

Total Elemental Analysis of Food Samples for Routine and Research Laboratories, using the Thermo Scientific iCAP RQ ICP-MS

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Key Words

Arsenic, Automation, Food Safety, He KED, High Matrix, High-throughput, iCAP RQ ICP-MS, Multi-Element, Quality Control, Rice, Speciation

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, multi-elemental 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.



Method

Sample preparation

The certified reference materials (Rice Flour IRMM-804 and Chicken NCS ZC73016) were prepared to evaluate the proposed SQ-ICP-MS method. Approximately 0.5g of each sample was acid digested using a mixture of HNO₃ and HCl in a closed vessel microwave digestion system.

After digestion, the samples were made up to volume (50mL) using ultra pure water. The standard calibration solutions, blank and rinse solution, were prepared in 1% (v/v) HNO₃. The major elements (Na, Mg, P, S, K and Ca) were prepared at calibration concentration levels of 25, 50 and 100 mg·L⁻¹ and the minor elements (balance of analytes) at concentrations of 25, 50 and 100 µg·L⁻¹. Internal standard correction was applied, with Ga, Rh, and Ir at 20, 10 and 10µg·L⁻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 spray chamber, PFA nebulizer and quartz torch with a 2.5 mm i.d. removable quartz injector. The instrument was operated in a single, comprehensive collision cell mode, with kinetic energy discrimination (KED), using pure He as the collision gas. All samples were presented for analysis using an Elemental Scientific SC4 DX Autosampler (Omaha, NE, USA).

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
QCell conditions	4.5mL·min ⁻¹ at He, 3V KED
Sample uptake/wash time	45 s each
Dwell times	Optimized per analyte
Number of points per week	1
Number of repeats per sample	3
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 level (Li, 0-100 µg·L⁻¹) and high (Na, 0-100 mg·L⁻¹) analytes determined simultaneously 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.

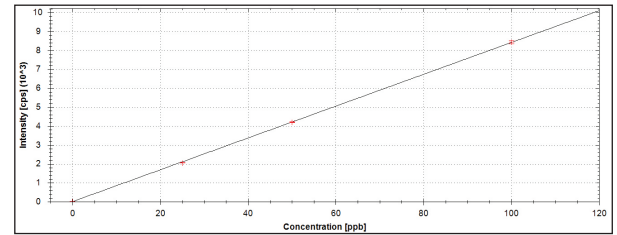


Figure 1. Calibration curve for ⁷Li in He KED mode.

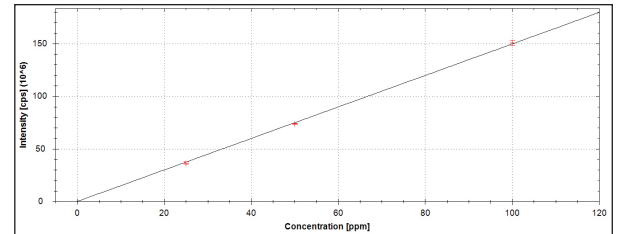


Figure 2. Calibration curve for ²³Na in He KED mode.



The iCAP RQ ICP-MS

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 $\mu\text{g}\cdot\text{L}^{-1}$ 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 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.

The analysis was evaluated for 8 hours over 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.

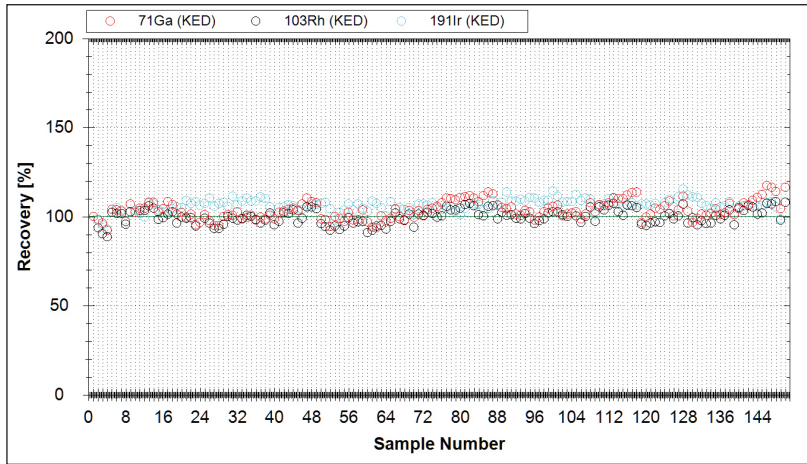


Figure 3. Variation of the internal standard intensities throughout the 8 hours analysis.

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.

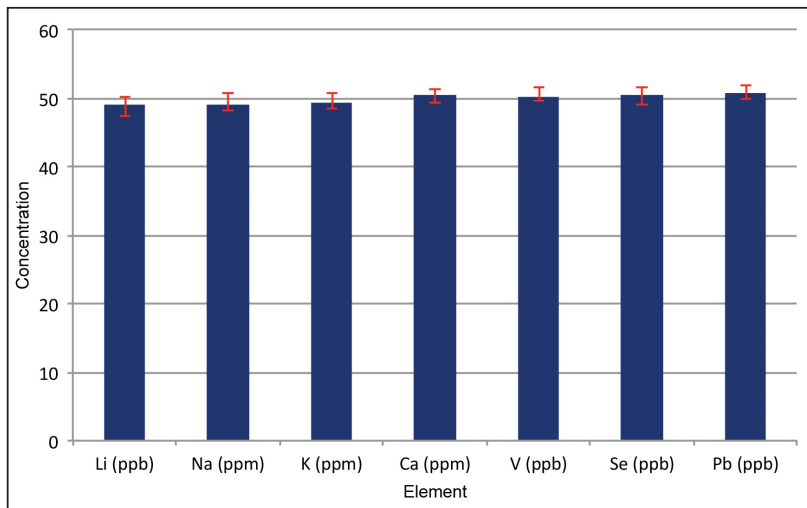


Figure 4. Calibration checks verification standards measured.

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	
²³ Na (KED)		0.01	1	0.1	KED	High
²⁴ Mg (KED)		0.01	1	0.1	KED	Normal
³⁹ K (KED)		0.01	1	0.1	KED	Normal

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

The normal resolution mode has 0.75amu peak width at 10% of the peak height and high resolution mode has a narrow 0.25 amu 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 (Na), where due to low ionization potential energy (5.1391eV) 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 ²³Na at 0, 5, 250, 500 and 1000 mg·L⁻¹ with R=1.000 linearity and background equivalent concentration (BEC) of only 6 µg·L⁻¹ using high resolution and He KED mode.

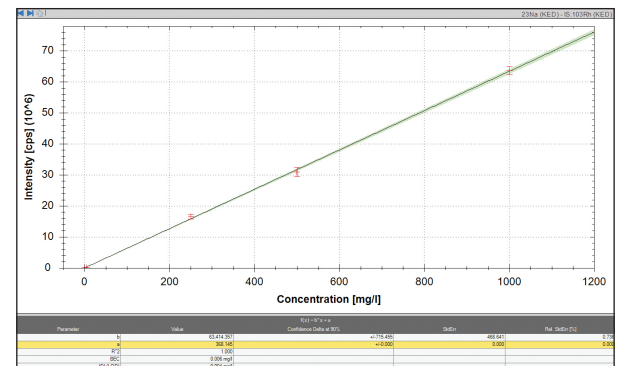


Figure 6. Calibration curve for ²³Na in He KED mode at 5, 250, 500 and 1000 mg·L⁻¹.

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

Media reports and scientific publications on the determination of arsenic (As) in foodstuffs have sparked renewed interest from consumer groups and politicians leading to responses from national regulatory bodies.

Following the publication of a report on high As levels in organic brown rice syrup (OBRS), an ingredient in a variety of organic foods, the United States Food and Drug Administration (FDA) conducted a study on As in rice and rice products, published September 6th 2013¹.

Based on previous work undertaken by Thermo Fisher Scientific Applications Specialists, OBRS samples were analyzed for their total arsenic content by ICP-MS and then subsequently by IC-ICP-MS to determine the concentration of six arsenic species: the two toxic inorganic species (As(III) and As(V)), and four organic species that are considered to be harmless.

Arsenic speciation analyses were performed in He KED mode to efficiently reduce polyatomic interferences for the analysis of (monoisotopic) arsenic at m/z 75. Chromatographic separations were carried out using the Thermo Scientific™ Dionex™ ICS-5000+ ion chromatography system coupled with the iCAP RQ ICP-MS as a highly sensitive and selective arsenic detector.

Preparation of the OBRS samples for As speciation analysis was achieved by taking 1.5 g of OBRS, adding 15 mL of 0.28 M HNO₃ and refluxing for 90 minutes.

Chromatographic separation of arsenic species in the OBRS sample is shown in Figure 7. Upon comparison of retention time with standards, each species of As was identified automatically by the Qtegra ISDS software.



The iCAP RQ ICP-MS paired with the Dionex ICS-5000 IC system.

Conclusion

The iCAP RQ ICP-MS has been shown to be an excellent tool for multi-elemental determination in complex food samples.

With its high sensitivity and analytical robustness, the iCAP RQ ICP-MS is capable of routinely measuring major and minor analyte concentrations in food, following a simple sample digestion step.

The analytical method is simplified using the iCAP RQ ICP-MS collision cell technology with single mode He KED for comprehensive interference removal and simultaneous determination of all elements of interest in a wide range of food samples. The iCAP RQ ICP-MS with Qtegra ISDS software provides the ideal solution for Quality Control and speciation analysis in both routine and research environments.

Reference

- (1) FDA Statement on Arsenic in Brown Rice Syrup, February 2012: <http://www.fda.gov/Food/FoodborneIllnessContaminants/Metals/ucm292531.htm>

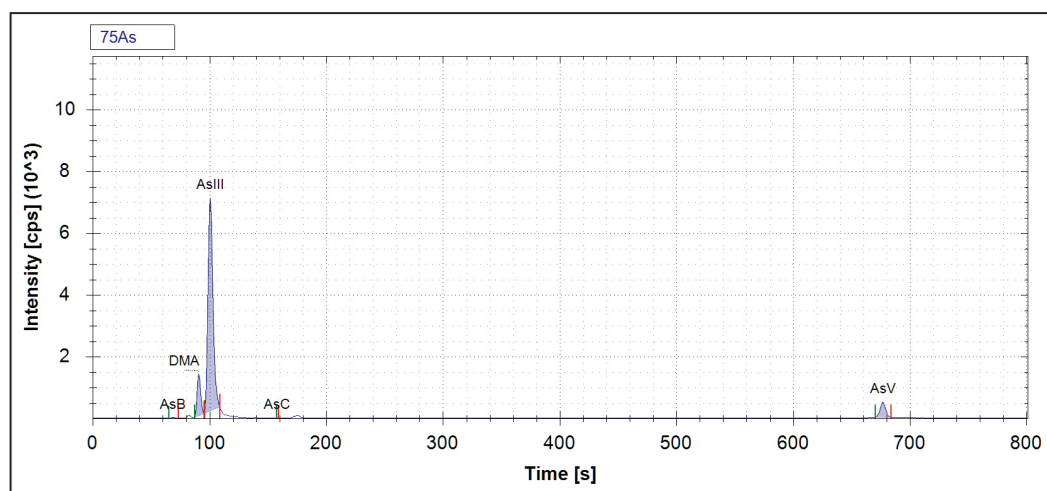


Figure 7. IC-ICP-MS chromatogram of Arsenic species found in a OBRS sample. As(III) was the most abundant species detected.

To find a local representative, visit:
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