

Combining Superior Interference Removal and Speed for Elemental Analysis Using ICP-MS

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ABSTRACT

This poster proposes a novel analysis mode using triple quadrupole ICP-MS, which combines the speed of analysis of a single quadrupole ICP-MS system with the added interference removal capabilities of a triple quadrupole ICP-MS. A thorough comparison of performance is shown, covering the most important analytical figures of merit. This novel approach for ICP-MS reliably eliminates critical interferences, simplifies method development, and decreases analysis time per sample¹.

INTRODUCTION

Analysis of metals is important for applied testing of food, environmental and industrial applications, among others. Typically occurring polyatomic interferences can be well controlled using single quadrupole ICP-MS instruments equipped with collision/reaction cells (CRC's), but some interferences can only be efficiently removed using triple quadrupole ICP-MS systems. These systems, however, are often viewed as not fit for purpose for applied analyses, as the use of multiple reaction gases for interference removal is necessary, making method development more difficult and increasing sample turnaround times. The combination of using O₂ as the only CRC gas and a triple quadrupole ICP-MS can be way to overcome the above-mentioned challenge, as is shown in Figure 1. Any addition of measurement time through a gas switch is eliminated, so that identical sample turnover times as compared to single quadrupole ICP-MS are feasible. At the same time, method development can be dramatically simplified, whilst confidence in results is increased.

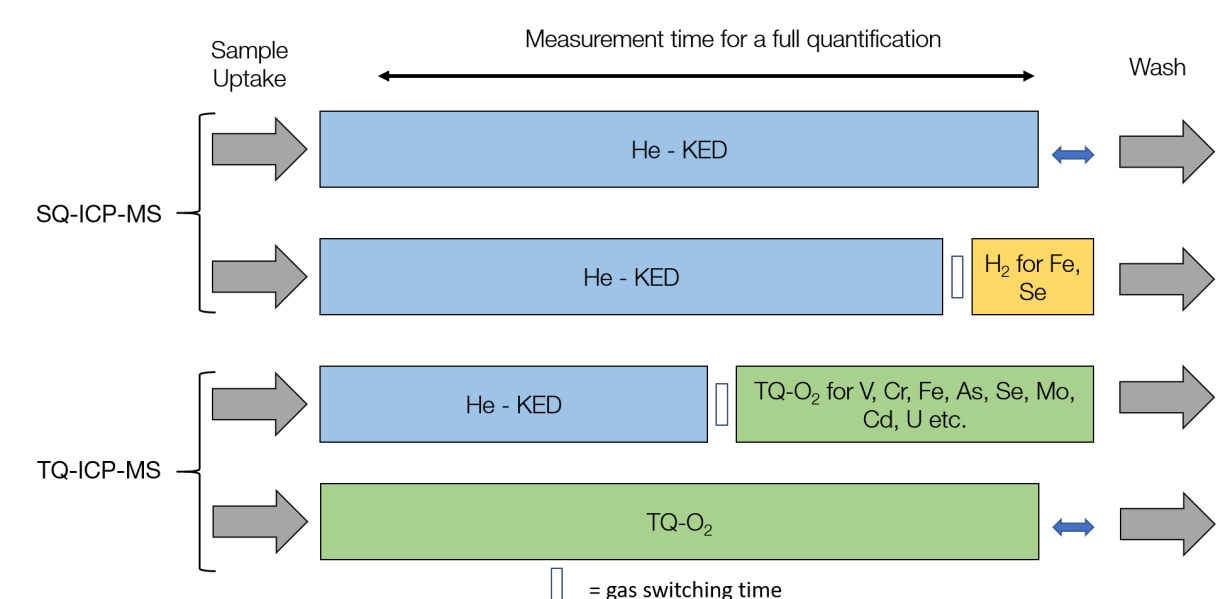


Figure 1. Concept of TQ-O₂ single mode analysis. The use of O₂ as the only reaction gas is reducing overall measurement time whilst improving interferences removal and detection limits for key contaminants.

The use of O₂ provides a wealth of opportunities to eliminate critical interferences on key contaminants (polyatomic and other types of interferences), whilst the mass analyzer setup eliminates the risk of unwanted side reactions through a mass filtration step prior to the CRC.

- Common polyatomics, for example ⁴⁰Ar³⁵Cl⁺ (on ⁷⁵As) are eliminated. At the same time, the sensitivity can be increased, returning lower detection limits. Polyatomic interferences in the high mass range are more effectively removed.
- The selection of default isotopes can be improved. For example, ⁸⁰Se⁺ is accessible as the ⁴⁰Ar₂⁺ interference is efficiently eliminated.
- Doubly charged interferences, caused for example by the presence of neodymium or gadolinium are removed. These interferences may cause a bias on ⁷⁵As⁺ and ⁷⁸Se⁺ when using a single quad instrument using kinetic energy discrimination.

MATERIALS AND METHODS

All measurements in this study were conducted using a Thermo Scientific[™] iCAP[™] TQe ICP-MS, coupled with an ASX-560 autosampler and the ASXpress[®] PLUS Rapid Sample Introduction System (Teledyne Cetac Technologies). The details of the sample introduction system and other parameters are listed in Table 1. The use of a single mode for analysis ultimately enabled the use of a segmented flow sample introduction system, so that a further reduction of the overall sample turnover time was possible.

Table 1. Typical operating parameters of the iCAP TQe ICP-MS

iCAP TQe ICP-MS	
Nebuliser	MicroMist Nebuliser (400 µl/min)
Interface	Ni Sample and Skimmer cone, High Matrix Skimmer cone insert
Spray chamber	Cyclonic quartz
Injector	Quartz, 2.5 mm ID
Nebuliser Flow	1.13 L·min ⁻¹
RF Power	1550 W
CRC Conditions	0.34 or 0.7 mL·min ⁻¹ O ₂ (analyte depending) 4.8 mL·min ⁻¹ Helium for comparative measurements using KED
Scan settings	0.2 s for As, Hg, Se; 0.1 s for Cd, Fe, Pb, Sb, Sn; 0.05 s for others. 5 sweeps, 3 main runs
Total Analysis time per sample	1:19 min

The following samples were prepared and analyzed as part of this study:

- Ten infant and baby food samples (two milk powders, two cereals, four meal substitute purees and two fruit juices/purees).
- A milk powder CRM (BCR 063 (European Commission, Joint Research Center, Geel, Belgium)
- Baby Food Composite CRM (NIST CRM 2383a))

Aliquots of 0.4 ± 0.05 g of homogenized powder sample or 2 ± 0.2 g of homogenized puree sample were weighed accurately. After the addition of 5 mL HNO₃ and 1 mL HCl (67 and 35–37 weight %, Optima[™] grade, Fisher Scientific), the digestion of the samples was accomplished using an Ethos microwave digestion system (Milestone SRL, Italy). After cooling, the digested solutions were quantitatively recovered and made up to a final volume of 50 mL using ultra-pure water. All food samples and reference materials were digested using the same method, irrespective of sample type.

RESULTS

Food samples are a mixture of various organic compounds, macro- and minor-nutrients, essential nutritional elements in varying amounts, and sometimes trace quantities of harmful or potentially toxic elements. The results presented in the following show an initial validation of the TQ-O₂ single mode analysis for the analysis of such samples, with special focus on improvement opportunities compared to a method using single quadrupole-based analysis. Further information (for example, spike recovery tests) can be found in reference 1.

To demonstrate the **superior interference removal** capabilities of this approach, a pooled sample was spiked with different potential interfering elements and the resulting concentrations were measured using both SQ-KED mode and TQ-O₂ mode. The results are displayed in **Table 2**.

To prove the **accuracy of the proposed method**, relevant CRM's were analyzed and the results are displayed in **Table 3**. both CRMs (NIST 2383a and BCR063) showed recoveries ranging from 85 - 119%.

Finally, an extended sequence, **analyzing more than 500 samples** (including QC checks and CRM analysis) and lasting for about 11 hours was run. The QC standard was repeated after each block of 10 unknown samples as a Continuous Calibration Verification (CCV) to ensure the validity of the calibration. The concentration in the CCV checks was 0.1 µg·L⁻¹ (Hg), 1 µg·L⁻¹ (common trace metals), 100 µg·L⁻¹ (Al, B, Be, Fe), 5,000 µg·L⁻¹ (Mn) and 10,000 µg·L⁻¹ (Ca, K, Mg, Na, P). The results are shown in **Figure 2**.

Table 2. Result of the analysis of a baby food sample spiked with a variety of potential interferences. Highlighted results exceed the maximum permissible limit as per the US Baby Food Safety Act² once the dilution factor incurred during sample preparation is included.

SQ KED				
	⁷⁵ As	⁷⁸ Se	¹¹¹ Cd	²⁰² Hg
Original sample	0.03	0.03	2.41	0.04
+ 20 µg·kg ⁻¹ REEs	1.00	6.46	-	-
+ 50 µg·kg ⁻¹ REEs	2.44	16.21	-	-
+ 10 µg·kg ⁻¹ W + 1 mg·kg ⁻¹ Mo			2.81	0.44
+ 10 µg·kg ⁻¹ W + 10 mg·kg ⁻¹ Mo			7.42	0.88
TQ-O ₂				
	⁷⁵ As ⁷⁵ As, ¹⁶ O	⁷⁸ Se ⁷⁸ Se, ¹⁶ O	¹¹¹ Cd ¹¹¹ Cd	²⁰² Hg ²⁰² Hg
Original sample	0.03	0.02	2.33	0.05
+ 20 µg·kg ⁻¹ REEs	0.03	0.02		
+ 50 µg·kg ⁻¹ REEs	0.03	0.02		
+ 10 µg·kg ⁻¹ W + 1 mg·kg ⁻¹ Mo			2.32	0.05
+ 10 µg·kg ⁻¹ W + 10 mg·kg ⁻¹ Mo			2.45	0.05

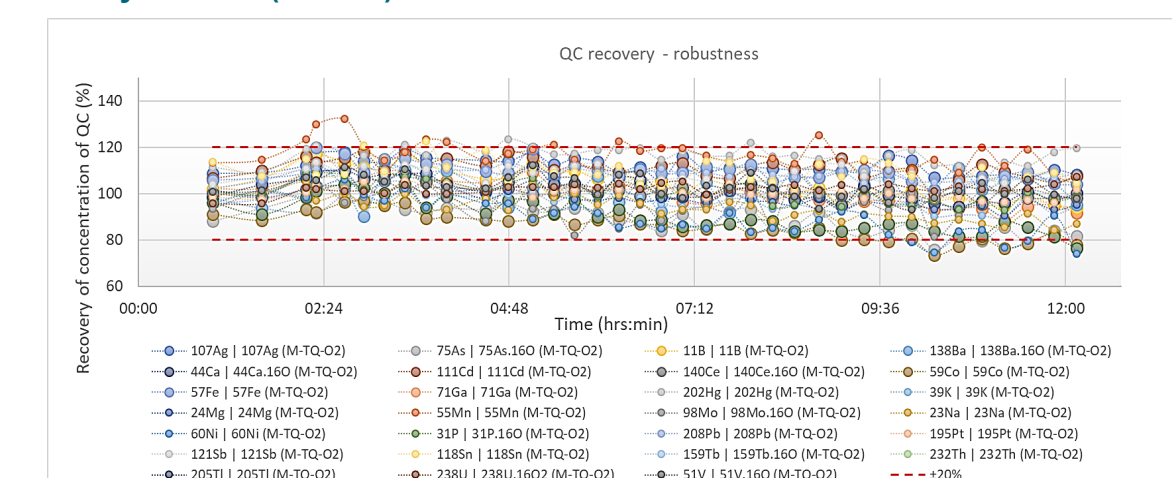
Note that both conventional analyses using kinetic energy discrimination and the proposed method using TQ-O₂ mode return identical results for the unspiked sample. However, with even just low concentrations of molybdenum and tungsten present in the sample, false positive results arise on the critical elements Cd and Hg. These interferences can only be efficiently removed using triple quadrupole technology.

Table 3. Certified and measured elemental concentrations two baby food CRMs. Values marked with * are known reference values.

Element	CRM NIST 2383a			CRM BCR 063		
	Certified [mg·kg ⁻¹]	Determined [mg·kg ⁻¹]	Recovery [%]	Certified [mg·kg ⁻¹]	Determined [mg·kg ⁻¹]	Recovery [%]
Ba	0.278 ± 0.020	0.243	88 ± 1.6	-	-	-
Ca	342.6 ± 5.0	377.3	110 ± 1.6	13,490 ± 100	14205	105 ± 4.8
Ce	-	-	-	1.5	1.2	83 ± 4.0
Co	0.048 ± 0.005	0.051	106 ± 3.9	-	-	-
Cu	0.758 ± 0.082	0.648	85 ± 3.2	0.602 ± 0.019	0.609	101 ± 6.2
Fe	4.420 ± 0.51	5.116	88 ± 1.5	2.32 ± 0.23	2.02	88 ± 1.8
K	2910 ± 220	3,341	115 ± 0.4	17680 ± 190	17556	102 ± 4.5
Mg	212 ± 4.0	229	108 ± 0.4	1263 ± 24	1362	110 ± 6.3
Mo	-	-	-	0.33	0.25	89 ± 2.2
Mn	0.963 ± 0.064	1.153	119 ± 0.5	-	-	-
Na	195 ± 29	202.5	104 ± 0.6	4370 ± 31	4329	95 ± 2.7
P	453 ± 11	402	89 ± 2.2	11100 ± 130	10598	95 ± 5.5
Pb	-	-	-	0.019 ± 0.001	0.018	95 ± 4.1
Se	-	-	-	0.129	0.121	93 ± 3.4
Zn	2.22 ± 0.18	1.77	89 ± 2.0	-	-	-

The accuracy of the method was tested using the reference materials mentioned above, which were representative of the different sample types analyzed in this study. By using the two reference materials, data on the method accuracy and precision could be retrieved for 15 elements. For the remaining analytes, selected samples were spiked (prior to digestion) at relevant levels, and the spike recovery determined (data not shown). This way, accuracy and precision could be assessed for 6 more analytes (e.g., V, Sn, Sb, Hg).

Figure 2. CCV recoveries for all analytes. The dashed line represents the accepted recovery interval (± 20%).



Blocks of ten unknown samples, which included two real baby food samples and eight simulated samples with matched matrix composition were analyzed. The recovery of the internal standard remained stable throughout the experiment with recoveries between 75 - 110% (data not shown). Almost all QC checks were found to be between within 80 - 120% over the full 11 hours of continuous analysis.

CONCLUSIONS

- A single method allowing the analysis of 30 elements, covering nutritional and toxic elements in baby food was developed and tested.
- All analytes were measured using a single measurement mode on the iCAP TQe ICP-MS using oxygen as the collision / reaction cell gas. This resulted in highly sensitive and accurate analysis of all analytes of interest, including potentially challenging analytes including arsenic, selenium, cadmium and mercury.
- Complete interference removal was demonstrated by spiking experiments and proved that the use of TQ technology is an effective way to overcome potential challenges.
- A wide linear dynamic range, starting from 0.005 µg·kg⁻¹ for trace elements and extending up to 100,000 µg·kg⁻¹ for major elements, was achieved, as well as excellent detection limits for almost all elements.
- Method validity and accuracy was demonstrated with the analysis of appropriate CRMs and RMs, typically obtaining a result between 85 - 120% of the certified concentration.

REFERENCES

1. S. Sengupta et al., Using triple quadrupole ICP-MS to improve the speed, sensitivity, and accuracy of the analysis of toxic and nutritional elements in baby foods; Application Note 000209, Thermo Fisher Scientific (2021)
2. S.1019 - Baby Food Safety Act of 2021. 117th Congress (2021-2022); Text - S.1019 - 117th Congress (2021-2022): Baby Food Safety Act of 2021 | Congress.gov | Library of Congress. <https://www.congress.gov/bills/117/congress/senate-bill/1019/text?r=1&s=4>

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