

Total elemental analysis of food samples using triple quadrupole ICP-MS with autodilution

Author: Tomoko Vincent

Keywords: Food safety, autodilution, rapid analysis, arsenic, selenium, interference removal

Goal

To demonstrate how simultaneous determination of all elements of interest in food samples can be efficiently, rapidly and automatically performed using the Thermo Scientific iCAP™ TQ™ ICP-MS coupled with an autodilution system.

Introduction

The measurement of toxic, essential and nutritional elements in food has become a major topic of public interest in recent years. Intergovernmental bodies sponsored by 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 chain via a series of pathways such as industrial pollution or environmental contamination. Once toxic elements are in the food chain they can pose significant health risks.



For these reasons, it is essential to have a simple, robust, multielemental analysis method for major and minor concentrations of elements in food.

This application note describes fully automated, rapid, food sample analysis using the Thermo Scientific™ iCAP™ TQ ICP-MS coupled with the prepFAST Autodilution System.

The autodilution system provides significant benefits for food samples containing different matrix composition, as it allows multielement calibration curves to be prepared via dilution of one parent stock standard and provides automatic dilution for unknown samples, prescriptively from the start of the analysis and/or intelligently during the run, as required. This function significantly reduces manual sample preparation time and method development time with regard to setting the correct working calibration range. Additionally, autodilution reduces the lab consumables required during manual dilution (such as pipette tips and sample tubes), as well as reducing reagent waste.

With respect to result accuracy, the majority of interferences from food 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 food samples, as it readily allows simultaneous determination of trace level contaminants and macro level nutrients. However, food samples such as vegetables 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. Unfortunately, the single quadrupole ICP-MS KED approach cannot remove these doubly-charged interferences, so an alternative technique is required.

The iCAP TQ ICP-MS provides the interference removal capability required to efficiently remove these doubly-charge REE interferences, using triple quadrupole technology to filter the ions in quadrupole 1 (Q1), before selective reaction chemistry interference removal using Q2 and finally mass selection of the product ion using Q3 (Figure 1).

This application note describes and compares performance of the iCAP TQ ICP-MS using triple quadrupole mode with O_2 reaction gas (TQ- O_2) and single quadrupole mode with He KED (SQ-KED) for analysis of food based certified reference materials.



Figure 1. Thermo Scientific iCAP TQ ICP-MS

Method

Sample preparation

Certified reference materials (Apple Leaves NIST 1515 and Tomato Leaves NIST 1573a) were prepared to evaluate the iCAP TQ ICP-MS for food analysis. Approximately 0.3 g of each sample was acid digested using a mixture of HNO_3 and HCl in a closed vessel microwave digestion system. After digestion, the samples were made up to volume (10 mL) using ultrapure water.

Multi-element calibration curves (see Table 1) were prepared using the prepFAST Autodilution System and internal standard correction was applied using Sc, Ga, In, and Tb, at $5 \mu\text{g}\cdot\text{L}^{-1}$.



Table 1. Calibration solutions concentration

Standard group	Element	Standard calibration concentrations
1	Al, As, Cd, Co, Cr, Cu, Mn, Ni, Mo, Sb, Se, Th, U, V, Zn, Pb	0.5, 1, 2, 4 and $10 \mu\text{g}\cdot\text{L}^{-1}$
2	Na, Mg, K, Ca, Fe	40, 100, 200 and $1,000 \text{ mg}\cdot\text{L}^{-1}$
3	S, P	200, 400 and $1,000 \text{ mg}\cdot\text{L}^{-1}$
4	B, Mn, Rb, Sr, Ba	20, 50, 100 and $200 \mu\text{g}\cdot\text{L}^{-1}$

Instrument configuration

A Thermo Scientific iCAP TQ ICP-MS was used for all measurements. The sample introduction system used consisted of a Peltier cooled (3 °C), baffled cyclonic spraychamber, PFA nebulizer and quartz torch with a 2.5 mm i.d. removable quartz injector. All samples were presented for analysis using an Elemental Scientific prepFAST Autodilution System (Omaha, NE, USA).

The iCAP TQ ICP-MS was operated in TQ-O₂ mode and SQ-KED mode using the parameters presented in Table 2.

Table 2. Instrument configuration and operating parameters

Parameter	Value
Nebulizer	PFA ST Nebulizer (Green) 100 µL·L ⁻¹
Sample Loop	1.5 mL
Spraychamber	Quartz cyclonic spraychamber 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	1.002 mL·min ⁻¹
TQ-O ₂	O ₂ gas at 0.3 mL·min ⁻¹
SQ-KED	He gas at 4.3 mL·min ⁻¹ with 3V KED
Dwell Time	0.1 second per analyte, 5 sweeps
Uptake Time	40 seconds
Wash Out Time	5 seconds
Lens Setting	Optimized using autotune routines

The following measurement modes were used for this analysis:

SQ-KED – single quadrupole mode with the CRC pressurized with helium as a collision gas and Kinetic Energy Discrimination (KED) applied.

TQ-O₂ – triple quadrupole mode with the CRC pressurized with oxygen as a reaction gas, Q1 set to analyte mass (M⁺) and Q3 set to product ion mass (MO⁺) (see Figure 6).

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

functionality ensures that plasma and interface related settings, such as nebulizer flow and extraction lens voltage, are automatically applied across all associated measurement modes so that the sample is processed in exactly the same way in the plasma, independent of the CRC and quadrupole settings. Details about the settings used for the different modes are shown in Table 2.

Reaction Finder (the method development assistant in Qtegra ISDS Software) automatically selects the best mode to use for the analyte measurements. In this evaluation exercise, in which the effectiveness of different measurement modes for the same analyte were investigated, replicate analytes were added and the additional measurement modes selected manually.

The Reaction Finder tool selects TQ-O₂ mode automatically for ³¹P, ³²S, ⁷⁵As and ⁷⁸Se as this is the default mode in the software. This mode uses pure O₂ in the CRC to create oxide ions of the arsenic and selenium isotopes. Phosphorus was measured as ³¹P¹⁶O at *m/z* 47, sulfur as ³²S¹⁶O at *m/z* 48, arsenic as ⁷⁵As¹⁶O at *m/z* 91 and selenium as ⁷⁸Se¹⁶O at *m/z* 94.

Acquisition Parameters, runtime estimation 31 seconds 500 milliseconds						
Identifier	Δ	Q3 Analyte	SQ / TQ	CR Gas	Dwell time (s)	Channels
11B (M-SQ-KED)			SQ	KED	0.1	1
23Na (M-SQ-KED)			SQ	KED	0.1	1
24Mg (M-SQ-KE)			SQ	KED	0.1	1
27Al (M-SQ-KED)			SQ	KED	0.1	1
31P 31P.16O (M	31P.16O		TQ	O ₂	0.1	1
32S 32S.16O (M	32S.16O		TQ	O ₂	0.1	1
39K (M-SQ-KED)			SQ	KED	0.1	1
44Ca (M-SQ-KED)			SQ	KED	0.1	1
Advanced Parameters						
Number of sweeps:			5			
Measurement order:			M-TQ-O2 M-SQ-KED			

Figure 2. Screenshot from Qtegra ISDS Software showing the definition of TQ-O₂ and SQ-KED per isotope and how to choose the order of the measurement modes used in an analysis

An internal standard was also associated with each analyte on a mass basis. Internal standard association and measurement modes for the final analysis are shown in Table 3.

Table 3. Measurement modes and internal standards used for each element

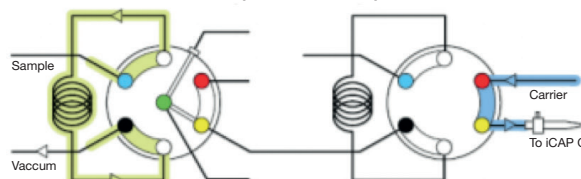
Analyte	Measurement mode	Internal standard
¹¹ B	SQ-KED	⁴⁵ Sc
²³ Na	SQ-KED	⁴⁵ Sc
²⁴ Mg	SQ-KED	⁴⁵ Sc
²⁷ Al	SQ-KED	⁴⁵ Sc
³¹ P as ³¹ P ¹⁶ O at 47 m/z	TQ-O ₂	¹¹⁵ In
³² S as ³² S ¹⁶ O at 48 m/z	TQ-O ₂	¹¹⁵ In
³⁹ K	SQ-KED	⁴⁵ Sc
⁴⁴ Ca	SQ-KED	⁴⁵ Sc
⁵¹ V	SQ-KED	⁷¹ Ga
⁵² Cr	SQ-KED	⁷¹ Ga
⁵⁵ Mn	SQ-KED	⁷¹ Ga
⁵⁷ Fe	SQ-KED	⁷¹ Ga
⁵⁹ Co	SQ-KED	⁷¹ Ga
⁶⁰ Ni	SQ-KED	⁷¹ Ga
⁶³ Cu	SQ-KED	⁷¹ Ga
⁶⁶ Zn	SQ-KED	⁷¹ Ga
⁷⁵ As as ⁷⁵ As ¹⁶ O at 91 m/z	TQ-O ₂	¹¹⁵ In
⁷⁵ As	SQ-KED	¹¹⁵ In
⁷⁸ Se as ⁷⁸ Se ¹⁶ O at 94 m/z	TQ-O ₂	¹¹⁵ In
⁷⁸ Se	SQ-KED	¹¹⁵ In
⁸⁵ Rb	SQ-KED	¹¹⁵ In
⁸⁸ Sr	SQ-KED	¹¹⁵ In
⁹⁸ Mo	SQ-KED	¹¹⁵ In
¹¹¹ Cd	SQ-KED	¹¹⁵ In
¹²¹ Sb	SQ-KED	¹¹⁵ In
¹³⁸ Ba	SQ-KED	¹⁵⁹ Tb
²⁰⁸ Pb	SQ-KED	¹⁵⁹ Tb
²³² Th	SQ-KED	¹⁵⁹ Tb
²³⁸ U	SQ-KED	¹⁵⁹ Tb

prepFAST Autodilution System operation

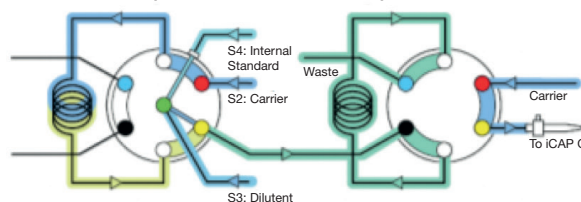
The prepFAST Autodilution System is based on dual FAST valves operated in combination with a bank of four syringe pumps (S1–S4) that provide improved precision and accuracy over peristaltic pumps. With flow rates of between 1 to 20,000 µL·min⁻¹ the S2 (carrier) and S3 (diluent) syringes can perform dilutions in seconds while the S4 syringe adds internal standard at a constant rate. Speed of dilution is independent of dilution factor (1 to 400) ensuring exact injection timing for all solutions

regardless of dilution. The operation of the prepFAST Autodilution System is summarized in the 4 steps shown in Figure 3: 1) Vacuum loading of the loop, 2) syringe dilution (S2 and S3) and addition of internal standard (S4), 3) sample injection and 4) loop rinsing (S4). The intelligent valve switching mechanism of the prepFAST Autodilution System allows minimum uptake and washout times to ensure rapid analysis.

1. Vacuum load sample into loop



2. Syringes add internal standard and dilute sample into second loop



3. Diluted sample is injected and sample loop is cleaned



4. Sample and dilution loops are cleaned

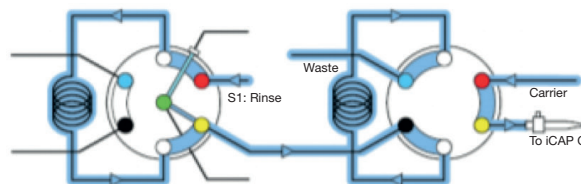


Figure 3. The 4 main steps of prepFAST Autodilution System operation, showing the combination of the 7 and 6-port FAST valves

Multiple stocks can be used to create combined calibration curves over extended concentration ranges, for example on this sample list at Figure 4, a 5-point calibration for “group 1” standard was generated from the single stock standard solution using the autodilution function. The 4 main steps of autodilution provide the same run time for diluted samples as for undiluted samples run through the system. The sample list configuration for generating the calibration solutions using the prepFAST Autodilution System is shown in Figure 4.

	Label	Sample Type	Standard	prepFAST D	Total Dilution Fact	Amount	Final Quantit	Rack Number	Vial Number	Dilution Fac
10	blank	AVERAGE BLK		2	2			3	1	
11	Low level element_0.5ppb	STD	low level element 10	200	200			3	2	
12	Low level element_1ppb	STD	low level element 10	100	100			3	2	
13	Low level element_2ppb	STD	low level element 10	50	50			3	2	
14	Low level element_4ppb	STD	low level element 10	25	25			3	2	
15	Low level element_10ppb	STD	low level element 10	10	10			3	2	
16	Major 2000ppm_40ppm	STD	Major 2000ppm	200	200			3	3	
17	Major 2000ppm_100ppm	STD	Major 2000ppm	100	100			3	3	
18	Major 2000ppm_200ppm	STD	Major 2000ppm	50	50			3	3	
19	Major 2000ppm_1000ppm	STD	Major 2000ppm	25	25			3	3	
20	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	50	50			3	4	
21	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	25	25			3	4	
22	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	10	10			3	4	
23	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	10	10			3	4	
24	wash	UNKNOWN		2	2			3	1	
25	Apple	UNKNOWN		4	130.718954248366	0.306 g	10 ml	1	1	
26	Apple	UNKNOWN		14	457.516339869281	0.306 g	10 ml	1	1	
27	Apple	UNKNOWN		14	457.516339869281	0.306 g	10 ml	1	1	

Figure 4. Generation of a multi-point calibration using prescriptive dilution factors in the Qtegra ISDS Software sample list

Results

The combination of the iCAP TQ ICP-MS and prepFAST Autodilution System promotes rapid and accurate analysis, with a total run time of just 2 min 30 seconds for a fully quantitative measurement of 24 elements in two different modes (SQ-KED and TQ-O₂), including sample uptake and washout.

Table 4 shows the instrument detection limit (IDL, measured as 3× standard deviation of the calibration blank, in µg·L⁻¹) achieved for a range of analytes using this method. Taking into account the dilution factor required for the samples (an automatic prescriptive 4-fold dilution was applied to each sample by the prepFAST Autodilution System) method detection limits (MDL's), in the µg·kg⁻¹ range were easily achieved for all analytes and all were well below the target levels required for food analysis. In samples where the measured analyte concentrations were above the highest calibration concentration range, the prepFAST Autodilution System was programmed to perform an additional dilution of 14-fold in a fully automated process with no user interaction necessary. Excellent agreement between the measured and certified concentrations in the two CRM's were obtained for all elements except As and Se in SQ-KED mode (Table 4). In SQ-KED mode, As and Se gave results that were above the certified range (particularly in the Apple Leaves material) as a result of REE doubly-charged ion interference. Figure 5 shows a survey scan of the Apple Leaves sample 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.

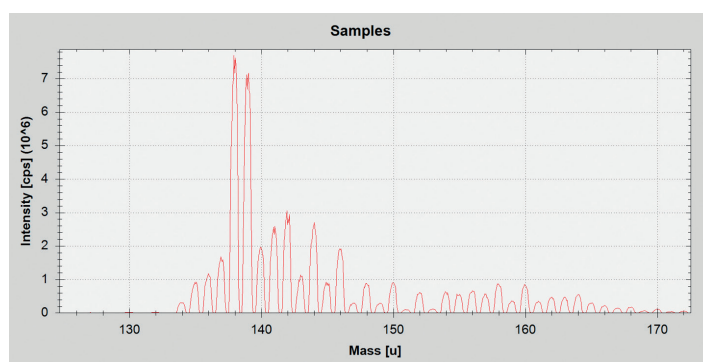


Figure 5. Survey scan of CRM NIST 1515 Apple Leaves in SQ-KED mode, REE mass region

Using the TQ-O₂ mass shift mode (schematically shown in Figure 6), the REE doubly-charged polyatomic interferences were efficiently removed leading to As and Se results that agreed well with the certified values. In TQ-O₂ mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (IMS) to reject unwanted ions. The second quadrupole (Q2) is used to selectively shift the As and Se target analytes to the product ions AsO and SeO using O₂ as the reaction gas, while the REE doubly-charged interference ions do not react with O₂. The third quadrupole (Q3) then isolates the product ions and removes any remaining interferences through a second stage of mass filtration allowing for completely interference free analysis of the analyte.

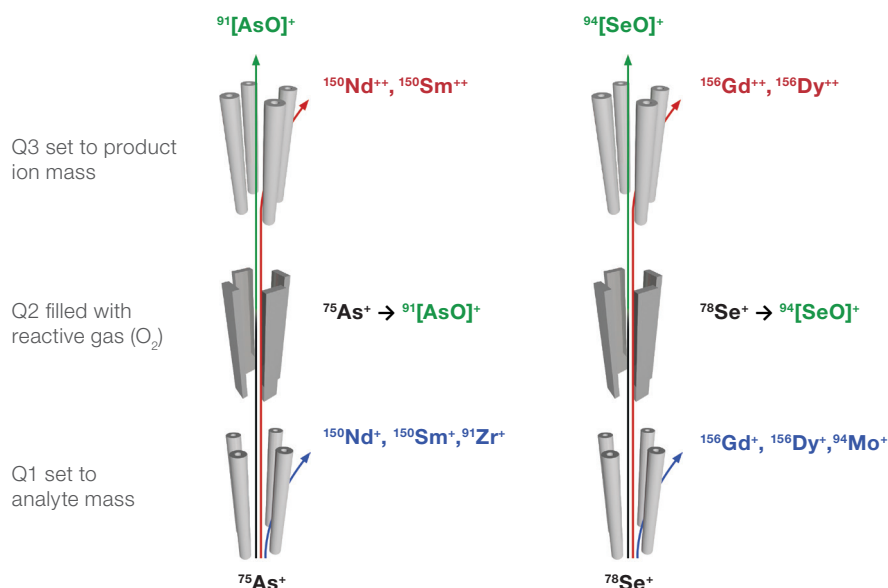


Figure 6. Schematic showing TQ mass shift modes for arsenic and selenium

Table 4. Results for the NIST CRM 1515 Apple leaves and NIST CRM 1673a Tomato leaves

Analyte	IDL ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL ($\mu\text{g}\cdot\text{kg}^{-1}$)	NIST 1515 apple leaves N=3		NIST 1573A tomato leaves N=3	
			Measured ($\text{mg}\cdot\text{kg}^{-1}$)	Certified ($\text{mg}\cdot\text{kg}^{-1}$)	Measured ($\text{mg}\cdot\text{kg}^{-1}$)	Certified ($\text{mg}\cdot\text{kg}^{-1}$)
^{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 $^{31}\text{P}^{16}\text{O}$ at m/z 47	0.05	6.0	1530 ± 10	1590^*	2040 ± 33	2160 ± 40
^{32}S as $^{32}\text{S}^{16}\text{O}$ at m/z 48	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 $^{75}\text{As}^{16}\text{O}$ at m/z 91	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 $^{78}\text{Se}^{16}\text{O}$ at m/z 94	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	1272 ± 187	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^*

Calibration curves

The wide dynamic range of the iCAP TQ ICP-MS detector, coupled with the use of SQ-KED mode to attenuate intense ion signals, allows high concentration analytes such as sodium (Na), to be calibrated up to 1000 mg·L⁻¹. Figure 7 shows a full calibration of ²³Na at 0, 40, 100, 200 and 1000 mg·L⁻¹ with a correlation coefficient, R², of better than 0.9999, using SQ-KED mode.

Arsenic and selenium calibrations with TQ-O₂ mass shift mode are shown in Figures 8 and 9. Both calibration curves have excellent linearity with an R² value of 0.999 for each calibration, consisting of a blank and four standards (0, 0.5, 1, 2, 4 and 10 µg·L⁻¹) prepared by the prepFAST Autodilution System.

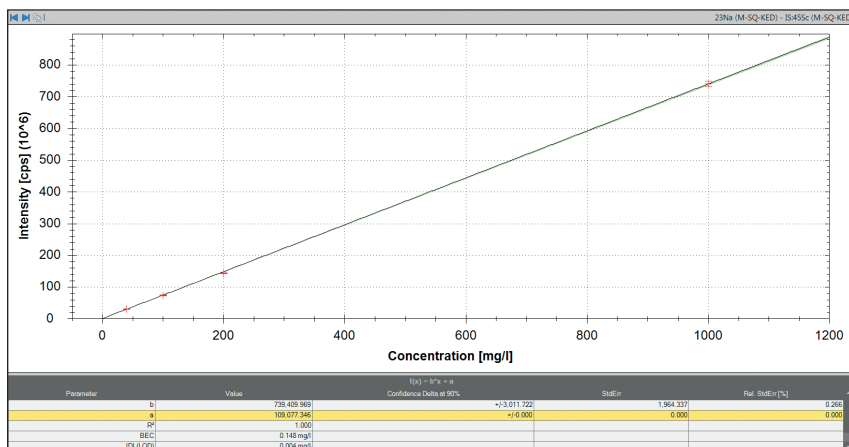


Figure 7. Calibration curve for ²³Na in SQ KED mode

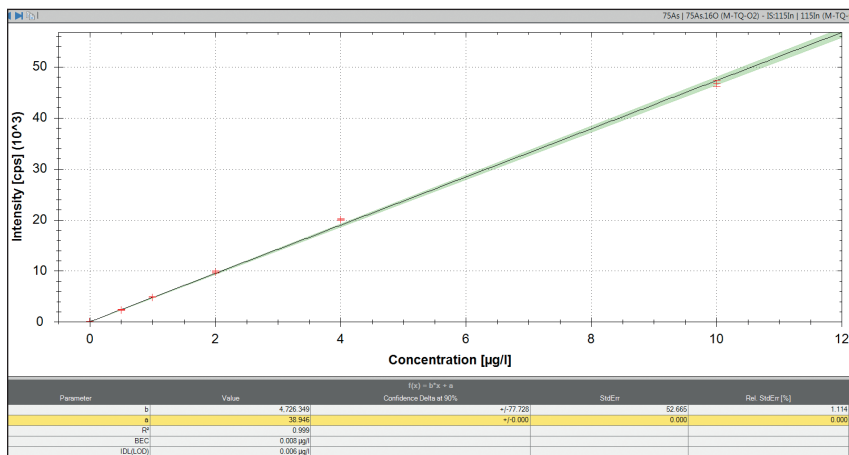


Figure 8. Calibration curve for ⁷⁵As as ⁷⁵As¹⁶O in TQ-O₂ mode

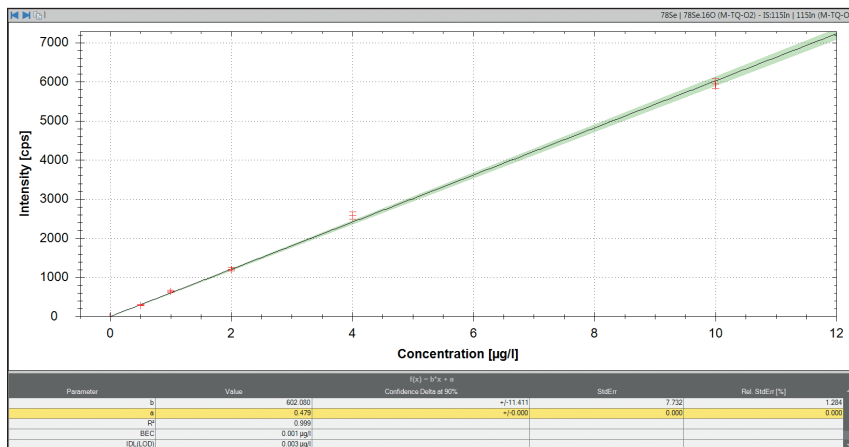


Figure 9. Calibration curve for ⁷⁸Se as ⁷⁸Se¹⁶O in TQ-O₂ mode

Conclusion

The Thermo Scientific iCAP TQ ICP-MS provides excellent performance for the determination of trace element analysis in food samples making it ideal for food safety and quality assurance measurements.

The combination of the prepFAST Autodilution System and the iCAP TQ ICP-MS provides the advanced performance required for the sensitive and accurate determination of As, Se and other elements in complex samples, whilst the Reaction Finder tool allows simple method development through automatic selection of the optimum analysis conditions for the analytes of interest.

Find out more at thermofisher.com/TQ-ICP-MS

For Research Use Only. Not for use in diagnostic procedures. © 2020 Thermo Fisher Scientific Inc. All rights reserved. FAST and prepFAST are used in trade by Elemental Scientific Inc., Omaha, IL, US. All other trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representatives for details. Not all products are available in all countries. Please consult your local sales representatives for details. **AN43446-EN 0620C**

ThermoFisher
SCIENTIFIC