Maximizing laboratory throughput: Robust and accurate analysis of trace metals in food samples with triple quadrupole ICP-MS

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Goal

To demonstrate the suitability of the Thermo Scientific™ iCAP™ TQe ICP-MS using a single measurement mode for the analysis of trace elements in a variety of food samples.

Introduction

The measurement of potentially harmful substances in food has become a major topic of public interest in recent years. The abundant use of pesticides/fertilizers in agricultural products and related health concerns have led customers to seek for organic alternatives. In addition to discrete molecules, toxic metals can also impose a significant risk of exposure through food, like the potential high concentration of arsenic in e.g. in rice and related products[1]. International regulatory bodies in conjunction with the Food and Agricultural Organization and the World Health Organization are responsible for developing standard test methods for the analysis of food samples. Alongside this regulatory compliance, it is important to monitor toxic contaminants that could potentially enter the food supply chain via a series of pathways, such as environmental contamination, industrial pollution, during food processing and by food fraud. The packaging of food may also contribute to the amount of toxic metals found in food products[2].

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is a powerful technique for the analysis of trace elements, as it allows a simultaneous determination of both toxic and nutritional elements in a single analysis. It´s outstanding detection sensitivity combined with a linear dynamic range of up to 10 orders of magnitude (for a single isotope) allow for the determination of both toxic metals, present in trace concentrations, as well as major components, present in concentrations as high as several hundreds of ppm at a time.

The high sensitivity of ICP-MS is required for the targeted analysis in food samples with the required detection limits becoming lower, as more insight is gained in food safety research. One of the main challenges for ICP-MS analysis for food sample is the potential of biased results through interferences, as well as adverse effects in the sample introduction system caused by the sample matrix, e.g. clogging of the nebulizer or instrumental drift.

The screening of food samples is often accomplished in laboratories working in high throughput conditions, so that short sample to sample time with consistent QC results, as well as robustness to cope with a variety of different sample matrices is key to achieve a high number of samples run per day. This application note describes an optimized method for the analysis of different types of food samples, including both organic as well as non-organic foods. In order to perform a basic validation of the method, different certified reference materials (apple leaves, bovine liver, rice flour and milk powder) were analysed. To facilitate short analysis time with full interference removal, an iCAP TQe ICP-MS was operated using a single measurement mode (TQ-O_2) to screen the entire mass range (lithium to uranium).

Experimental

Experimental optimization of instrument parameters

An iCAP TQe ICP-MS was used for all measurements. The sample introduction system consisted of a Peltier cooled (2.7 ˚C), baffled cyclonic spray chamber, PFA nebulizer, and quartz torch with a 2.5 mm i.d. removable quartz injector. In order to avoid any unwanted matrix effects when analysing a wide variety of sample types, the robust skimmer cone insert was selected for this application. For automation of the sample introduction process, a Teledyne CETAC ASX-560 autosampler (Omaha, NE, USA) was used. In order to remove all potentially occurring interferences, the ICP-MS was operated in TQ-O_2 mode using the parameters presented in Table 1. In short, the TQ-O_2 mode removes spectral interferences in following way:

Table 1. Instrument configuration and operating parameters

Parameter	Value
Nebulizer	Borosilicate glass micromist, 400 µL·min^{-1}, pumped at 40 rpm
Pump tubing	Orange – green, 0.38 mm i.d.
Spraychamber	Quartz cyclonic, cooled at 2.7 ˚C
Injector	2.5 mm i.d., quartz
Interface	Nickel sampler and nickel skimmer cone with robust insert
Plasma power	1,550 W
Nebulizer gas	1.08 L·min^{-1}
QCell setting	**TQ-O_2**
Gas flow	100% O_2, 0.34 mL·min^{-1}
CR bias	-6.3 V
Q3 bias	-12 V
Scan setting	0.2 sec dwell time for P, S, As and Se, 0.05 sec dwell time for others, 5 sweeps, 3 main runs
Lens setting	Optimized using autotune
Sample up take	55 sec
Wash time	45 sec
Total analysis time	2 min 57 sec

The collision reaction cell (CRC) is pressurized with oxygen as a reaction gas. For all analytes, Q1 set to analyte mass (M^+), whereas Q3 is set to either the the same mass (for elements unreactive or with low reactivity towards oxygen), or MO^+ or even MO_2^+ (for analytes reactive to oxygen). Based on the mass filtration in the first quadrupole, potential side reactions of other elements are suppressed, and other elements, potentially occupying the intended product ion mass of MO^+, are removed. This mode allows for complete interference removal and improved detection sensitivity for key analytes. With respect to accuracy, some food samples can contain trace levels of rare earth elements (REEs) arising from the soil in which the plant was grown. In the ICP, REEs generate a proportion of doubly charged ions (such as Nd^{2+} and Gd^{2+}) which then interfere on arsenic and selenium respectively, causing a positive bias in the results. The principle of how the iCAP TQe ICP-MS removes these interferences is highlighted in Figure 1.

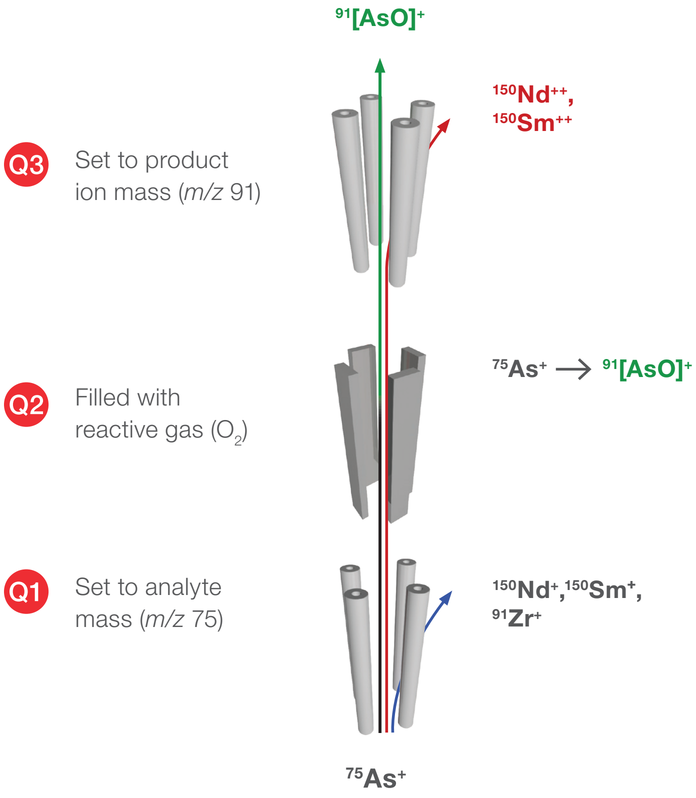

Figure 1. Schematic showing TQ mass shift modes for arsenic

Although for some elements, other modes such as kinetic energy discrimination might provide at least equivalent interference removal and, in some cases, also slightly improved detection limits, the advantage of using a single mode for all elements was preferred in order to reduce the analysis time per sample by omitting a gas switching cycle in the CRC. Especially when using valve-based systems for discrete sampling, a time saving of 10 seconds (corresponding to a typical flush/fill cycle in a CRC) makes up for a significant amount of the turnover time per sample.

Data acquisition and data processing

All parameters in the measurement modes was defined automatically using the autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

The autosampler was controlled using the Qtegra ISDS Software as well using a dedicated software plug-in. In total, 37 elements were screened including the internal standards.

Quality control is critical in routine analysis, especially when running long batches containing different sample matrices. To ensure quality control, the internal standards were monitored and continuing calibration checks (CCVs) were performed periodically throughout the analytical run.

The absolute suppression and relative drift of the internal standards was evaluated throughout the analysis, further demonstrating the stability and robustness of the iCAP TQe ICP-MS for prolonged measurement of high matrix samples. A full suite of quality control tests is included in the Qtegra ISDS Software and can be configured (with respect to applicable % limits, repetition rate and actions on warning/failure) as required. This includes also testing for spike recovery, as used in continuation of this note.

Sample preparation

Precleaned polypropylene bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ·cm^{-1}) and left to dry in a laminar flow clean hood before use.

Four certified reference materials (Apple Leaves, NIST (National Institute of Standards and Technology) 1515; Bovine liver, NIST 1577c; Rice flour NIST 1568b and milk powder BCR 685 (European Commission)) and a total of 18 individual food samples, comprising both organic as well as inorganic grown food (details are shown Figure 2 and Table 2) were prepared to evaluate the iCAP TQe ICP-MS for this analysis. All samples were digested before analysis.

Figure 2. Analysed the food sample image

Table 2. Overview of the samples analysed, including condition, packaging material and origin

	Item	Status	Package	Product origin
1	Organic raspberry	Freeze dry	Aluminum foil bag	Germany
2	Raspberry	Freeze dry	Aluminum foil bag	Germany
3	Organic strawberry	Freeze dry	Aluminum foil bag	Germany
4	Strawberry	Freeze dry	Aluminum foil bag	Germany
5	Orange powder	Freeze dry	Aluminum foil bag	Germany
6	Blueberry powder	Freeze dry	Aluminum foil bag	Germany
7	Rice	Uncooked	Plastic bag	Netherland
8	Hazel nuts	Uncooked	Plastic bag	Turkey
9	Peanuts	Uncooked	Plastic bag	South America
10	Chia seed	Uncooked	Plastic bag	South America
11	Curry mix spice powder	Powder	Plastic bag	India
12	Oregano	Dried	Glass bottle	Germany
13	Chili	Dried	Plastic bottle	China
14	Paprika powder	Powder	Glass bottle	Hungary
15	Basil	Dried	Glass bottle	Germany
16	Yeast	Dried	Aluminum foil bag	Germany
17	All-purpose flour (type 405)	Uncooked	Paper bag	Germany
18	Bread flour (type 550)	Uncooked	Paper bag	Germany

An aliquot of approximately 0.3–0.4 g of each sample was accurately weighed and acid digested using a mixture of 5 ml HNO_3 (68% Optima™ grade, Fisher Chemicals) and 1 ml HCl (35% Optima™ grade, Fisher Chemicals) in a closed vessel microwave digestion system (Milestone ETHOS 1). After digestion, the samples were made up to 50 mL using ultrapure water, so that the amount of total dissolved solids was around 0.6% in the measured sample solution. No further dilution was applied prior to analysis.

All blanks, calibration standards, and quality control samples (QC) were prepared using 2% v/v HNO_3, replacing the certified reference material with single element standards (SPEX CertiPrep, Metuchen, NJ, USA) to result in the concentrations listed in Table 3.

Table 3. Calibration solutions concentration (all values as in $mg·L^{-1}$)

Standard group	Element	STD-1	STD-2	STD-3	STD-4	QC (CCV)
Group 1	Ag, Al, As, Au, Be, Cd, Ce, Co, Cr, Cu, Hg, Mo, Ni, Th, U, V, Zn, Pb, Pt, Sb, Se, Sn	0.0001	0.001	0.005	0.01	0.001
Group 2	Li, B, Mn, Ba, Rb, Sr	0.002	0.02	0.1	0.2	0.02
Group 3	Na, Ca, K, Fe, Mg, P, S	2	20	100	200	-

An internal standard solution, containing Sc, Ga, In, Tb and Tl, all at 5 µg·L^{-1} in 2% v/v HNO_3 was added to all samples via a T-piece (mixing rate between internal standard and samples 1:1) before entering the nebulizer. The internal standards were selected to cover the entire mass range of the analytes selected in order to get the best possible correction for potentially occurring matrix effects or drifts. The allocation of the different internal standards to the individual elements is highlighted in Table 3.

The details of the measurement modes, acquisition parameters, and internal standards used for each element are summarized in Table 4. In order to analyse all elements using a single mode, the default settings of the Reaction Finder Method Development Assistant were modified accordingly.

Table 4. Internal standards used for each element with corresponding target isotopes, Q1, Q3 and dwell times

Analyte	Dwell time (s)	Q1 resolution	Q3 resolution	Internal standard
^{7}Li	0.1	High	Normal	^{45}Sc^{16}O
^{9}Be	0.1	High	Normal	^{45}Sc^{16}O
^{11}B	0.1	High	Normal	^{45}Sc^{16}O
^{23}Na	0.05	High	High	^{45}Sc^{16}O
^{24}Mg	0.05	High	High	^{45}Sc^{16}O
^{27}Al	0.1	Normal	Normal	^{45}Sc^{16}O
^{31}P as ^{31}P^{16}O at *m/z* 47	0.1	High	High	^{45}Sc^{16}O
^{32}S as ^{32}S^{16}O at *m/z* 48	0.1	High	High	^{45}Sc^{16}O
^{39}K	0.05	High	High	^{45}Sc^{16}O
^{40}Ca as ^{40}Ca^{16}O at *m/z* 56	0.05	High	High	^{45}Sc^{16}O
^{51}V as ^{51}V^{16}O at *m/z* 67	0.1	Normal	Normal	^{45}Sc^{16}O
^{52}Cr as ^{52}Cr^{16}O at *m/z* 68	0.1	Normal	Normal	^{45}Sc^{16}O
^{55}Mn	0.1	Normal	Normal	^{45}Sc^{16}O
^{56}Fe	0.05	High	High	^{45}Sc^{16}O
^{59}Co	0.1	Normal	Normal	^{71}Ga
^{60}Ni	0.1	Normal	Normal	^{71}Ga
^{63}Cu	0.1	Normal	Normal	^{71}Ga
^{66}Zn	0.1	Normal	Normal	^{71}Ga
^{75}As as ^{75}As^{16}O at *m/z* 91	0.1	Normal	Normal	^{71}Ga
^{80}Se as ^{80}Se^{16}O at *m/z* 96	0.1	Normal	Normal	^{71}Ga
^{85}Rb	0.1	Normal	Normal	^{71}Ga
^{88}Sr as ^{88}Sr^{16}O at *m/z* 104	0.1	Normal	Normal	^{71}Ga
^{98}Mo as ^{98}Mo^{16}O at *m/z* 114	0.1	Normal	Normal	^{115}In
^{107}Ag	0.1	Normal	Normal	^{115}In
^{111}Cd	0.1	Normal	Normal	^{115}In
^{118}Sn	0.1	Normal	Normal	^{115}In
^{121}Sb	0.1	Normal	Normal	^{115}In
^{138}Ba as ^{138}Ba^{16}O at *m/z* 154	0.1	Normal	Normal	^{159}Tb^{16}O
^{197}Au	0.1	Normal	Normal	^{159}Tb^{16}O
^{202}Hg	0.1	Normal	Normal	^{159}Tb^{16}O
^{208}Pb	0.1	Normal	Normal	^{205}Tl
^{238}U as ^{238}U^{16}O^{16}O at *m/z* 270	0.1	Normal	Normal	^{205}Tl

Result and discussion

Linearity assessment

In a first step to assess the overall method performance for the analysis of trace elements in food samples, the achievable detection limits and the linear dynamic range were determined through acquisition of a calibration curve. For all analytes, the linearity of the method was demonstrated over a concentration range covering at least four orders of magnitude (see Table 3 for applicable calibration ranges). ICP-MS can cover a linear dynamic range of up to 10 orders of magnitude for a single isotope, so that even large differences in concentration between individual samples are not of concern.

Sensitivity (limit of detection)

In general, the sensitivity obtained in modes using the CRC is reduced compared to standard mode (no interference removal), especially for low mass elements such as lithium (Li), beryllium (Be) or boron (B). Especially in kinetic energy discrimination (KED), using an additional positive bias potential towards the inlet of the analysing quadrupole, the sensitivity per unit concentration can be reduced by several orders of magnitude. Due to a reduced background signal, however, detection limits are often at least comparable. In a triple quadrupole mode, the bias potential between CRC and Q3 are typically set to a negative difference of up to 7V, so that part of the signal loss due to collisions with gas molecules can be offset. Therefore, elements with low mass can be analysed successfully and with good detection limits using the same analysis mode as “typical” transition metals, requiring the use of the CRC to eliminate interferences. Figure 3 shows that the analyte with the lowest mass investigated in this study (^{7}Li) can be detected with an excellent correlation, R^2 >0.9999, and good detection limits.

To measure nutritious elements, potentially present in high concentrations (standard calibration group 3) and causing very high signal intensities, the iCAP TQe ICP-MS can use variable resolution settings for both quadrupoles (Q1 and Q3). Changing the average resolution of the third quadrupole (Q3) from normal resolution (about 0.75 amu peak width) to high resolution (about 0.35 amu peak width) can attenuate signals to enable their direct measurement without negative impact on the lifetime of the detector. The results obtained with the iCAP TQe ICP-MS show excellent results based on the correlation coefficients (R^2) of the obtained calibration curves. Figure 4 shows the calibration curve for ^{39}K for concentrations of 0, 5, 20, 100 and 500 $mg\cdot L^{-1}$ with R^2 = 0.9999. This allows the verification of the concentration of nutritious elements in food sample without additional dilution.

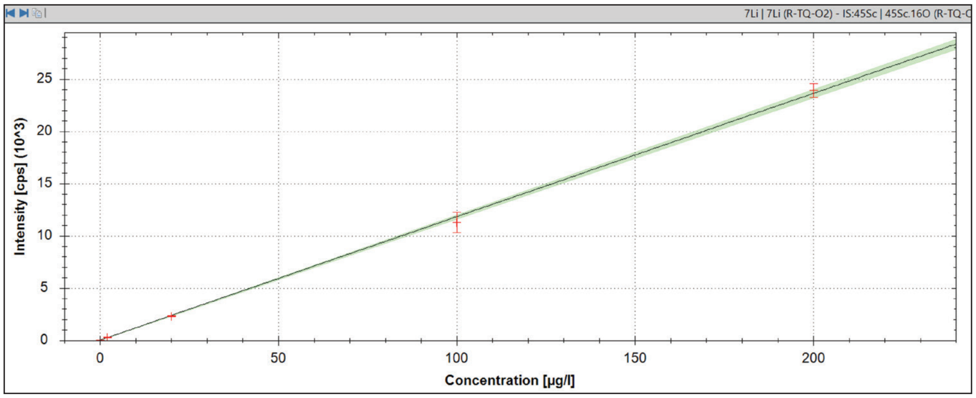

Figure 3. Calibration curve for ^{7}Li 7 *m/z* in TQ-O_2 on mass mode

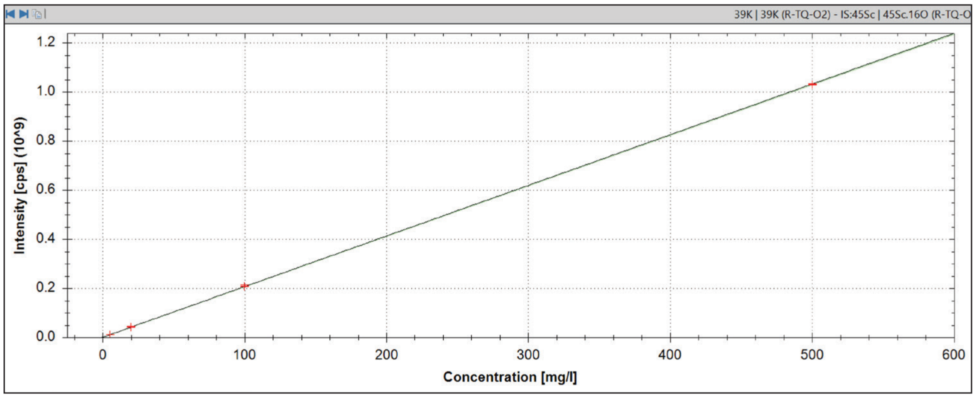

Figure 4. Calibration curve for ^{39}K 39 *m/z* in TQ-O_2 on mass mode

Table 5 shows the R^{2}, limits of detection (LOD) and background equivalent concentration (BEC). The LODs were calculated from three times the standard deviation of ten replicate measurements of the calibration blank. The LODs for all the elements of interest are significantly below the expected levels required for food sample analysis.

Table 5. Results for R^{2}, LOD and BEC data for the analysis of 32 elements in 2% HNO_3

Analyte	Correlation coefficient, R^{2}	BEC (μg·L^{-1})	LOD (μg·L^{-1})
^{7}Li	>0.9999	0.06	0.15
^{9}Be	0.9997	0.01	0.07
^{11}B	0.9998	0.67	0.38
^{23}Na	>0.9999	16.1	0.92
^{24}Mg	0.9999	0.31	0.20
^{27}Al	>0.9999	0.98	0.19
^{31}P as ^{31}P^{16}O at *m/z* 47	0.9999	4.0	0.77
^{32}S as ^{32}S^{16}O at *m/z* 48	0.9999	7.3	0.45
^{39}K	0.9999	14.8	0.17
^{40}Ca as ^{40}Ca^{16}O at *m/z* 56	0.9998	13.8	0.15
^{51}V as ^{51}V^{16}O at *m/z* 67	0.9999	0.004	0.004
^{52}Cr as ^{52}Cr^{16}O at *m/z* 68	0.9997	0.07	0.02
^{55}Mn	0.9998	0.009	0.006
^{56}Fe	0.9986	0.2	0.06
^{59}Co	0.9996	0.007	0.003
^{60}Ni	0.9995	0.04	0.005
^{63}Cu	0.9996	0.04	0.02
^{66}Zn	0.9996	0.11	0.04
^{75}As as ^{75}As^{16}O at *m/z* 91	0.9994	0.004	0.01
^{80}Se as ^{80}Se^{16}O at *m/z* 96	0.9995	0.004	0.02
^{85}Rb	0.9999	0.005	0.003
^{88}Sr as ^{88}Sr^{16}O at *m/z* 104	0.9996	0.009	0.01
^{98}Mo as ^{98}Mo^{16}O at *m/z* 114	>0.9999	0.008	0.01
^{107}Ag	>0.9999	0.004	0.002
^{111}Cd	0.9997	0.0004	0.002
^{118}Sn	>0.9999	0.03	0.01
^{121}Sb	>0.9999	0.003	0.004
^{138}Ba as ^{138}Ba^{16}O at *m/z* 154	0.9999	0.007	0.006
^{197}Au	0.9999	0.02	0.005
^{202}Hg	>0.9999	0.009	0.009
^{208}Pb	0.9999	0.005	0.003
^{238}U as ^{238}U^{16}O^{16}O at *m/z* 270	>0.9999	0.0003	0.0004

Method validation

As part of this study, four food reference materials (apple leaves, bovine liver, rice flour and milk powder) and 18 different food samples were analysed as technical replicates to assess the repeatability of the results. The results obtained show that the calculated concentrations of the target elements matched the certified values accurately, demonstrating the accuracy of method. For all reference materials, at least 10 individual samples were measured, so that the method was also demonstrated to deliver excellent precision (Table 6).

Out of the reference materials selected, NIST SRM 1515 (apple leaves) poses a significant challenge for the analysis using single quadrupole ICP-MS. Since this reference material contains approximately 17 mg·kg^{-1} neodymium (Nd) and 3 mg·kg^{-1} Gadolinium (Gd), respectively, the resulting doubly charged interferences are leading to considerable bias to the results for arsenic and selenium. Even considering the dilution during sample preparation, the final concentrations in the measured solutions may result in signals of several hundred thousand of cps. Using the TQ-O_2 mass shift mode (as shown in Figure 1), the doubly charged interferences were efficiently removed, leading to excellent agreement of the results with the certified concentrations. The results obtained for all CRM´s and method detection limits (MDLs) are summarized in Table 6. MDLs are based on the instrumental detection limits summarized in Table 5 but considering the dilution factor of 150 incurred during the digestion process.

The typical concentrations found in the analysed reference materials cover a wide concentration range, from sub µg·kg^{-1} to low % levels, demonstrating the importance of the linear dynamic range of the iCAP TQe ICP-MS.

Table 6. Quantitative results obtained for the CRM food samples. Analytes concentration are reported as mg·L^{-1}. All numbers annotated with * are known reference values (expected values).

Analyte	MDL	Apple leaves, NIST 1515, (n=28)		Rice flour, NIST 1568b, (n=10)	
		Certified	Measured	Certified	Measured
^{7}Li	0.02	-	0.1 ± 0.03	0.01 ± 0.004	-
^{9}Be	0.01	-	0.02 ± 0.01	<MDL	-
^{11}B	0.06	27.6 ± 2.8	33.1 ± 3.3	0.68 ± 0.08	-
^{23}Na	0.14	24.4 ± 2.1	25.9 ± 3.3	7.1 ± 0.8	6.74 ± 0.19
^{24}Mg	0.03	2,710 ± 120	2,761 ± 78	552 ± 26	559 ± 10
^{27}Al	0.03	284.5 ± 5.8	269 ± 2.9	4.6 ± 0.42	4.21 ± 0.34
^{31}P as ^{31}P^{16}O at *m/z* 47	0.12	1,593 ± 68	1,611 ± 114	1,158 ± 57	1,530 ± 40
^{32}S as ^{32}S^{16}O at *m/z* 48	0.07	1,800*	1,751 ± 116	1,159 ± 46	1,200 ± 10
^{39}K	0.25	16,080 ± 210	16,483 ± 83	1,185 ± 0.6	1,281 ± 11
^{40}Ca as ^{40}Ca^{16}O at *m/z* 56	0.22	15,250 ± 100	15,108 ± 121	120 ± 4	118.4 ± 3.1
^{51}V as ^{51}V^{16}O at *m/z* 67	0.001	0.254 ± 0.027	0.22 ± 0.01	0.01 ± 0.003	-
^{52}Cr as ^{52}Cr^{16}O at *m/z* 68	0.003	0.3*	0.3 ± 0.02	0.05 ± 0.002	-
^{55}Mn	0.001	54.1 ± 1.1	54.0 ± 2	19.3 ± 0.57	19.2 ± 1.8
^{56}Fe	0.01	82.7 ± 2.6	84.8 ± 5.6	8.2 ± 0.6	7.42 ± 0.44
^{59}Co	0.0004	0.09*	0.095 ± 0.004	0.019 ± 0.0009	0.0177 ± 0.0005
^{60}Ni	0.001	0.936 ± 0.094	0.9 ± 0.04	0.21 ± 0.008	
^{63}Cu	0.003	5.69 ± 0.13	5.1 ± 0.2	2.3 ± 0.05	2.35 ± 0.16
^{66}Zn	0.01	12.45 ± 0.43	11.8 ± 0.4	18.5 ± 0.4	19.42 ± 0.26
^{75}As as ^{75}As^{16}O at *m/z* 91	0.002	-	0.04 ± 0.004	0.29 ± 0.01	0.285 ± 0.014
^{80}Se as ^{80}Se^{16}O at *m/z* 96	0.003	-	0.05 ± 0.01	0.31 ± 0.02	0.365 ± 0.029
^{85}Rb	0.0005	10.2 ± 1.6	9.0 ± 1.1	6.18 ± 0.21	6.198 ± 0.026
^{88}Sr as ^{88}Sr^{16}O at *m/z* 104	0.002	25.1 ± 1.1	24.7 ± 4.2	0.156 ± 0.007	-
^{98}Mo as ^{98}Mo^{16}O at *m/z* 114	0.002	0.095 ± 0.011	0.09 ± 0.01	1.51 ± 0.05	1.451 ± 0.048
^{107}Ag	0.0004	-	0.01 ± 0.0002	0.002 ± 0.0001	-
^{111}Cd	0.0003	0.0132 ± 0.0015	0.01 ± 0.002	0.020 ± 0.0001	0.0224 ± 0.0013

Table 6 continued. Quantitative results obtained for the CRM food samples. Analytes concentration are reported as mg·L^{-1}. All numbers annotated with * are known reference values (expected values).

Analyte	MDL	Apple leaves, NIST 1515, (n=28)		Rice flour, NIST 1568b, (n=10)	
		Certified	Measured	Certified	Measured
^{118}Sn	0.002	-	0.2 ± 0.01	0.007 ± 0.002	0.005 ± 0.0001
^{121}Sb	0.001	0.013*	0.02 ± 0.001	0.004 ± 0.0005	-
^{138}Ba as ^{138}Ba^{16}O at *m/z* 154	0.001	48.8 ± 2.3	46.8 ± 2.3	0.14 ± 0.01	-
^{197}Au	0.001	0.001*	0.001 ± 0.002	0.002 ± 0.001	-
^{202}Hg	0.001	0.0432 ± 0.0023	0.04 ± 0.002	0.0066 ± 0.0008	0.00591 ± 0.00036
^{208}Pb	0.0004	0.47 ± 0.024	0.49 ± 0.02	0.008 ± 0.0003	0.008 ± 0.0003
^{238}U as ^{238}U^{16}O^{16}O at *m/z* 270	0.0001	0.006*	0.007 ± 0.0004	0.0004 ± 0.00001	-

Analyte	MDL	Bovine liver, NIST 1577c (n=10)		Milk powder BCR 685 (n=10)	
		Certified	Measured	Certified	Measured
^{7}Li	0.02	0.01 ± 0.004	-	0.03 ± 0.003	-
^{9}Be	0.01	<MDL	-	<MDL	-
^{11}B	0.06	0.34 ± 0.03	-	1.5 ± 0.06	-
^{23}Na	0.24	2,239 ± 31	2,300 ± 64	4,312 ± 5	4,370 ± 31
^{24}Mg	0.03	614 ± 8	620 ± 42	1260 ± 5	1,263 ± 0.024
^{27}Al	0.03	6.9 ± 0.7	-	2.9 ± 0.1	-
^{31}P as ^{31}P^{16}O at *m/z* 47	0.12	10,149 ± 287	-	10,156 ± 50	11,100 ± 130
^{32}S as ^{32}S^{16}O at *m/z* 48	0.07	7,755 ± 204	7,490 ± 340	3,338 ± 50	
^{39}K	0.25	10,361 ± 381	10,230 ± 640	17,105 ± 184	17,680 ± 190
^{40}Ca as ^{40}Ca^{16}O at *m/z* 56	0.22	134 ± 2	131 ± 10	13,287 ± 103	13,490 ± 100
^{51}V as ^{51}V^{16}O at *m/z* 67	0.001	0.01 ± 0.0006	0.0092 ± 0.0007	0.072 ± 0.0004	-
^{52}Cr as ^{52}Cr^{16}O at *m/z* 68	0.003	0.06 ± 0.014	0.053 ± 0.014	0.046 ± 0.009	-
^{55}Mn	0.001	10.5 ± 0.2	10.46 ± 0.47	0.23 ± 0.02	
^{56}Fe	0.01	222 ± 12	197.94 ± 0.65	2.6 ± 0.06	2.32 ± 0.23
^{59}Co	0.0004	0.35 ± 0.0016	0.300 ± 0.018	0.01 ± 0.005	-
^{60}Ni	0.001	0.05 ± 0.002	0.0445 ± 0.0092	0.09 ± 0.009	-
^{63}Cu	0.003	299 ± 13	275.2 ± 4.6	0.64 ± 0.003	0.602 ± 0.019
^{66}Zn	0.01	188 ± 3	181.1 ± 1	48.6 ± 0.2	49.0 ± 0.6
^{75}As as ^{75}As^{16}O at *m/z* 91	0.002	0.02 ± 0.002	0.0196 ± 0.0014	0.004 ± 0.001	-
^{80}Se as ^{80}Se^{16}O at *m/z* 96	0.003	2.0 ± 0.05	2.031 ± 0.045	0.13 ± 0.06	0.129*
^{85}Rb	0.0005	35 ± 0.9	-	19.9 ± 0.2	-
^{88}Sr as ^{88}Sr^{16}O at *m/z* 104	0.002	0.109 ± 0.006	0.0953 ± 0.0042	4.3 ± 0.03	-
^{98}Mo as ^{98}Mo^{16}O at *m/z* 114	0.002	3.2 ± 0.02	3.3 ± 0.13	0.33 ± 0.02	0.33*
^{107}Ag	0.0004	0.006 ± 0.0002	-	0.0007 ± 0.0002	-
^{111}Cd	0.0003	0.099 ± 0.0002	0.097 ± 0.0014	0.013 ± 0.0002	-
^{118}Sn	0.002	0.011 ± 0.0002	-	0.056 ± 0.0002	-
^{121}Sb	0.001	0.003 ± 0.0006	-	0.0009 ± 0.0002	-
^{138}Ba as ^{138}Ba^{16}O at *m/z* 154	0.001	0.042 ± 0.002	-	0.975 ± 0.004	-
^{197}Au	0.001	0.0036 ± 0.002	-	0.0032 ± 0.0004	-
^{202}Hg	0.001	0.0068 ± 0.0009	-	0.001 ± 0.0002	-
^{208}Pb	0.0004	0.0067 ± 0.001	0.0628 ± 0.001	0.021 ± 0.006	0.0185 ± 0.0027
^{238}U as ^{238}U^{16}O^{16}O at *m/z* 270	0.0001	0.0008 ± 0.00005	-	0.0003 ± 0.00002	-

Table 7 shows the results obtained for different food samples and provides detailed information on the concentrations for both toxic and nutritious elements. No significant differences were observed in the concentrations of toxic or nutritious elements between organic and non-organic grown food.

Table 7. Quantification results for different food samples. All concentrations are reported as mg·L^{-1}.

Analyte	Raspberry organic	Raspberry	Strawberry organic	Strawberry	Orange organic	Blueberry organic	Rice	Hazel nuts	Peanuts
^{7}Li	0.01	0.01	0.02	0.01	0.05	0.004	0.01	0.01	0.01
^{9}Be	0.01	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
^{11}B	10.9	6.6	13.1	13.6	12.6	6.8	0.8	18.6	19.4
^{23}Na	6.0	5.5	13.8	156	76.6	2.2	8.2	5.5	239
^{24}Mg	1,352	968	1,283	1,148	731	384	270	1,376	1,784
^{27}Al	6.2	5.5	17.4	9.9	2.4	8.9	4.1	6.7	1.6
^{31}P as ^{31}P^{16}O at *m/z* 47	1,667	1,282	1,963	2,287	1,256	732	1,075	2,686	3,935
^{32}S as ^{32}S^{16}O at *m/z* 48	706	632	758	789	491	449	942	1,274	1,760
^{39}K	12,207	11,110	12,782	14,953	12,697	4,657	850	6,028	7,343
^{40}Ca as ^{40}Ca^{16}O at *m/z* 56	1,644	1,527	2,169	1,201	1,363	1,135	55.2	1,323	630
^{51}V as ^{51}V^{16}O at *m/z* 67	0.01	0.01	0.04	0.04	0.01	0.01	0.01	0.01	0.01
^{52}Cr as ^{52}Cr^{16}O at *m/z* 68	0.02	0.02	0.1	0.09	0.10	0.07	0.004	0.02	0.002
^{55}Mn	132	100	28.3	26.2	1.5	155	9.9	31.7	11.1
^{56}Fe	28.7	24.3	42.9	17.2	6.9	9.9	2.7	28.3	14.2
^{59}Co	0.4	0.2	0.3	0.1	0.02	0.004	0.01	0.1	0.08
^{60}Ni	3.6	2.8	2.1	0.2	0.2	0.7	0.5	1.4	0.4
^{63}Cu	6.2	6.8	3.8	2.9	2.2	2.9	3.0	14.3	5.5
^{66}Zn	21.3	18.6	9.5	9.3	2.5	4.8	19.1	18.7	46.1
^{75}As as ^{75}As^{16}O at *m/z* 91	0.02	0.01	0.02	0.01	0.003	0.004	0.1	0.01	0.004
^{80}Se as ^{80}Se^{16}O at *m/z* 96	0.004	0.003	0.003	0.01	0.01	0.01	0.04	0.01	0.04
^{85}Rb	3.5	4.3	10.1	3.7	9.5	15.3	0.4	7.6	1.4
^{88}Sr as ^{88}Sr^{16}O at *m/z* 104	5.2	6.1	7.7	9.6	8.7	2.4	0.2	8.0	4.3
^{98}Mo as ^{98}Mo^{16}O at *m/z* 114	0.2	0.1	0.3	0.5	0.1	0.1	1.2	0.03	5.3
^{107}Ag	0.003	0.003	0.001	0.001	0.001	0.001	0.002	0.003	0.001
^{111}Cd	0.2	0.13	0.02	0.005	0.0003	0.01	0.04	0.02	0.03
^{118}Sn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.003
^{121}Sb	0.002	0.001	0.001	0.002	0.0004	0.001	0.004	0.003	0.0005
^{138}Ba as ^{138}Ba^{16}O at *m/z* 154	3.6	3.6	11.2	5.4	1.3	13.3	0.1	3.4	1.4
^{197}Au	0.002	0.005	0.003	0.004	0.002	0.003	0.003	0.003	0.004
^{202}Hg	0.002	0.002	0.003	0.002	0.001	0.002	0.003	0.002	0.002
^{208}Pb	0.01	0.01	0.01	0.02	0.01	0.005	0.004	0.01	0.001
^{238}U as ^{238}U^{16}O^{16}O at *m/z* 270	0.0003	0.0002	0.001	0.003	0.001	0.0002	0.0001	0.0003	0.0002

■ <1 mg·L^{-1} ■ 1–10 mg·L^{-1} ■ 1–01000 mg·L^{-1} ■ >1000 mg·L^{-1}

Table 7 continued. Quantification results for different food samples. All concentrations are reported as mg·L^{-1}.

Analyte	Chia sheed	Curry spice	Oregano	Chili	Paprika	Basil	Yeast	All-purpose flour	Bread flour
^{7}Li	0.05	0.3	5.2	0.5	1.1	0.2	0.07	0.01	0.01
^{9}Be	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
^{11}B	12.3	15.9	126	21.9	9.7	21.9	0.7	0.4	0.3
^{23}Na	4.5	355	150	117	346	315	708	6.1	4.6
^{24}Mg	3,952	2,719	2,509	1,708	2,243	3,704	848	230	299
^{27}Al	10.2	235	195	34.3	177	57.0	3.9	4.1	1.4
^{31}P as ^{31}P^{16}O at *m/z* 47	8,733	3,474	1,985	3,214	3,811	3,355	8,644	977	1,117
^{32}S as ^{32}S^{16}O at *m/z* 48	2,877	1,996	3,227	2,289	2,021	2,532	2,871	997	997
^{39}K	8,505	17,400	21,066	33,302	15,122	30,062	18,581	1,833	1,630
^{40}Ca as ^{40}Ca^{16}O at *m/z* 56	5,541	6,463	17,495	1,056	1,257	17,976	305	200	164
51V as 51V16O at *m/z* 67	0.01	0.6	0.5	0.07	0.4	0.3	0.03	0.01	0.004
^{52}Cr as ^{52}Cr^{16}O at *m/z* 68	0.01	1.2	0.4	0.6	3.0	0.4	0.01	0.02	0.01
^{55}Mn	47.3	122	143.5	10.0	17.8	166	6.9	8.2	6.3
^{56}Fe	85.0	254	220	67.4	308	110	26.4	11.1	9.4
^{59}Co	0.5	0.2	0.3	0.1	0.2	0.5	0.4	0.002	0.001
^{60}Ni	3.0	2.1	3.0	0.6	1.7	1.6	0.1	0.03	0.05
^{63}Cu	21.2	8.5	14.1	9.4	11.1	15.3	3.3	1.3	1.7
^{66}Zn	64.8	31.8	59.2	14.2	18.4	61.2	126	8.6	9.0
^{75}As as ^{75}As^{16}O at *m/z* 91	0.03	0.05	0.96	0.04	0.2	0.3	0.03	0.003	0.001
^{80}Se as ^{80}Se^{16}O at *m/z* 96	0.06	0.05	0.03	0.02	0.1	0.05	0.03	0.04	0.04
^{85}Rb	1.9	15.8	26.9	25.3	12.3	13.7	25.4	0.6	1.6
^{88}Sr as ^{88}Sr^{16}O at *m/z* 104	59.6	41.0	135	4.4	12.8	75.0	7.3	0.7	0.6
^{98}Mo as ^{98}Mo^{16}O at *m/z* 114	0.7	0.4	1.3	0.4	0.4	0.2	0.03	0.3	0.8
^{107}Ag	0.007	0.003	0.02	0.001	0.01	0.03	0.002	0.005	0.001
^{111}Cd	0.02	0.1	0.1	0.1	0.1	0.4	0.04	0.05	0.02
^{118}Sn	0.01	0.02	0.06	0.01	0.07	0.3	0.02	0.01	0.005
^{121}Sb	0.002	0.009	0.02	0.005	0.01	0.02	0.006	0.001	0.0006
^{138}Ba as ^{138}Ba^{16}O at *m/z* 154	13.8	17.8	30.3	1.2	4.2	27.7	0.4	1.4	0.8
^{197}Au	0.003	0.002	0.02	0.004	0.004	0.03	0.005	0.002	0.003
^{202}Hg	0.001	0.004	0.02	0.002	0.002	0.02	0.002	0.001	0.001
^{208}Pb	0.004	0.2	0.4	0.1	0.4	0.7	0.006	0.01	0.002
^{238}U as ^{238}U^{16}O^{16}O at *m/z* 270	0.0003	0.01	0.007	0.002	0.03	0.01	0.03	0.0001	0.0001

⬜ <1 mg·L^{-1} ▩ 1–10 mg·L^{-1} ▢ 1–01000 mg·L^{-1} ■ >1000 mg·L^{-1}

With respect to toxic elements, a relatively high concentration of lead (Pb) was observed in oregano, basil, chili, curry spice and paprika than other food samples and could potentially be explained due to exposure to pollution from agricultural machinery or traffic.

In order to also verify the accuracy of the determination in these samples, all samples were also subjected to a spike recovery check, meaning that a fixed amount of all analytes (concentration as per standard 3, refer to Table 2 for details) was added into each sample after the microwave digestion step. The recovery results showed good agreement with the expected values with recoveries between 82–120%, once again demonstrating the applicability of the proposed method.

Robustness

For reliable analysis in a routine laboratory, it is important that the results obtained are accurate and precise also in longer batches. Often, the response of the internal standard is a good indicator and there are acceptable limits that define whether a result can be reported or not. Commonly, the response of the internal standard should be between 80–120%, which has been achieved in all measurements. In addition, quality control (QC) samples containing a known concentration of all analytes are analysed periodically during a longer batch to monitor instrument performance.

To simulate a typical routine sample analysis, a larger sample batch was scheduled for analysis containing a preparation blank and 22 food samples (CRM and food samples). Each sample sequence in the batch was concluded with a quality control standard (CCB and CCV) before restarting the next sequence. In summary, a set of QC tests was analysed every 22 samples. The entire batch contained a total of 283 samples and was analysed in a total time of approximately 14 hours.

Figure 5 shows the results obtained for all QC samples. The RSD for all CCVs are well within ±10% over 14 h and indicates that the iCAP TQe ICP-MS allows for robust and reliable long-term analysis even for samples containing a relatively high amount of TDS and varying composition of the sample matrix.

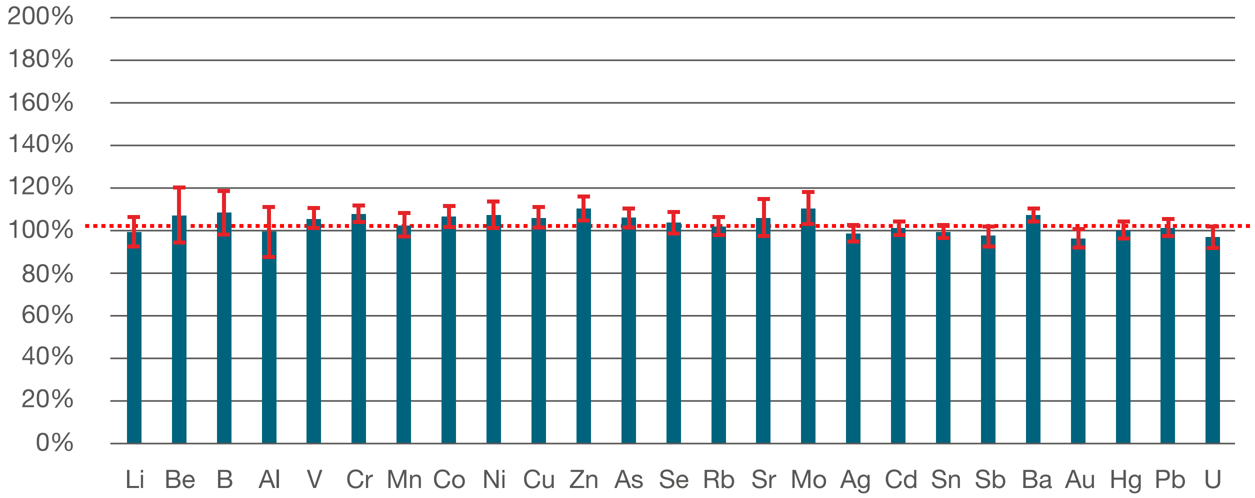

Figure 5. QC calibration verification results. Error bars indicate standard deviation calculated from n=14 repeat measurements. Dotted line represents the average value (in %).

Conclusion

The iCAP TQe ICP-MS was employed to analyse 32 elements in 22 different food sample types following simple microwave digestion. Both nutritious and toxic elements were targeted in organically grown and non-organic food samples analysed over large sample batches under routine laboratory conditions. This analytical method was rigorously tested, and the results obtained clearly demonstrated the fowling analytical advantages:

- High sensitivity TQ-O_2 mode provided the advanced performance required for the accurate determination of As, Se and other elements in complex food matrix samples showing outstanding LODs and linear response.
- Using a single measurement (TQ-O_2) mode reduced the total analysis time to <3 min/sample (including uptake and wash time) for 32 elements (nutritious and toxic). This sample turnover time can be reduced further using a discrete sampling valve and will positively impact the sample throughput in routine laboratories.
- The method allowed for a linear dynamic range of up to nine orders of magnitude (0.0001–33,000 $mg \cdot kg^{-1}$) for precise determination of multi elements at low and high concentrations.
- Robust and stable analytical performance was demonstrated over 14 hours of continuous acquisition of 270 food samples containing an average of 0.6% TDS.
- User friendly Qtegra ISDS software supported comprehensive evaluation of the large amount of results.

The iCAP-TQe ICP-MS system provides superior performance for the determination of trace elements in a variety of food samples, making it an ideal tool for quantitative determinations of elemental nutrients as well as toxic elements in food.

References and acknowledgements

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