The Determination of Major and Trace Elements in Milk using ICP-Q-MS

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Overview

Purpose: To demonstrate the power of ICP-Q-MS for the determination of analytes in milk and milk products.

Methods: Total elemental determinations, including iodine, were performed using the Thermo Scientific™ iCAP Q™ ICP-Q-MS in a single operation mode. A Thermo Scientific ICS-5000 was coupled to the iCAP Q for subsequent speciation determinations.

Results: Good agreement with the certified values of a milk reference material was obtained. Speciation analysis showed iodide was present as the major iodine species in all samples and two unknown species were observed in cow milk.

Introduction

Milk and milk products form a major part of a healthy diet. The FDA recommends a daily consumption of two and three cups of milk daily for children and adults respectively. As well as being a high source of calcium and potassium, milk contains a number of essential elements such as iron, copper and zinc. Multi-elemental analysis of milk can determine whether milk is meeting the expected nutritional requirements or is lacking either due to regional soil deficiencies in the case of cow milk or poor diet in the case of breast milk. Alternatively, the analysis of trace elements that are toxic in nature can alert us to the possible risk of contamination in milk.

As the sole source of nutrition for young babies and as a major constituent of the diet for older babies and toddlers, nutritionists are also eager to investigate the differences in bioavailability of some of the essential elements. As bioavailability is dependent on the chemical form of the element, speciation analysis is perceived as the most promising approach to indentifying differences between baby formulas and breastmilk for example.

Methods

Sample Preparation

1 cow milk, 1 baby formula, 1 breast milk and the CRM BCR®-063 were each subjected to the procedures shown in Table 1.

TABLE 1. Sample preparation procedures.

Procedure	Description
Microwave digestion	Add 5 mL conc. HNO_3 and 2 mL H_2O_2 to 0.5 - 1 g material and digest at 1600 W for a total of 50 mins in closed PTFE vessels. Make up to 50 mL with 18.2 MΩ water.
Total Iodine extraction	Add 50 mL 0.5% ammonia to 0.25 - 0.35 g powder material or approx. 1 mL milk and shake. Leave overnight, then shake for 2 hrs. Centrifuge and analyze the same day.
Speciation	Powder samples were diluted in milli-Q water according to the manufacturers protocol and then all samples were diluted 25 fold in the mobile phase just prior to injection.

Mass Spectrometry

The iCAP Qc was used for acquisition of all data. A SC4S autosampler was used for the total element quantification (TEQ). The iCAP Q was operated in single He KED mode for all measurements.

FIGURE 1. Thermo Scientific iCAP Qc and ICS-5000.

Ion Chromatography Separation

An ICS-5000 was coupled to the iCAP Qc for speciation determinations of iodine and Table 2 outlines the column and elution conditions used.

TABLE 2. Speciation parameters.

Analyte	Column (Dimensions)	Elution (Duration)
Iodine	IonPac AG19-AS19 (2 x 40 and 2 x 250 mm)	Isocratic with 10 to 100 mM NaOH (14 mins)

Data Analysis

Thermo Scientific Qtegra™ software was used for both TEQ by external quantification and speciation analyses. Embedded Thermo Scientific Chromeleon™ plug-ins within Qtegra allowed the seamless integration of the ICS-5000 with the iCAP Q. Single software control of the coupled system allows for highly flexible data processing, one sample list and emergency shut-off for reliable unattended operation.

Results

Total Elemental Quantification

The microwave digestion procedure outlined in Table 1 was used to prepare the milk samples in triplicate for total elemental quantification, with the exception of iodine. Iodine tends to be volatile in acidic media and therefore requires an extraction in basic media to prevent losses. The iodine extracts, also prepared in triplicate, were analyzed as soon as possible after the extraction procedure.

Table 3 shows the TEQ and recovery data for the milk and milk powder samples. The high linear dynamic range of the iCAP Q meant that major food components, such as calcium and potassium could be determined in the same analytical run as the minor elements such as cadmium and mercury.

TABLE 3. Total elemental concentrations found in milk, baby formulas and BCR-063 (blue in g/kg, white in mg/kg and pink in µg/kg).

	BCR-063		Baby Formula		Cow milk	Breast milk
	Conc	%	Conc	%	Conc	Conc
23Na	4.12	94	2.08	87	0.333	0.047
24Mg	1.14	91	0.46	92	0.102	0.03
31P	11.2	101	3.17	83	0.697	0.089
39K	16.9	96	6.21		1.42	0.531
44Ca	12.9	96	5.98	93	1.12	0.245
56Fe	2.35	101	72.5	88	0.322	0.215
65Cu	0.553	92	4.05	94	0.245	0.244
66Zn	40.3	82	58.2	90	3.36	0.857
127I	0.873	108	1.01	94	0.128	0.072
55Mn	221		466	82	17.1	2.26
75As	3.04		2.12		0.19	0.3
78Se	107		79.1	66	13.6	9.26
111Cd	0.95		0.56		ND	0.07
120Sn	2.36		0.24		ND	ND
202Hg	0.60		0.20		0.10	0.17
208Pb	20.7	112	3.75		0.88	0.59

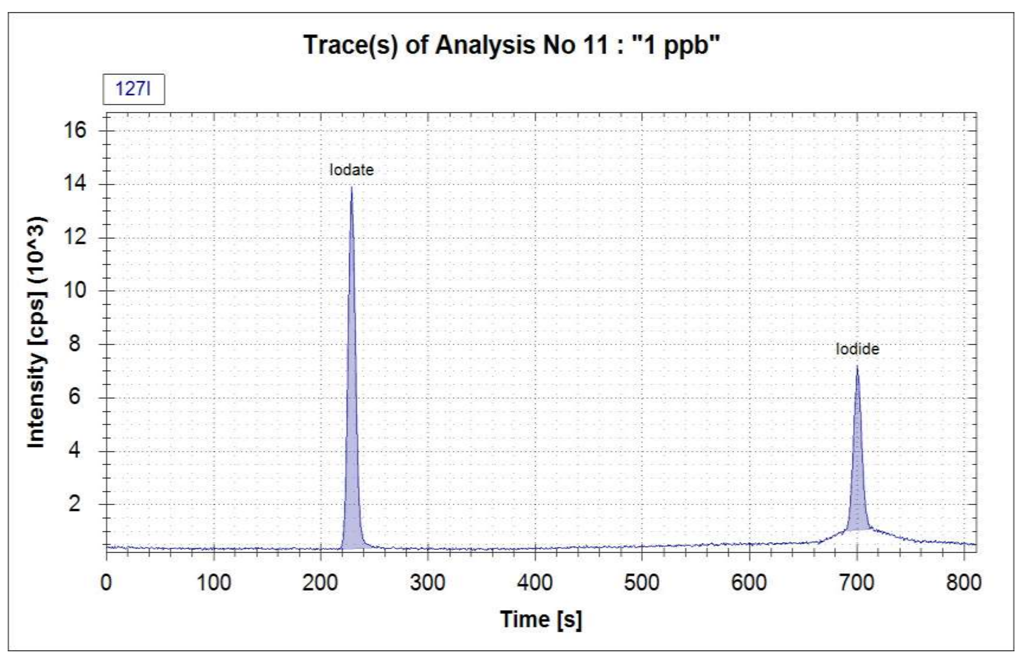
The concentrations for the analytes certified in BCR-063 all lie between 90 and 110% of the reference value, with the exception of zinc and lead. Zinc showed a low recovery at 82%. The slightly high lead recovery was attributed to the very low levels of this analyte in the sample. The concentrations of analytes in the baby formula also agreed with the values reported on the packing, although the selenium recovery was low. Other analyte concentrations in the cow milk and breast milk, in general agree with values that are reported in the literature.

Speciation

Iodine is a micronutrient, essential for thyroid hormone stores and central nervous system development. The bioavailability of iodine is dependent on the chemical form and therefore speciation can shed light on uptake pathways. The principal form of iodine in milk is iodide. Hormonal iodine has also been found in breast milk. How the iodide is present in the milk, as free iodide or bound into proteins or lipids for example is still not fully clarified.

In this study, we have opted to look at a simple ion exchange chromatography, to determine if 'free' iodide is present in the milk. Figure 2 shows the separation of 1 ppb of iodide and iodate on a Dionex™ AS-19 anion exchange column.

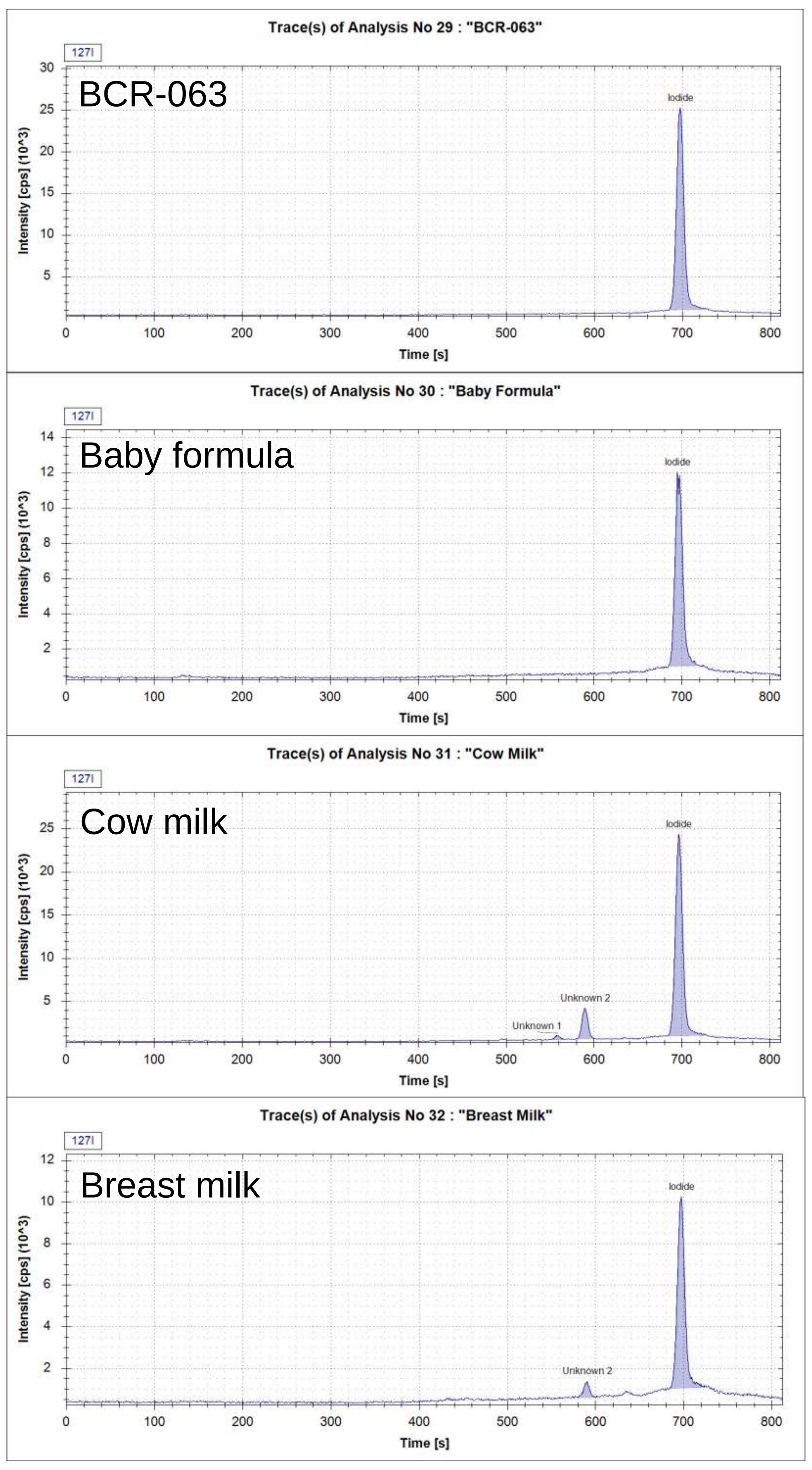
FIGURE 2. Speciation of iodine with Dionex AS-19.



The anion exchange separation was used to determine iodine species in the milk samples. Milk samples were prepared according to the speciation procedure in Table 1 on the day of analysis.

Figure 3 shows the chromatograms for the diluted milk samples.

FIGURE 3. Speciation of iodine in milk samples.



Only Iodide was recovered from the CRM and the baby formula. Unknown iodine species were found in both the cow and breast milk samples. Table 4 shows the quantitative data for the iodine species.

TABLE 4. Quantification of iodine species in the milk samples (µg/g).

	Speciation in diluted samples		
	Iodide	Unknown 1	Unknown 2
BCR-063	1.007		
Baby Formula	0.452		
Cow Milk	0.131	0.002	0.018
Breast Milk	0.043	0.004	

Conclusion

The high sensitivity of the iCAP Qc across the entire mass range, even in He KED mode, means that a single set of operating conditions could be used for all measurements. TEQ data showed:

- Good agreement between determined and certified values for BCR-063 and baby formula
- A 108% and 94% recovery of iodine from the BCR-063 and the baby formula respectively

Qtegra allowed fully integrated IC-ICP-MS operation. A simple IC separation mechanism showed:

- Separation of iodate and iodide in 12 minutes on an AS-19 anion exchange column
- Two unknowns in cow milk and one unknown in breast milk that were not present in the baby formula or the reference material

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