Accelerating Food Analysis using Advanced ICP-MS Technology

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ABSTRACT

To ascertain the quality of food and food products, the analysis of toxic, essential and nutritional elements becomes a routine task for food quality monitoring. Elements such as arsenic, cadmium, mercury or lead may enter the food chain via a series of pathways including, but not limited to, industrial pollution or environmental contamination. Recent public alerts on arsenic or lead contaminations in our daily food or water supply have contributed to an increased attention, but there is also a high demand for clear information on nutrients and contaminants through health-conscious consumers.

To keep up with the demands of the market, analytical laboratories need to be capable of analysing a high number of samples, containing both major and trace levels of a variety of elements, in the shortest possible time. Therefore, highly productive analytical systems are needed. This can be accomplished for example by using single quadrupole ICP-MS instruments enabling a single measurement mode to analyse all elements in a suite, and therefore dramatically reducing the time needed per sample. Additional accessories enabling automated in line dilution can furthermore liberate operator time and free up valuable resources.

At the same time, certain elements present only occasionally (for example, rare earth elements) may cause significant false positive signals on critical analytes such as arsenic or selenium, and may not be eliminated fully using single quadrupole based ICP-MS systems and require advanced interference only possible with triple quadrupole technology.

This paper reviews different strategies including collision/reaction cell (CRC) strategies in both single and triple quadrupole ICP-MS for the accurate analysis of trace elements in different food samples.
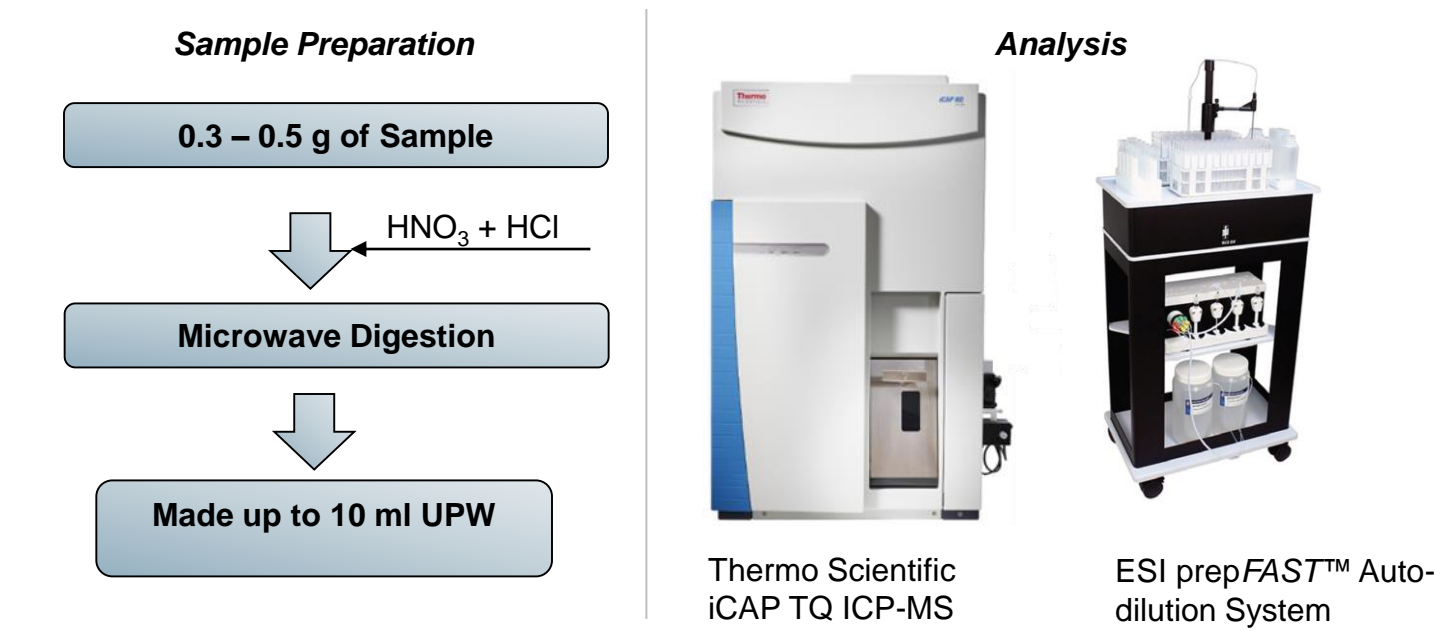
INTRODUCTION

ICP-MS is a sensitive and rapid techniques with wide linear dynamic range and as such are ideal tools for the analysis of trace and major analytes in food in one analytical run. The accuracy of these techniques is demonstrated through the analysis of food based certified materials following microwave digestion.

The principal challenge for trace elemental ICP-based techniques are interferences that stem from the complex food matrix, the reagents used to prepare the sample and the plasma source. This paper reviews different strategies including collision/reaction cell (CRC) strategies in triple quadrupole ICP-MS for the accurate analysis of trace elements in more challenging matrices.

MATERIALS AND METHODS

Samples were prepared from certified reference materials NIST 1515 Apple Leaves, NIST 1573a Tomato Leaves. High purity standards (1000 mg·kg^{-1} single element standards) were used to prepare the stock calibration standards.

Figure 1. Sample preparation and analysis

Sample Preparation

- 0.3 – 0.5 g of Sample
- HNO$_3$ + HCl
- Microwave Digestion
- Made up to 10 ml UPW

Analysis

Thermo Scientific iCAP TQ ICP-MS

ESI prepFAST™ Auto-dilution System

Instrumentation

A Thermo Scientific™ iCAP™ TQ ICP-MS was operated in SQ-KED mode and TQ-O$_2$ mode using the parameters presented in Table 1. All instruments were controlled using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Table 1. ICP-MS and ICP-OES operating parameters.

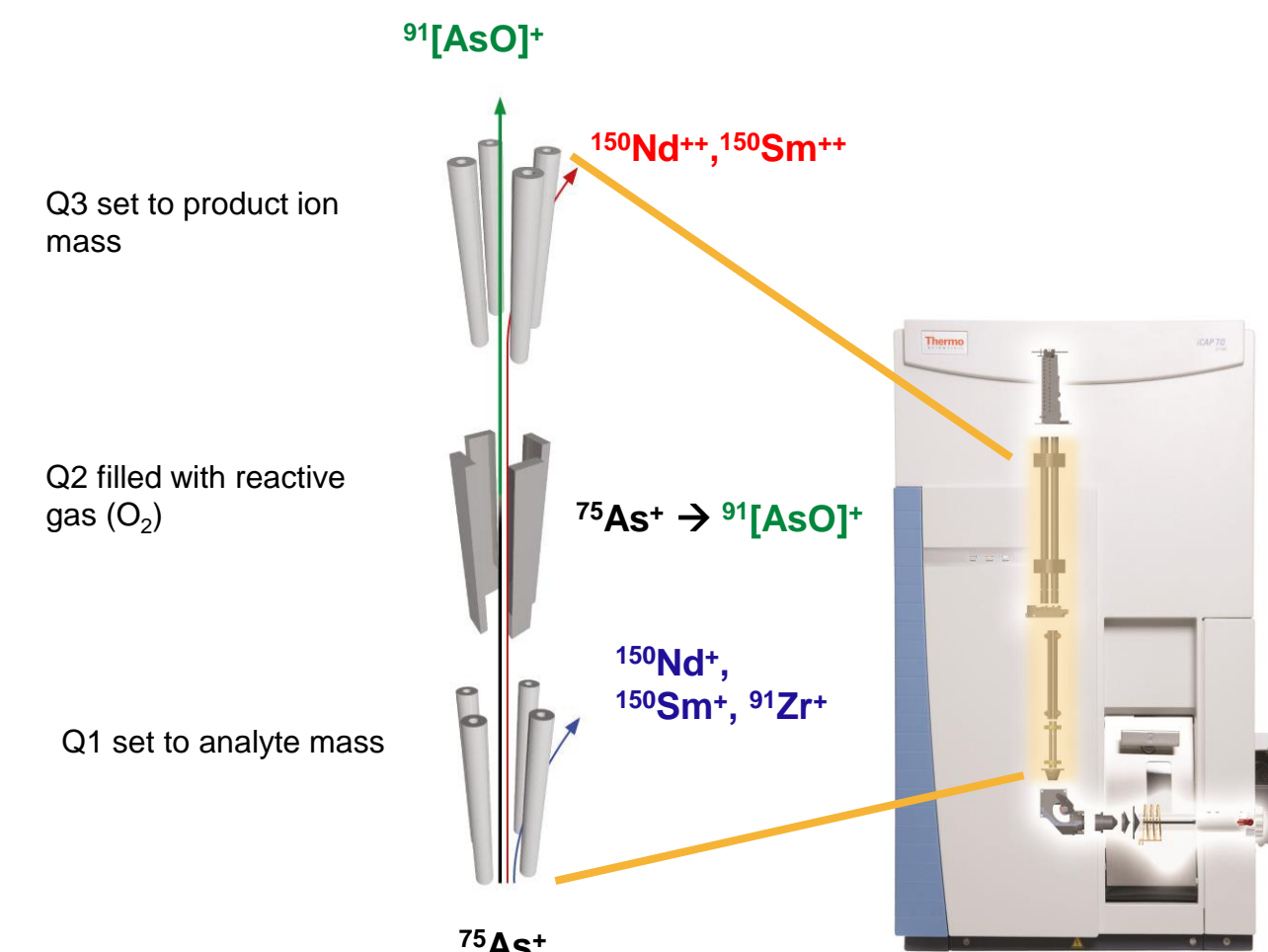| Parameter	iCAP TQ ICP-MS
Nebulizer	PFA ST Nebulizer (Green) 100 µL·L^{-1}
Spray chamber	Quartz cyclonic spraychamber cooled @ 3° C
Injector	2.5 mm Quartz
Interface	Ni sampler and Ni skimmer with High Matrix insert
RF Power	1550 W
Nebulizer Gas	1.0 mL·min^{-1}
TQ-O$_2$	100% O$_2$ gas @ 0.3 mL·min^{-1}
SQ-KED	100 % He gas @ 4.3 mL·min^{-1} with 3V KED
Dwell Time	0.1 second per analyte, 5 sweeps
Lens Setting	Optimized using autotune routines

Autodilution System

Samples were presented for analysis with the iCAP TQ ICP-MS using an Elemental Scientific prepFAST Autodilution System. Using prescriptive dilution, all samples were automatically diluted directly before the analysis using ICP-MS. Again, the autodilution unit was controlled within the Qtegra ISDS Software, allowing to use both user defined prescriptive as well as intelligent autodilution for samples falling outside of previously defined ranges (calibration range or internal standard recovery).
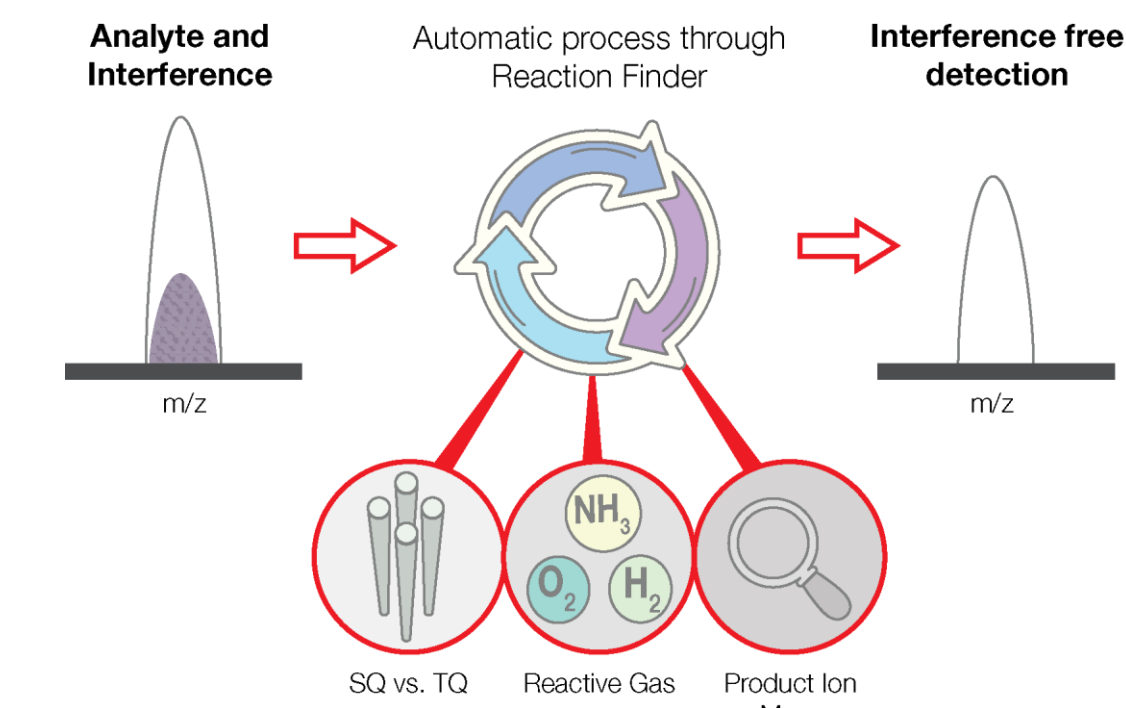
RESULTS

Whilst ICP-OES is an excellent and powerful tool for the analysis of trace elements in food samples, ICP-MS can offer even lower detection limits and higher dynamic range to analyze both trace and major elements in one run. However, ICP-MS is affected by different types of spectral interferences. Most interferences observed are polyatomic in nature (e.g. $^{40}Ar^{35}Cl^+$ resulting in a false positive signal on ^{75}As) and can be removed using helium and kinetic energy discrimination on single quadrupole based systems. In some cases, other interferences may be observed, for example, doubly charged ions formed form rare earth elements, also resulting in false positive signals on elements such as arsenic or selenium. To overcome these interferences, the use of triple quadrupole ICP-MS instrumentation, like the iCAP TQ ICP-MS, is required.

Figure 2. Interference Removal for ^{75}As using the iCAP TQ ICP-MS with O$_2$ as Reactive Gas

$^{91}[AsO]^+$

$^{150}Nd^{++}, ^{150}Sm^{++}$

Q3 set to product ion mass

Q2 filled with reactive gas (O$_2$)

$^{75}As^+ \rightarrow ^{91}[AsO]^+$

$^{150}Nd^+, ^{150}Sm^+, ^{91}Zr^+$

Q1 set to analyte mass

$^{75}As^+$

Selection of the most appropriate combination of reactive gas and scan settings however may be difficult for some users of ICP-MS instrumentation. For most elements, measurement modes as used on a single quadrupole based instrument will also give the lowest detection limits while fully eliminating potential interferences. In order to facilitate the process of setting up methods for the iCAP TQ ICP-MS leveraging the full potential of advanced interference removal using triple quadrupole technology, the Qtegra ISDS Software contains the Reaction Finder Method Development Assistant. The process of setting up a method using Reaction Finder is outlined in Figure 3:

Figure 3. Workflow of the Reaction Finder Method Development Assistant.

Analyte and Interference

Automatic process through Reaction Finder

Interference free detection

SQ vs. TQ   Reactive Gas   Product Ion Mass

One example for a sample leading to potentially unresolved interferences is NIST 1515 apple leaves. A full spectrum reveals the presence of a variety of rare earth elements with considerable concentrations, as shown in Figure 4. Therefore, the results for elements such arsenic and selenium will be showing false positives when analyzed without triple quadrupole technology due to the formation of e.g. Nd^{++} or Gd^{++} ions. However, the Reaction Finder Method Development Assistant will automatically select a measurement mode based on triple quadrupole ICP-MS to effectively eliminate these interferences. Other modes (or alternative product ions where applicable) can be manually added and are automatically applied intelligently in just one aspiration of a sample.

Figure 4. Mass spectrum showing mass range between 125-175. The observed signals correspond to Ba, as well as different rare earth elements, such as Nd or Gd, among others.
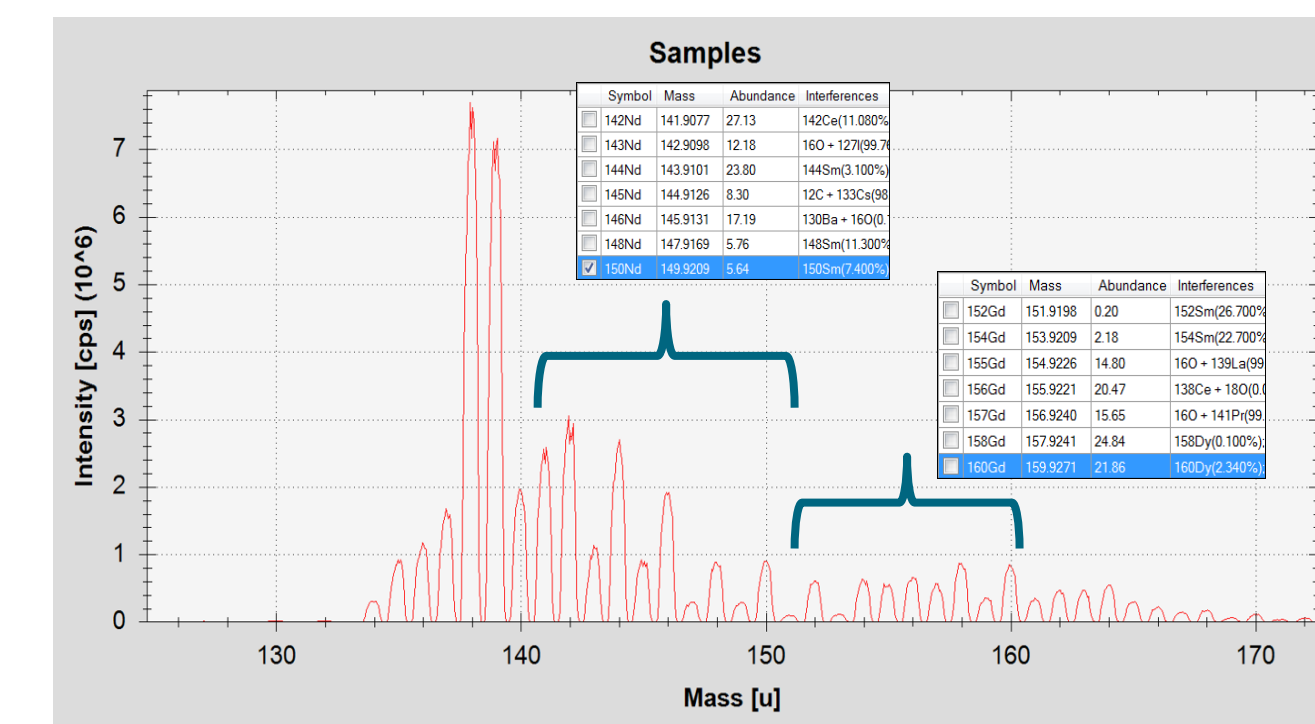

Table 2 shows the results obtained for the analysis of both reference materials under investigation, NIST 1515 (apple leaves) and 1573A (tomato leaves). As can be seen, all reported concentrations are in perfect agreement with certified values, including arsenic and selenium. At the same time, also sulfur and phosphorous can be analyzed, which are normally heavily interfered in single quadrupole based ICP-MS, and therefore typically measured using ICP-OES in an independent analysis

Table 2. Results for the NIST CRM 1515 Apple leaves and NIST CRM 1673a Tomato leaves by iCAP TQ ICP-MS.

Analyte	IDL (µg·L^{-1})	MDL (µg·kg^{-1})	NIST 1515 apple leaves N=3		NIST 1573A tomato leaves N=3	
			Measured (mg·kg^{-1})	Certified (mg·kg^{-1})	Measured (mg·kg^{-1})	Certified (mg·kg^{-1})
^{11}B	0.4	52.4	25.2±0.6	27±2	30.0±0.2	33.3±0.7
^{23}Na	4	524	29.3±0.8	24.4±1.2	123±1.5	136±4
^{24}Mg	1	131	2686±84	2710±80	10556±210	12000*
^{27}Al	0.1	13.1	258±8.4	286±9	532±13	598±12
^{31}P as $^{31}P^{16}O$	0.05	6	1530±10	1590*	2040±33	2160±40
^{32}S as $^{32}S^{16}O$	0.02	2.6	1819±15	1800*	9779±0.2	9600*
^{39}K	3	393	16106±75	16100±200	27299±198	27000±500
^{44}Ca	1	131	15218±2300	15260±1500	49339±235	50500±900
^{51}V	0.001	0.13	0.24±0.01	0.26±0.03	0.80±0.01	0.835±0.010
^{52}Cr	0.005	0.66	0.29±0.01	0.3*	1.97±0.02	1.99±0.06
^{55}Mn	0.003	0.39	52.6±0.6	54±3	242±1.9	246±8
^{57}Fe	1	131	81.5±1.6	80*	366±4.8	368±7
^{59}Co	0.011	1.44	0.08±0.003	0.09*	0.57±0.01	0.57±0.02
^{60}Ni	0.023	3.01	0.85±0.13	0.91±0.12	1.57±0.02	1.59±0.07
^{63}Cu	0.088	11	5.59±0.05	5.64±0.24	4.7±0.1	4.7±0.14
^{66}Zn	0.026	3.41	11.3±0.16	12.5±0.3	28.2±0.37	30.9±0.7
^{75}As as $^{75}As^{16}O$	0.006	0.79	0.036±0.003	0.038±0.007	0.117±0.03	0.112±0.004
^{75}As	0.004	0.52	0.469±0.012	0.038±0.007	0.143±0.01	0.112±0.004
^{78}Se as $^{78}Se^{16}O$	0.003	0.39	0.052±0.006	0.050±0.009	0.053±0.01	0.054±0.003
^{78}Se	0.046	6.03	1.272±0.19	0.050±0.009	0.11±0.01	0.054±0.003
^{85}Rb	0.004	0.52	9.1±0.17	9*	13.97±0.03	14.89±0.27
^{88}Sr	0.002	0.26	25.5±0.34	25±2	84.8±0.49	85*
^{98}Mo	0.003	0.39	0.094±0.01	0.094±0.013	0.47±0.06	0.46*
^{111}Cd	0.001	0.13	0.013±0.001	0.014*	1.45±0.03	1.52±0.04
^{121}Sb	0.001	0.13	0.012±0.005	0.013*	0.057±0.003	0.063±0.006
^{138}Ba	0.002	0.262	48.8±0.1	49±2	60.2±0.7	63*
^{208}Pb	0.001	0.131	0.422±0.002	0.470±0.024	-	N.D.
^{232}Th	0.001	0.131	0.03±0.002	0.03	0.107±0.002	0.12*
^{238}U	0.001	0.131	0.008±0.002	0.006*	0.033±0.001	0.035*

CONCLUSIONS

- Using triple quadrupole ICP-MS, excellent performance for the determination of trace element analysis in food samples can be achieved, making it ideal for food safety and quality assurance measurements.

- The Reaction Finder Method Development Assistant allows simple method development through automatic selection of the optimum analysis conditions for the analytes of interest.

REFERENCES

1. Total elemental analysis of food samples using the Thermo Scientific iCAP TQ ICP-MS with autodilution, Application Note 43446; Thermo Fisher Scientific

TRADEMARKS/LICENSING

Thermo Fisher SCIENTIFIC