

Overcome unexpected interferences and accelerate environmental analysis using triple quadrupole ICP-MS

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Goal

To highlight the benefits of triple quadrupole ICP-MS for the analysis of elemental contaminants in waters, waste, soils, and sediments.

Introduction

Toxic elements, such as arsenic, cadmium, mercury, and lead, need to be monitored in the environment to protect the surrounding nature from contamination and keep water resources safe. Therefore, the analysis of drinking waters, surface waters and waste waters, as well as monitoring the level of potential contaminants in solid waste or sewage sludges, is an important task. Regulated methods with applicable sample preparation procedures¹ and stringent protocols to assure system suitability and quality control have been established globally. ICP-MS is the preferred analytical solution for trace element determination at the lowest concentration levels. Modern instruments offer comprehensive interference removal and innovative solutions to increase sample throughput. Moreover, although the handling of samples containing more than 0.3% (m/v) of total dissolved solids has been historically a challenge for ICP-MS, today's instruments can be easily



configured for the direct analysis of solutions containing 3% TDS (for example undiluted sea water)² or more. Special sampling accessories, like automatic dilution systems, allow for prescriptive dilution of each sample without any user interaction and therefore open new possibilities to analyze a wide range of sample types under optimized conditions.

Single quadrupole ICP-MS systems are commonly used in many laboratories, combining consistent interference removal with short measurement times, and hence enabling robust, high-throughput analysis. Interference removal is accomplished by using a collision/reaction cell (CRC) filled with helium in order to remove the most common polyatomic interferences. Reactive gases, such as hydrogen, oxygen, or ammonia are occasionally used to eliminate certain interferences (e.g., H₂ for reduction of ⁴⁰Ar₂⁺ on ⁸⁰Se), but often, the formation of new interferences in the collision cell is possible, as other ions present in the ion beam can lead to uncontrolled side reactions.

One way to overcome these interference challenges is to use triple quadrupole ICP-MS (TQ-ICP-MS) instrumentation,³ such as the Thermo Scientific™ iCAP™ TQe ICP-MS. TQ-ICP-MS instruments eliminate interferences using reactive gases in the CRC (often referred to as quadrupole 2 (Q2), independent of the number of rods). Interference removal is accomplished as analyte and interferent react differently with the reactive gas and can be separated from each other in the analyzing quadrupole (Q3). Suppression of side reactions is accomplished through a mass filtration step in the first quadrupole (Q1), added axially in front of the CRC (Q2).

Experimental

An iCAP TQe ICP-MS system was used for all analysis. On each day of measurement, performance of the instrument was verified using an automatic performance report wizard and tuned using the autotune routines in case performance criteria were not met. The optimized parameters for the analysis are summarized in Table 1.

Table 1. Instrument configuration and operating parameters

Parameter	Value
Nebulizer	Borosilicate glass MicroMist (Glass Expansion, Australia), 400 $\mu\text{L}\cdot\text{min}^{-1}$, pumped at 40 rpm
Spray chamber	Quartz cyclonic spray chamber cooled at 3 °C
Injector	2.5 mm quartz
Interface	Ni sampler and Ni skimmer with 3.5 mm insert
Forward power	1,550 W
Nebulizer gas	1.00 $\text{mL}\cdot\text{min}^{-1}$
TQ- O_2	O_2 at 0.34 $\text{mL}\cdot\text{min}^{-1}$ (Low gas flow) or 0.8 $\text{mL}\cdot\text{min}^{-1}$ (High gas flow)
SQ-KED	He at 4.3 $\text{mL}\cdot\text{min}^{-1}$ with 3 V KED

The selection of the optimum measurement mode for each analyte can be accomplished easily using the Reaction Finder Method Development Assistant included in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software. For single mode analysis, all settings made by Reaction Finder were modified manually.

Results and discussion

False positive results caused by the presence of interfering elements can lead to a significant disruption to the daily workplan in a busy laboratory. During the required troubleshooting, the instrument affected will have to stop productive analysis, and affected samples will need to be repeated. Kinetic energy discrimination (KED) allows the full mass range (typically lithium to uranium) to be analyzed, with consistent removal of polyatomic interferences in the most affected area of the mass range (m/z 40–100).

To illustrate the process of interference removal on a triple quadrupole ICP-MS, Figure 1 contains an overview on the analysis of ^{75}As and ^{202}Hg , demonstrating the two potential pathways of measurement: Either in a mass shift reaction (where the analyte is reactive to a specific gas), or an on-mass reaction (where the interference reacts while the analyte is detected on its original m/z ratio).

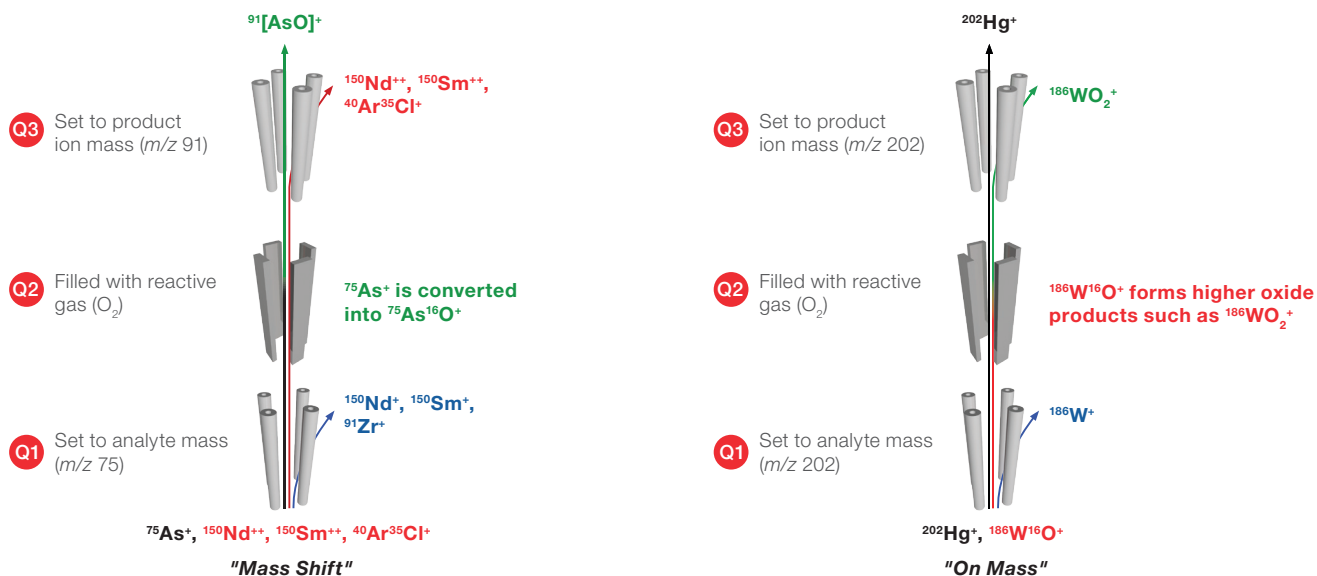


Figure 1. Interference removal using a mass shift reaction (e.g., ^{75}As) or an on-mass reaction (e.g., ^{202}Hg) on a triple quadrupole ICP-MS

For some analytes, predominantly measured in on-mass mode, the use of a higher flow rate of the reaction gas provides lower backgrounds and hence superior interference removal. One example for this is cadmium, where the potential interferent molybdenum (leading to formation of $^{95}\text{Mo}^{16}\text{O}^+$ on $^{111}\text{Cd}^+$) can be present in elevated concentrations, potentially requiring a higher flow of the reactive gas O_2 for interference removal.

Arsenic is a critical contaminant and under regulation in a wide variety of sample types. Whereas the most predominant interference on arsenic is caused by chlorine ($^{40}\text{Ar}^{35}\text{Cl}^+$ and $^{40}\text{Ca}^{35}\text{Cl}^+$ interfering on the only available isotope ^{75}As), bias can also arise from the potential presence of rare earth elements, specifically neodymium and samarium, through the formation of doubly charged ions ($^{150}\text{Nd}^{++}$ and $^{150}\text{Sm}^{++}$). The latter cannot be removed by KED and are even elevated in this measurement mode. The resulting concentrations for arsenic (measured in different modes) in a series of samples is shown in Table 2.

Table 2. Results obtained for the analysis of arsenic in a variety of sample matrices. No arsenic was added to any of the solutions.

Sample	SQ-KED [$\mu\text{g}\cdot\text{L}^{-1}$]	TQ- O_2 [$\mu\text{g}\cdot\text{L}^{-1}$]	SQ- O_2 [$\mu\text{g}\cdot\text{L}^{-1}$]	Comment
100 $\text{mg}\cdot\text{L}^{-1}$ Ca, 5% HCl	0.06	0.00	0.2	KED is generally suitable, but the combination of calcium and chlorine leads to a small bias. SQ- O_2 shows a significant bias due to the formation of $^{43}\text{Ca}^{16}\text{O}_2^+$
10 $\mu\text{g}\cdot\text{L}^{-1}$ REE Mix	1.05	0.00	0.02	KED shows (as expected) false positive result.
100 $\mu\text{g}\cdot\text{L}^{-1}$ REE Mix	11.97	0.00	0.04	SQ- O_2 is less effective compared to TQ- O_2 to remove these interferences.
0.5 $\text{mg}\cdot\text{L}^{-1}$ Zr	0.00	0.00	148.72	No mass filtration in Q1 leads to a completely wrong result in SQ- O_2 mode. A false positive is observed due to unreacted $^{91}\text{Zr}^+$.

As can be seen from the data, chlorine-based polyatomic interferences are generally well controlled using KED and will not cause major bias in most samples. However, the potential presence of rare earth elements can create a significant false positive result already at low levels. The use of oxygen and a subsequent oxidation of $^{75}\text{As}^+$ to $^{75}\text{As}^{16}\text{O}^+$

fully removes these interferences. The control of other ions entering the cell is essential, as can be seen from the results observed in SQ- O_2 mode (with no mass filtration before the CRC). Here, new interferences are formed, leading to increased backgrounds, as observed in the presence of calcium. The analysis of a solution containing $0.5 \text{ mg}\cdot\text{L}^{-1}$ of zirconium shows another critical reason for having a mass filtration stage before the CRC. Although zirconium effectively reacts with oxygen to form ZrO (and higher oxides), the reaction does not completely remove all zirconium from (in this case) m/z 91, the resulting product ion mass of $^{75}\text{As}^{16}\text{O}^+$.

Mercury is another example of a critical element frequently required for analysis. The high mass range is often considered interference free in ICP-MS. However, this statement is only valid relative to the low and mid mass range, where abundant polyatomic interferences based on argon species cause significant backgrounds. As the difference in size between a polyatomic interference (consisting of at least two atoms) and an analyte ion is significantly lower for higher masses, KED is less effective, and hence, even small contributions can lead to a noticeable signal increase. For mercury, the presence of tungsten can lead to a potential false positive result. This is highlighted in Table 3, summarizing the results of the analysis of a series of solutions containing increasing amounts of tungsten. Even for a concentration of tungsten as low as $5 \mu\text{g}\cdot\text{L}^{-1}$, a false positive bias for mercury is obtained that could potentially exceed the applicable reporting limit in a regulated method ($0.1 \mu\text{g}\cdot\text{L}^{-1}$ is set in a variety of regulations). Note that all major isotopes of mercury (e.g., ^{199}Hg or ^{200}Hg) would be similarly affected by comparable interferences from other isotopes of tungsten. Other isotopes, such as ^{196}Hg , ^{198}Hg , or ^{204}Hg are not useful due to potential overlaps with gold (^{197}Au), which is commonly used as a stabilizer for mercury, and an isobaric overlap with ^{204}Pb . At the same time, analysis of mercury using TQ- O_2 mode fully removes the potential interferences with no bias observed. It is important to note here that the use of O_2 as a reactive gas on a single quadrupole ICP-MS instrument would lead to an immediate reaction of W^+ ions (and hence formation of WO^+). Only after completely eliminating W^+ from the ion beam can the selective oxidation of WO^+ into higher oxides to remove the interference on mercury be achieved.

Table 3. Measured concentrations for different isotopes of mercury when analyzing solutions containing increasing concentrations of tungsten. Isotopic abundance of mercury isotopes is noted in parentheses. n.d. - not detected

Concentration of W in solution [$\mu\text{g}\cdot\text{L}^{-1}$]	¹⁹⁹ Hg (16.84%)		²⁰⁰ Hg (23.13%)		²⁰¹ Hg (13.22%)		²⁰² Hg (29.60%)	
	Result SQ-KED [$\mu\text{g}\cdot\text{L}^{-1}$]	Result TQ-O ₂ [$\mu\text{g}\cdot\text{L}^{-1}$]	Result SQ-KED [$\mu\text{g}\cdot\text{L}^{-1}$]	Result TQ-O ₂ [$\mu\text{g}\cdot\text{L}^{-1}$]	Result SQ-KED [$\mu\text{g}\cdot\text{L}^{-1}$]	Result TQ-O ₂ [$\mu\text{g}\cdot\text{L}^{-1}$]	Result SQ-KED [$\mu\text{g}\cdot\text{L}^{-1}$]	Result TQ-O ₂ [$\mu\text{g}\cdot\text{L}^{-1}$]
5	0.154	n.d.	0.186	n.d.	0.070	n.d.	0.120	n.d.
10	0.360	n.d.	0.436	n.d.	0.170	n.d.	0.287	n.d.
20	0.891	n.d.	1.088	n.d.	0.425	n.d.	0.720	n.d.
50	1.549	n.d.	1.882	n.d.	0.734	n.d.	1.241	n.d.
Interference caused by	¹⁸³ W ¹⁶ O ⁺		¹⁸⁴ W ¹⁶ O ⁺		¹⁸⁴ W ¹⁷ O ⁺ , ¹⁸⁴ W ¹⁶ O ¹ H ⁺		¹⁸⁶ W ¹⁶ O ⁺	

Impact on sample throughput

A common challenge is the need to analyze a high number of samples to keep up with the backlog and achieve return on investment. TQ-ICP-MS systems are therefore less commonly found in analytical testing laboratories, as each specialized set of measurement parameters (e.g., for multiple reactive gases) adds to the total method runtime. In contrast, SQ-ICP-MS allow for the analysis of samples using one or two acquisition modes only.

To achieve high throughput with full interference removal, the use of a single mode method using triple quadrupole technology and oxygen as a reactive cell gas is a great alternative. In this case, the iCAP TQe ICP-MS is operated in a single mode for all elements. This allows for effective removal of all interferences across the entire mass range.

Table 4 compares the resulting data acquisition times for a method analyzing a total of 29 individual masses (simulating a common set of analytes and typical internal standards), with different methods typically used on single and triple quadrupole ICP-MS. In all cases, an identical sample delivery system was used (a standard autosampler) with identical uptake and rinse times (30 seconds each). From the turnover time per sample, the total runtime of a batch containing 100 samples was calculated and compared between different methods.

Table 4. Comparison of acquisition time per sample, total runtime for 100 samples, and interference removal capability for different ICP-MS methods

	STD or KED Single Mode [*]	KED and H ₂ [*]	TQ-O ₂ Single Mode	TQ-ICP-MS using Reaction Finder defaults
Acquisition time per sample not including uptake/wash [s]	91	139	121	125
Total runtime [min] and time saving for 100 samples	251 + 0 minutes	331 + 80 minutes	301 + 50 minutes	308 minutes + 57 minutes
Polyatomic interferences removed	No/Yes	Yes	Yes	Yes
Doubly charged interferences removed (e.g., REE)	No	No	Yes	Yes
Confidence all interferences are under control	No	No	Yes	Yes

^{*} Data acquired on a Thermo Scientific™ iCAP™ RQ ICP-MS

As can be seen, a method based on single mode analysis has a clear potential for the realization of time savings, especially compared to a method combining the use of KED with H₂. Here, the sample turnover time is not only extended because of the need to evacuate and flush the CRC with two different gases (He, for KED operation, and H₂), but additionally through the longer duration of this process when adding a gas with a high flow rate (often in the range of 7 to 10 mL·min⁻¹ for H₂). Importantly, the single mode analysis using the TQ-O₂ mode includes an increase of the gas flow rate for some analytes, which requires a short stabilization time, but significantly shorter as compared to a full gas exchange in the CRC. With no change of the gas flow rate, identical turnover times could be achieved. Even though the measurement time is increased over a single mode approach using KED, the use of a triple quadrupole ICP-MS allows the full removal of all types of interferences (including those previously highlighted) and increases the confidence in the data generated.

Conclusion

As demonstrated in this note, the use of TQ ICP-MS with a combination of helium and oxygen as collision/reaction gases is a powerful approach to address common and potential challenges found in environmental analysis. With this technology, existing and established methods can be transferred and extended for improved interference removal on key analytes and new options become available.

There are many benefits, not only in research driven laboratories, but also for laboratories tasked with screening high numbers of samples in a high-throughput environment.

- A reduction of the data acquisition time of more than 10% can be achieved compared to methods based on single quadrupole ICP-MS using different collision/reaction gases.
- This can be achieved with no or negligible impact on the detection limits. The iCAP TQe ICP-MS enables complete removal of many commonly encountered interferences, eliminating the need to re-analyze the samples and ultimately increasing confidence in data quality.
- With no additional investment in laboratory infrastructure on top of what is required for a single quadrupole instrument (only the common gases helium and oxygen are required for interference removal), unnecessary interruptions to the daily laboratory routine caused by unexpected false positives can be avoided.

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