Total elemental analysis of food samples for routine and research laboratories using the Thermo Scientific iCAP RQ ICP-MS

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Goal

To demonstrate how simultaneous determination of all elements of interest in a wide range of food samples can be efficiently and rapidly performed using the Thermo Scientific™ iCAP™ RQ ICP-MS.

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. The elemental and dynamic range of single quadrupole (SQ) ICP-MS makes it particularly suited to the analysis of food, simultaneously determining trace level contaminants and macro level nutrients. In some cases, a sample may contain matrix that leads to specific interferences that can only be effectively resolved using triple quadrupole (TQ) ICP-MS.

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Method

Sample preparation

Certified Reference Materials (Rice Flour IRMM-804 and Chicken NCS ZC73016) were prepared to evaluate the proposed SQ-ICP-MS method. Approximately 0.5 g of each sample were 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 (50 mL) using ultrapure water. The standard calibration solutions, blank and rinse solution were all prepared in 1% (v/v) HNO_3. The major elements (Na, Mg, P, S, K and Ca) were prepared at calibration concentration levels of 25, 50 and 100 mg·L^{-1}, while the minor elements (balance of analytes) were prepared at concentrations of 25, 50 and 100 µg·L^{-1}. Internal standard correction was applied with Ga, Rh, and Ir at 20, 10 and 10 µ·gL^{-1} respectively.

Instrument configuration

A Thermo Scientific™ iCAP™ RQ 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. The instrument was operated using kinetic energy discrimination (KED) using pure He as the collision gas in the collision/reaction cell (CRC). To automate the sampling process, an Elemental Scientific SC-4 DX Autosampler (Omaha, NE, USA) was used.

General analytical conditions

The iCAP RQ ICP-MS was operated in a single He KED mode using the parameters presented in Table 1.

Table 1. Instrument operating parameters.

Parameter	Value
Forward Power	1500 W
Nebulizer Gas	0.9 L·min^{-1}
Auxiliary Gas	0.8 L·min^{-1}
Cool Gas Flow	14.0 L·min^{-1}
CRC Conditions	4.5 mL·min^{-1} at He, 3V KED
Sample Uptake/Wash Time	45 s each
Dwell Times	Optimized per analyte
Total Acquisition Time	3 min

Results

The use of a single, comprehensive He KED mode is made possible through the use of unique Thermo Scientific QCell™ flatapole technology. Sample throughput is significantly improved with the single analysis mode – a key advantage for the analysis of food, since large numbers of samples may have to be screened rapidly. High transmission of the iCAP RQ ICP-MS QCell provides sufficient low mass sensitivity for accurate analysis of low mass analytes such as Li, so that all analytes can be reliably measured in one single measurement mode.

Table 2 shows the typical detection limits achievable for a range of analytes measured by this method. Taking into account the 1:100 dilution factor required for this analysis, the data shows that µg·kg^{-1} range method detection limits are achieved with ease for all analytes. Detection limits for all the major constituent elements are well below the target levels required for food analysis.

Figures 1 and 2 show typical external calibration curves for the low concentration (Li, 0-100 µg·L^{-1}) and high concentration (Na, 0-100 mg·L^{-1}) analytes determined in the same analytical run with the iCAP RQ ICP-MS in single He KED mode. The results of the rice flour and chicken reference material measurements are presented in Table 2.

Excellent agreement was observed between the measured and reference values for all target analytes in the two reference materials analyzed.
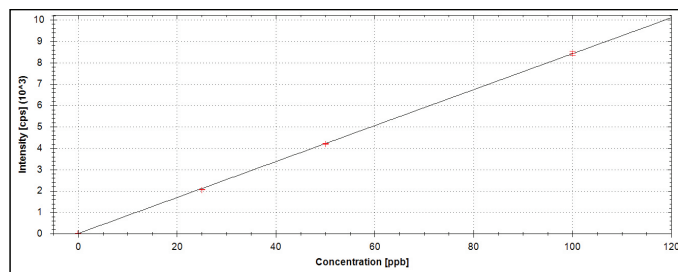

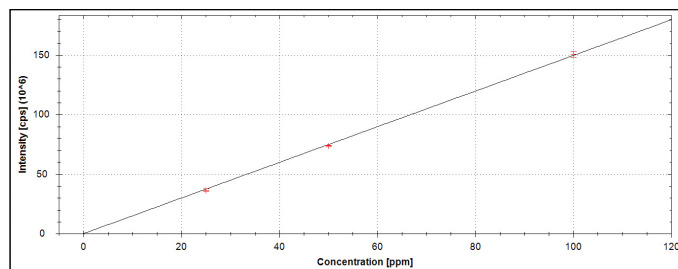Figure 1. Calibration curve for ^{7}Li in He KED mode.

Figure 2. Calibration curve for ^{23}Na in He KED mode.

Table 2. Dilution corrected MDLs and results for two certified reference materials: relative standard deviation is calculated for 5 independent analyses. All concentrations reported in µg·L^{-1} except where stated.

Isotope	Method detection limit (MDL)	IRMM-804 Rice			NCS ZC73016 Chicken		
		Measured	Certified	% RSD	Measured	Certified	% RSD
^{7}Li	3	-	-	-	28 ± 1	34 ± 7	1.9
^{11}B	10	-	-	-	730 ± 23	760 ± 130	1.9
^{23}Na	0.3 (mg·L^{-1})	-	-	-	1310 ± 25	1440 ± 90	1.3
^{25}Mg	0.01 (mg·L^{-1})	-	-	-	1200 ± 22	1280 ± 100	1.1
^{31}P	0.6 (mg·L^{-1})	-	-	-	8950 ± 220	9600 ± 800	1.7
^{34}S	9 (mg·L^{-1})	-	-	-	8310 ± 220	8600 ± 500	1.9
^{39}K	0.5 (mg·L^{-1})	-	-	-	14000 ± 480	14600 ± 700	1.8
^{44}Ca	0.2 (mg·L^{-1})	-	-	-	200 ± 4	220 ± 20	1.7
^{52}Cr	0.2	-	-	-	450 ± 10	590 ± 110	0.9
^{55}Mn	1	35800 ± 470	34200 ± 2300	0.5	1640 ± 20	1650 ± 70	0.8
^{56}Fe	4	-	-	-	32700 ± 260	31300 ± 3000	0.7
^{60}Ni	2	-	-	-	153 ± 2	150 ± 30	0.8
^{65}Cu	0.8	2650 ± 30	2740 ± 240	0.4	1350 ± 11	1460 ± 120	0.7
^{66}Zn	2	23100 ± 270	23100 ± 1900	0.7	25300 ± 220	26000 ± 1000	0.6
^{75}As	0.2	52.3 ± 0.8	49 ± 4	1.4	115 ± 1	109 ± 13	0.9
^{78}Se	1	35.1 ± 1.0	38 (Reference value)	1.3	549 ± 11	490 ± 60	1.6
^{88}Sr	0.1	-	-	-	611 ± 11	640 ± 80	1.6
^{98}Mo	1	-	-	-	112 ± 1	110 ± 10	1.9
^{111}Cd	0.3	1620 ± 9	1610 ± 70	0.7	-	-	-
^{138}Ba	0.3	-	-	-	1610 ± 16	1500 ± 400	1.4
^{141}Pr	0.02	-	-	-	2.6 ± 0.1	2.8 ± 0.6	1.6
^{208}Pb	0.1	460 ± 8	420 ± 70	0.8	90.7 ± 2.0	110 ± 20	1.0

As part of this study, the reference materials were repeatedly analyzed during the analysis. Five independent measurements were made of separate aliquots of each reference material to assess the repeatability of the method.

The results in Table 2 demonstrate that excellent reproducibility was achieved for the five repeat analyses of rice flour and chicken reference materials over 8 hours, with RSD's of <2 % obtained for all of the elements determined.

Quality control with Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software

Quality control is critical in routine analysis. To ensure quality control with the high matrix samples described in this method, 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 RQ ICP-MS for prolonged measurement of high matrix samples. The variation in the internal standard signals during the run is shown in Figure 3.
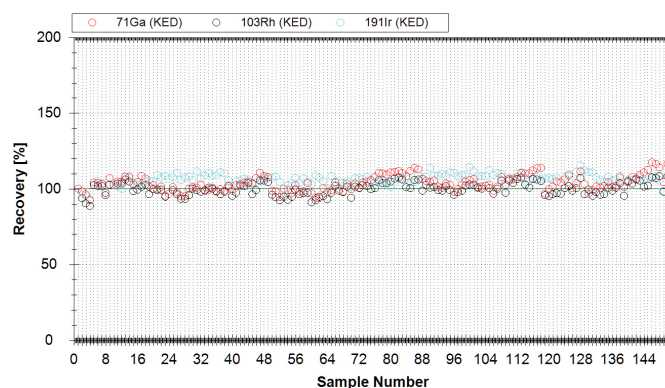

Figure 3. Variation of the internal standard intensities throughout the 8 hours analysis.

The analysis was evaluated for 8 hours, allowing the analysis of more than 150 samples. The minimal variation in the internal standard signals highlights the excellent robustness of the iCAP RQ ICP-MS in terms of both matrix resistance and interference removal for food samples analysis. Powerful, comprehensive He KED mode effectively removed complicated interferences and delivered accurate measurement results.

Continuing calibration checks (CCVs) and the reference materials were periodically analyzed throughout the analytical run with good agreement to expected levels illustrating the robustness of the method.

Six CCV checks were analyzed at intervals during the 8 hour analysis. Figure 4 shows the average concentration of the CCV standard and the in-run relative error for a range of high and low level analytes. The results from the CCV checks throughout the analysis show that there was minimal drift between the batches of food samples, eliminating the need for any sensitivity re-calibration within the 8 hour analysis period.
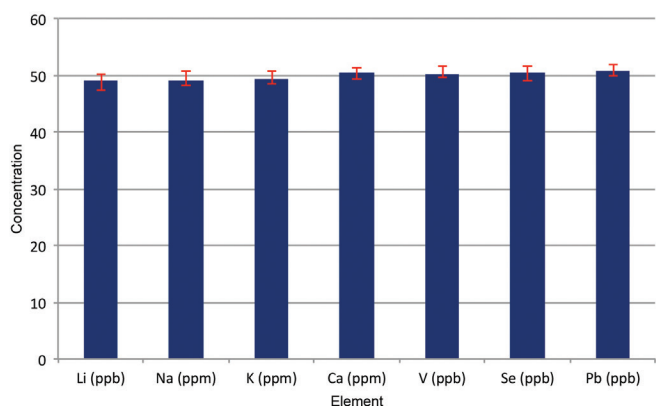
Figure 4. Calibration checks verification standards measured.

The iCAP RQ ICP-MS

Dynamic range control with user defined mass resolution

Normal resolution or high resolution modes can be selected easily within the Qtegra ISDS Software (Figure 5). This function is particularly useful to extend dynamic range, in food, environmental and clinical research samples.

Identifier	Δ	Dwell time (s)	Channels	Spacing (u)	Measurement mode	
23Na (KED)		0.01	1	0.1	KED	High
24Mg (KED)		0.01	1	0.1	KED	Normal
39K (KED)		0.01	1	0.1	KED	Normal

Figure 5. Screen shot measurement mode from Qtegra ISDS Software.

The normal resolution mode has 0.75 u peak width at 10% of the peak height and high resolution mode has a narrow 0.25 u peak width. Using this user selectable, high resolution mode, sensitivity is reduced in order to generate a linear calibration curve with a wide concentration range.

This feature can be used for analytes such as sodium, where due to low ionization potential energy (5.1 eV) and high sensitivity in hot plasma, a calibration up to 1000 mg·L^{-1} can be outside the performance capabilities of the SQ-ICP-MS detector's dynamic range.

Figure 6 shows a full calibration of ^{23}Na at 0, 5, 250, 500 and 1000 mg·L^{-1} with R^2=1.000 linearity and background equivalent concentration (BEC) of only 6 µg·L^{-1} using high resolution and He KED mode.
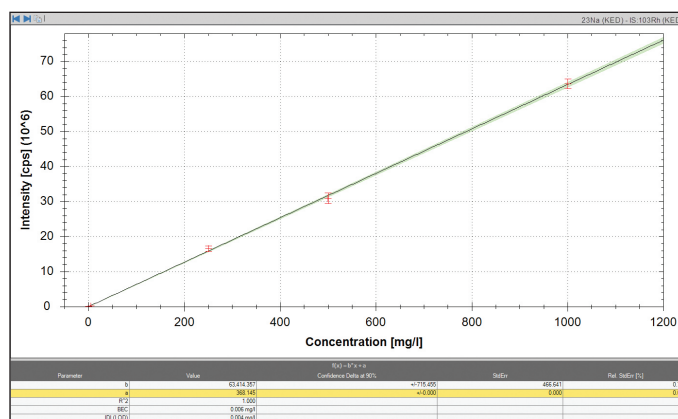
Figure 6. Calibration curve for ^{23}Na in He KED mode at 5, 250, 500 and 1000 mg·L^{-1}.

IC-ICP-MS speciation analysis in organic brown rice syrup with the iCAP RQ ICP-MS

For some types of food, the concentration of a given element may not be sufficient to judge potential hazards. For example, As may be present in both inorganic forms, such as As (III) and As (V), as well as organic forms (e.g. arsenobetaine and methylated forms), which exhibit different toxicological properties. Elevated concentrations of As in foodstuffs such as rice or rice derived products are occasionally reported in the media, and speciation analysis is required to determine whether the As found is either toxic inorganic As or rather harmless organic As. Currently, regulatory authorities strive for maximum concentration levels for As in a variety of foodstuffs.

Speciation analysis comprises the separation of different compounds containing a given element using, for example, Ion Chromatography (IC) followed by selective and sensitive detection of the element using ICP-MS. Based on previous work undertaken by Thermo Fisher Scientific Application Specialists, speciation analysis of As was accomplished using the Thermo Scientific Dionex™ ICS-5000+ ion chromatography system coupled to the iCAP RQ ICP-MS. The hyphenated system can be integrated into the Qtegra ISDS Software used for operation of the iCAP RQ ICP-MS using the Thermo Scientific ChromControl Plug-in.

As for conventional As analysis, He KED mode was used to efficiently reduce polyatomic interferences affecting the detection of monoisotopic As at m/z 75. The method allows the determination of six As species often encountered in food analysis: The two toxic inorganic As species, and four organic species which are considered harmless.

Whereas some samples, for example water or beverages may be simply diluted, for rice and rice derived products such as organic brown rice syrup (OBRS, often used as an organic sweetener for example in cereals and cereal bars), a mild extraction is required.

Preparation of OBRS samples for As speciation was achieved by taking 1.5 g of sample, adding 15 mL of 0.28 M HNO_3 and refluxing for 90 minutes. This procedure is also suitable for As species extraction from rice grains.

Chromatographic separation of the As species under investigation is shown in Figure 7. As can be seen, OBRS contains mostly As (III) and As (V), so one of the toxic forms of As, but also methylated DMA can be observed. Each species of As was identified using comparative retention times of a standard, and automatic peak area integration for quantification was accomplished using the tQuant data evaluation plugin included in the Qtegra ISDS Software.
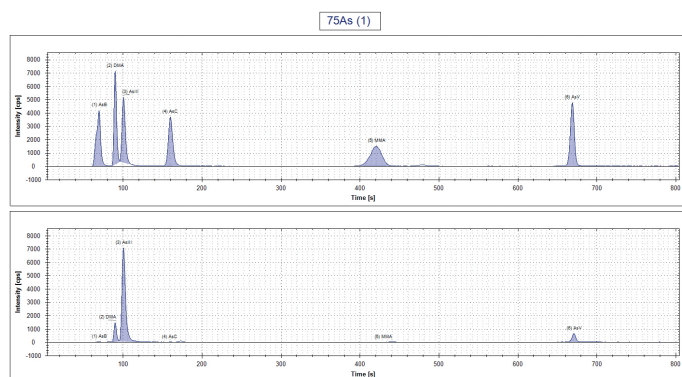

Figure 7. IC-ICP-MS chromatogram of (top) arsenic standards and (bottom) Arsenic species found in a OBRS sample. As(III) was the most abundant species detected.

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