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™ ICP-Q™ ICP-Q-MS in a single operation mode. A Thermo Scientific ICS-5000 was coupled to the ICP 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 to three cups of milk 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 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>
<thead>
<tr>
<th>Procedure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave Digestion</td>
<td>Add 5 g of conc. HNO3, and 2 mL H2O2 to 0.5 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.</td>
</tr>
<tr>
<td>Total Iodine Extraction</td>
<td>Add 50 mL 0.5% sodium 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.</td>
</tr>
<tr>
<td>Speciation</td>
<td>Powder samples were digested in Milli-Q water according to the manufacturers protocol and then all samples were digested 25 fold in the mobile phase just prior to injection.</td>
</tr>
</tbody>
</table>

Mass Spectrometry

The ICP Qc was used for acquisition of all data. A SCAS autosampler was used for the total element quantification (TEQ). The ICP 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 ICP Qc for speciation determinations of iodine and Table 2 outlines the column and elution conditions used.

TABLE 2. Speciation parameters.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Column (Dimensions)</th>
<th>Elution (Duration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodide</td>
<td>IonPac AS19-AS19</td>
<td>2 x 40 and 2 x 250 mm</td>
</tr>
</tbody>
</table>

Data Analysis

Thermo Scientific Oqtegra™ software was used for both TEQ by external quantification and speciation analyses. Embedded Thermo Scientific Chromel® plug ins within Oqtegra allowed the seamless integration of the ICS-5000 with the ICP 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 extracted, 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 ICP 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 kg/g, white in mg/kg and pink in μg/kg).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iodine</th>
<th>Ca</th>
<th>K</th>
<th>P</th>
<th>Mg</th>
<th>Cu</th>
<th>Zn</th>
<th>Se</th>
<th>Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cow milk</td>
<td>0.043</td>
<td>221</td>
<td>11.2</td>
<td>0.87</td>
<td>0.56</td>
<td>0.33</td>
<td>0.53</td>
<td>0.46</td>
<td>0.24</td>
</tr>
<tr>
<td>Baby formula</td>
<td>0.017</td>
<td>112</td>
<td>221</td>
<td>0.87</td>
<td>0.56</td>
<td>0.33</td>
<td>0.53</td>
<td>0.46</td>
<td>0.24</td>
</tr>
<tr>
<td>Breast milk</td>
<td>0.002</td>
<td>112</td>
<td>221</td>
<td>0.87</td>
<td>0.56</td>
<td>0.33</td>
<td>0.53</td>
<td>0.46</td>
<td>0.24</td>
</tr>
</tbody>
</table>

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 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.


Acknowledgements

The authors would like to thank Lutz Effe and Caroline Iordor from InterTek, Bremen for the preparation of the samples for TEQ determinations.

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.