸ Sn	0.4	0.5	0.2 [¹¹⁸ Sn]	–
¹²¹ Sb	0.1	0.5	0.5 [¹²¹ Sb]	0.3 [¹²¹ Sb]
¹²⁵ Te	1.0	< 0.01	0.3 [¹²⁵ Te]	0.3 [¹²⁵ Te]
¹³³ Cs	0.04	0.05	0.04 [¹³³ Cs]	0.03 [¹³³ Cs]
¹³⁷ Ba	0.7	0.3	2.1 [¹³⁷ Ba ¹⁶ O] ⁺	0.4 [¹³⁷ Ba]
¹³⁹ La	0.02	0.03	0.04 [¹³⁹ La ¹⁶ O] ⁺	0.09 [¹³⁹ La]
¹⁴⁰ Ce	0.02	0.03	0.1 [¹⁴⁰ Ce ¹⁶ O] ⁺	0.2 [¹⁴⁰ Ce]
¹⁴¹ Pr	<0.01	<0.01	<0.01 [¹⁴¹ Pr ¹⁶ O] ⁺	0.01 [¹⁴¹ Pr]
¹⁴⁶ Nd	0.02	0.08	0.05 [¹⁴⁶ Nd ¹⁶ O] ⁺	0.1 [¹⁴⁶ Nd]
¹⁴⁷ Sm	0.01	0.02	0.03 [¹⁴⁷ Nd ¹⁶ O] ⁺	0.05 [¹⁴⁷ Sm]

Table 2 (part 2). Typical LODs achieved with the iCAP MTX ICP-MS in STD and He KED mode, as well as TQ-O₂ and TQ-NH₃ modes. All results are reported in ng·L⁻¹.

	Standard mode	KED mode	TQ-O ₂ mode	TQ-NH ₃ mode
	2% HNO ₃		2% HNO ₃ , 0.5% HCl	
¹⁵³ Eu	<0.01	<0.01	<0.01 [¹⁵³ Eu]	<0.01 [¹⁵³ Eu]
¹⁵⁷ Gd	0.02	0.02	0.01 [¹⁵⁷ Gd]	0.09 [¹⁵⁷ Gd]
¹⁵⁹ Tb	<0.01	0.004	<0.01 [¹⁵⁹ Tb ¹⁶ O] ⁺	0.01 [¹⁵⁹ Tb]
¹⁶³ Dy	0.01	0.01	0.01 [¹⁶³ Dy ¹⁶ O] ⁺	0.05 [¹⁶³ Dy]
¹⁶⁵ Ho	<0.01	0.003	0.02 [¹⁶⁵ Ho ¹⁶ O] ⁺	0.04 [¹⁶⁵ Ho]
¹⁶⁶ Er	<0.01	0.01	0.01 [¹⁶⁶ Er ¹⁶ O] ⁺	0.03 [¹⁶⁶ Er]
¹⁶⁹ Tm	<0.01	0.002	<0.01 [¹⁶⁹ Tm ¹⁶ O] ⁺	<0.01 [¹⁶⁹ Tm]
¹⁷² Yb	<0.01	<0.01	<0.01 [¹⁷² Yb ¹⁶ O] ⁺	0.03 [¹⁷² Yb]
¹⁷⁵ Lu	<0.01	<0.01	<0.01 [¹⁷⁵ Lu ¹⁶ O] ⁺	<0.01 [¹⁷⁵ Lu]
¹⁷⁸ Hf	0.2	0.3	0.8 [¹⁷⁸ Hf ¹⁶ O] ⁺	0.6 [¹⁷⁸ Hf ¹⁴ N(¹⁴ N'H ₃) ₃]
¹⁸¹ Ta	0.1	0.3	1.3 [¹⁸¹ Ta ¹⁶ O] ⁺	2.5 [¹⁸¹ Ta]
¹⁸² W	0.2	0.8	1.5 [¹⁸² W ¹⁶ O] ⁺	1.0 [¹⁸² W ¹⁴ N'H(¹⁴ N'H ₃) ₃]
¹⁸⁵ Re	0.01	< 0.01	0.03 [¹⁸⁵ Re]	0.02 [¹⁸⁵ Re]
¹⁸⁹ Os	0.7	3.4	4.5 [¹⁸⁹ Os ¹⁶ O] ⁺	–
¹⁹³ Ir	0.2	0.2	0.4 [¹⁹³ Ir]	1.7 [¹⁹³ Ir(¹⁴ N'H)]
¹⁹⁵ Pt	0.03	0.3	0.4 [¹⁹⁵ Pt]	1.4 [¹⁹⁵ Pt ¹⁴ N'H(¹⁴ N'H ₃) ₃]
¹⁹⁷ Au	0.2	0.5	1.2 [¹⁹⁷ Au]	–
²⁰² Hg	1.02	1.00	1.11 [²⁰² Hg]	–
²⁰⁵ Tl	0.1	0.2	0.3 [²⁰⁵ Tl]	0.09 [²⁰⁵ Tl]
²⁰⁸ Pb	0.2	0.3	0.5 [²⁰⁸ Pb]	2.3 [²⁰⁸ Pb]
²⁰⁹ Bi	0.04	0.04	0.04 [²⁰⁹ Bi]	1.7 [²⁰⁹ Bi]
²³² Th	0.01	0.05	0.07 [²³² Th ¹⁶ O] ⁺	1.0 [²³² Th]
²³⁸ U	0.05	<0.01	<0.01 [²³⁸ U ¹⁶ O] ⁺	–

Conclusions

The iCAP MTX ICP-MS system with its integrated Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software demonstrates excellent performance and provides a significant improvement to analytical laboratory capabilities

through simplicity, productivity, and robustness. The flexible configuration delivers a complete solution for a wide range of trace elemental analysis in both research and analytical testing applications.

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