

Strategies for Improving Analytical Performance of ICP-MS For Environmental Sample Analysis

Simon Nelms^{1*}, Daniel Kutscher² and Shona McSheehy Ducos²

1. Thermo Fisher Scientific, Hemel Hempstead, UK 2. Thermo Fisher Scientific (Bremen) GmbH, Bremen, Germany *simon.nelms@thermofisher.com

ABSTRACT

Single quadrupole ICP-MS is now a standard technology for routine trace elemental analysis of a range of environmental samples including surface waters, sediment digests, soil extracts and sea waters. For the most part, it is straightforward to achieve stable, reproducible and accurate results for these types of sample, but specific problems such as interference, drift and signal suppression still remain with the most challenging sample matrices.

For example, soil and sediment samples give rise to unexpected interferences on the key analytes As and Se, caused by the formation of doubly charged rare earth element ions (specifically Nd²⁺, Sm²⁺ and Gd²⁺) in the plasma. In addition, the presence of carbon in these samples (either from carbonates or dissolved organic material) leads to signal enhancement on Se, leading to false positive results. Finally, the high salt matrix content of sea waters causes considerable problems of signal suppression, drift and increased maintenance of the ICP-MS interface, leading to the need to dilute this type of sample prior to analysis, which compromises achievable detection and quantitation limits, and introduces the potential for contamination.

INTRODUCTION

The development of triple quadrupole ICP-MS has provided a new way to overcome a wide range of interferences, including rare earth doubly charged ions, leading to greatly improved accuracy, but this technology still faces the challenges posed by high matrix environmental samples.

This presentation will describe the application of triple quadrupole ICP-MS for improving data quality for routine analysis of environmental samples. With regard to higher matrix, sea water samples, approaches for solving contamination problems, enhancing productivity, decreasing drift and reducing signal suppression caused by higher matrix samples, will be presented.

MATERIALS AND METHODS

Method Development For Complete Interference Removal

Different solutions containing arsenic and selenium were prepared from single element standard solutions and diluted in clean nitric acid (2% w/w). In a similar manner, a mixed solution containing 100 ng·mL⁻¹ of neodymium, gadolinium, dysprosium, molybdenum and zirconium was prepared to check for complete interference removal on both analytes. In addition, solutions containing 50 µg·L⁻¹ calcium and iron, which can both be present in environmental samples at these levels were tested for their impact on the analytes. Finally, solutions containing defined concentrations of arsenic and selenium were prepared in the mixed matrix solution to check for accurate spike recovery¹.

Analysis of Water Reference Materials

The water samples were diluted manually 10 times using 2% nitric acid before analysis. In this dilution step, addition of an internal standard was included. The samples were subsequently analyzed using a Teledyne CETAC Technologies ASX-560 autosampler (Teledyne CETAC Technologies, Omaha, NE).

ICP-MS Analysis

All measurements were accomplished using a Thermo Scientific™ iCAP™ TQ ICP-MS system (Thermo Fisher Scientific, Bremen, Germany). The selection of analytes, appropriate analysis mode (single quad vs. triple quad, choice of reactive gas) was accomplished using the Reaction Finder method development assistant. Further analysis modes for particular isotopes were added manually for comparison. The mass selection in the first quadrupole was controlled using intelligent Mass Selection (IMS) in all cases. The typical parameters are summarized in Table 1.

Table 1. Typical operating parameters for the iCAP TQ ICP-MS

Parameter	Value
Nebulizer	MicroMist™ (Glass Expansion Ltd, Australia), Quartz nebulizer 0.4mL·min ⁻¹ , pumped at 40rpm
Spray chamber	Quartz cyclonic spray chamber cooled to 2.7 °C
Injector	2.5mm id, Quartz
Interface	High Matrix (3.5mm) insert, Ni cones
RF Power	1550W
Nebulizer Gas Flow	1.11 L·min ⁻¹
QCell settings	SQ-KED TQ-O ₂
Gas Flow	100% He, 4.5 mL·min ⁻¹ 100% O ₂ , 0.7 mL·min ⁻¹
CR Bias	-21 V -7.5 V
Q3 Bias	-18 V -12 V
Scan Settings	0.1s dwell time per analyte, 10 sweeps, 3 main runs



Workflow

Setting up a method using a triple quadrupole ICP-MS system includes a few more relevant decisions to be taken by the operator as compared to single quadrupole systems:

- Is there a different choice of the isotope of a given element to be selected?
- Which reactive gas (if any) should be chosen for best results?
- What is the resulting product ion (if any)?

All these decisions require knowledge and are a limiting factor for some laboratories, which would indeed benefit from leveraging triple quadrupole technology for interference removal.

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software contains the Reaction Finder method development assistant for the iCAP TQ ICP-MS. Reaction Finder automatically provides a set of acquisition modes suitable for the range of elements previously selected by the user. The proposed settings can be accepted and the analysis can be started right away.

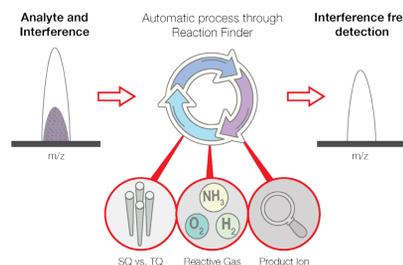


Figure 1. Reaction Finder Workflow

For method development, comparison of results obtained in different modes is often required. Reaction Finder therefore also offers complete flexibility to modify or add additional acquisition settings:

- Choice of alternative reactive gases (e.g. NH₃ as an alternative for the analysis of ⁶³Cu)
- Alternative product ions (see ⁴⁸Ti in Figure 2)
- Low or High gas flow rates for all gas channels
- Different resolution settings for Q1: intelligent Mass Selection (IMS) or High Resolution (< 1 u)
- Optional resolution settings on Q3 (Normal, High and XS)

Method	Q1 Mode	Q2 Gas Flow	Q3 Gas Flow	Q3 Resolution	Q3 Interference	Q3 Resolution	Q3 Interference
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	High
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal
238U-SQ-KED	SQ	Normal	KED	0.1	1	0.1	Normal

Figure 2. Default method setup and user customization allowing full flexibility with Reaction Finder

Modifications or additions to the settings can be made through simple clicks or automatically updated right-click context menus.

RESULTS

Interference Removal Using Triple Quadrupole ICP-MS

The majority of interferences from environmental sample matrices can be efficiently removed using collision/reaction cell (CRC) operation with kinetic energy discrimination (KED). This approach is well suited to the analysis of most samples, as it readily allows simultaneous determination of trace level contaminants and macro level constituents. However, some samples such as soils can, depending on the geological surroundings, contain trace levels of rare earth elements (REEs). In the ICP, REEs generate a proportion of doubly-charged ions (such as Nd²⁺ and Gd²⁺) which then interfere on arsenic and selenium respectively, causing a positive bias in the results. Unfortunately, the single quadrupole ICP-MS KED approach cannot remove these doubly-charged interferences, so an alternative technique is required. Figure 4 shows the effect of false positive bias caused by the presence of REE's when using KED as interference removal mechanism.

Figure 3 shows a survey scan of sample of Apple Leaves reference material, in which high signals are apparent for all the REE's (from ¹⁴⁰Ce to ¹⁷⁵Lu), leading to considerable interference from Nd²⁺ on As and Gd²⁺ on Se. The uptake of these elements is a direct consequence of their presence in the soil.

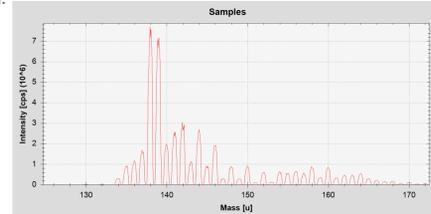


Figure 3. Survey scan of CRM NIST 1515 Apple Leaves in SQ-KED mode, REE mass region

Using triple quadrupole based ICP-MS systems, these interferences can be eliminated efficiently using O₂ as a reactive cell gas and the resulting mass shift reaction of either As or Se. However, it is crucial to ensure that the intended product ion mass is not interfered by other elements present in the samples, such as Zr (⁹¹Zr⁺ would interfere on ⁷⁵As¹⁶O⁺) or Mo (⁹⁶Mo⁺ would interfere on ⁸⁰Se¹⁶O⁺). The principle of interference removal is illustrated in Figure 4.

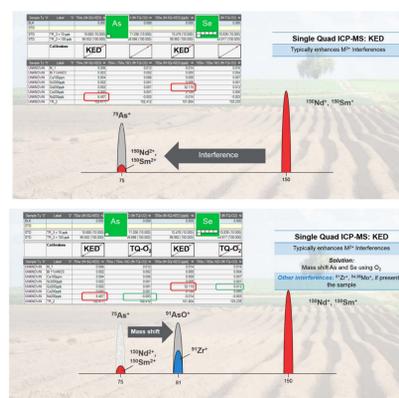


Figure 4. Interferences caused on ⁷⁵As through presence of rare earth elements and how they can be resolved using O₂ and a mass shift reaction

The results for the quantitative assessment of successful interference removal are shown in Table 2.

As can be seen from the results, some components of the matrix induce false positive signals and often, interferences can be aggravated in single quadrupole modes when using non-KED analysis conditions and reactive gases in the CRC.

Table 2. Results for the analysis of arsenic and selenium using reactive gases in single and triple quadrupole modes

Analyte	Gas	Mode	BEC in Matrix [µg·L ⁻¹]	1 µg·L ⁻¹ Spike Recovery [%] in Matrix	BEC in 50ppm Ca [µg·L ⁻¹]	BEC in 50ppm Fe [µg·L ⁻¹]
⁷⁵ As	O ₂	SQ (75As ¹⁶ O ⁺)	0.08	93 ± 2	0.01	3.00
		TQ (75As ¹⁶ O ⁺)	0.004	101 ± 1	0.002	0.04
⁷⁸ Se	O ₂	SQ (78Se ¹⁶ O ⁺)	26.6	-27 ± 1	0.33	0.66
		TQ (78Se ¹⁶ O ⁺)	0.003	103 ± 3	0.01	0.02
⁸⁰ Se	O ₂	SQ (80Se ¹⁶ O ⁺)	22.0	17 ± 2	0.01	0.67
		TQ (80Se ¹⁶ O ⁺)	0.005	102 ± 2	0.002	0.02

Whilst the analysis of arsenic and selenium using a mass shift reaction with oxygen may be a viable option for a triple quadrupole based system, there are several limitations on a single quad instrument:

- ✓ Elements of higher mass than the analyte may potentially cause interferences at the intended product ion mass of the reaction: Significantly higher background signals are observed due to unresolved ⁹¹Zr⁺ (interfering with ⁷⁵As¹⁶O⁺) and ⁹⁴Mo⁺ (interfering with ⁷⁸Se¹⁶O⁺), rendering Se quantitation practically useless.
- ✓ Elements with lower mass may react with the cell gas as well and create new interferences with same m/z charge as the analyte: The presence of Fe causes a false positive signal on m/z 91, 94 and 96 (e.g. [Fe(OH)₂]⁺).
- ✓ Using the TQ-O₂ mass shift mode, the REE doubly-charged polyatomic interferences were efficiently removed leading to As and Se results that agreed well with spiked concentrations. No elevated BEC's for higher concentrations of Ca and Fe were detected.

Water Analysis

The analysis of water samples typically poses different challenges, such as varying content of salts (e.g. for sea water as compared to river water), affecting internal standard responses. Sample composition may also lead to significant contributions of interferences, for example chlorine based interferences, such as ³⁵Cl¹⁶O⁻ (interfering on ⁵¹V), or ⁴⁰Ar³⁵Cl⁺ (interfering on ⁷⁵As). Again, these can be removed efficiently through kinetic energy discrimination, but also reactive gases and triple quadrupole technology can perfectly overcome these interferences. To show the potential of the iCAP TQ ICP-MS to do a complete analysis of the most common analytes in water samples, a certified reference material was analysed. For elements which were not certified, a spike recovery test was performed to address the accuracy of the analysis. The results are displayed in Table 3.

Table 3. Results for a Multielement Analysis of an SLRS River Water CRM

Analyte	Mode	Measured	Spike Recovery	Certified Value [µg·L ⁻¹]	Recovery
²³ Na	KED	5085	100%	5380	95%
²⁴ Mg	KED	2665	105%		
²⁷ Al	KED	55.3		49.5	112%
³⁹ K	KED	863	101%	839	103%
⁵¹ V	TQ-O ₂	0.33	98%	0.32	104%
⁵² Cr	TQ-O ₂	0.23	100%	0.208	110%
⁵⁶ Fe	KED	93.2		91.2	102%
⁵⁸ Co	KED	0.05	98%	0.05	107%
⁶⁰ Ni	KED	0.52	91%	0.48	110%
⁶³ Cu	KED	18.2		17.4	105%
⁷⁵ As	TQ-O ₂	0.43		0.41	104%
⁷⁸ Se	TQ-O ₂	0.10			
⁸⁵ Rb	KED	1.20	103%		
¹⁰⁷ Ag	KED	0.00	101%		
¹¹¹ Cd	TQ-O ₂	0.0057		0.006	95%
¹¹⁵ In	KED	0.001	105%		
¹³³ Cs	KED	0.004	103%		
¹³⁸ Ba	TQ-O ₂	14.7		14.0	105%
²⁰⁸ Pb	KED	0.08	106%		
²³⁸ U	KED	0.10		0.09	109%

As can be seen, KED still is the preferred interference removal mechanism as it allows the generic removal of all polyatomic interferences. However, for some elements triple quadrupole based modes either remove other types of interferences that KED mode cannot (as shown before), or they achieve better limits of detection and are therefore automatically selected by Reaction Finder.

As can be seen from the results, all elements agree well with certified concentrations (where available) or indicate quantitative spike recovery. In total, more than 20 elements were analyzed in two different measurement modes. To comprehensively remove all interferences, the use of only two gases, He and O₂, was sufficient.

CONCLUSIONS

- The use of triple quadrupole ICP-MS technology removes critical interferences on certain key analytes using reactive gases and subsequent chemical reactions in the CRC system. However, to effectively leverage reactive gases, an active pre-filter must remove other ions from the ion beam that could potentially interfere on dedicated product ion masses. Overall, this approach allows the reliable removal of all interferences, regardless of their nature.
- The use of a dedicated method development assistant to set up a method combining different modes (SQ vs. TQ), reactive gases (He vs. O₂ vs. other), etc., greatly simplifies the use of the triple quadrupole techniques, especially in routine, high throughput laboratories.
- O₂ and He are a powerful combination of gases to allow comprehensive interferences removal for most regulated methods, and other gases are not necessary in these situations.

REFERENCES

1. Smart Note 44415; Thermo Fisher Scientific

TRADEMARKS

Teledyne CETAC Technologies is a trademark of Teledyne Instruments Inc.. All other trademarks are the property of Thermo Fisher Scientific and its subsidiaries

ThermoFisher
SCIENTIFIC