

Coupling of an Inert Ion Chromatographic System with ICP-Q-MS for robust and accurate Elemental Speciation

Tomoko Vincent¹, Daniel Kutscher¹, Lothar Rottmann¹, Julian Wills¹, Shona McSheehy-Ducos¹, Detlef Jensen²

1: Thermo Fisher Scientific, Bremen, Germany 2: Thermo Fisher Scientific, Olten, Switzerland

Overview

Purpose: In this poster, the coupling of the Thermo Scientific Dionex ICS-5000 ion chromatography system to the new Thermo Scientific iCAP Q™ ICP-MS is assessed for the speciation analysis of As (inorganic and organic) species in Organic Brown Rice Syrup (ORBS, a toddler formula ingredient) and Cr (Cr³⁺ and CrO₄²⁻) in potable water.

Methods: Anion exchange chromatography coupled to the iCAP Q™ ICP-MS was used. The Dionex AS7 (for As) and AG7 (for Cr) columns used contain capacities for the separation of both cationic and anionic species¹ and are therefore ideally suited for such applications.

Results: Routine coupling between the Thermo Scientific Dionex ICS-5000 and iCAP Q™ ICP-MS was achieved and was shown to provide a highly sensitive speciation technique for the speciation of trace elements.

Introduction

Interest in the speciation analysis of As in OBRS has recently been triggered by a study indicating high As concentrations in it and products that contain OBRS as a ingredient, e.g. toddler formulas or cereal bars². However, determination of the total amount of As is not sufficient to judge potential hazards as toxicity depends on the chemical form of the As found – inorganic As species (As (III) and As (V)) are highly toxic, as opposed to the non-toxic organic As species (e.g. arsenobetaine). When it comes to Cr, toxicity is also species dependent: while Cr (III) is considered essential, Cr (VI) is highly toxic. Therefore, both species need to be routinely monitored.

Methods

Sample Preparation

Three different OBRS samples were sourced and prepared for analysis. For the total As analysis, the closed microwave digestion method described by Jackson et al² was used. 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 minutes³. For Cr speciation, a drinking water sample was collected in a rinsed PFA container and analyzed directly without any prior dilution or pH adjustment.

Liquid Chromatography

Chromatographic separations were carried out using the Thermo Scientific Dionex ICS-5000 ion chromatography system. Further details can be found in Table 1.

Table 1. Conditions for As speciation analysis.

Parameter	Value
Column	Dionex AS7 (2 mm I.D., 250 mm length)
Elution	Gradient elution (0.3 mL min ⁻¹)
Mobile phase	A: 20 mmol L ⁻¹ Ammoniumcarbonate, pH 9 B: 200 mmol L ⁻¹ Ammoniumcarbonate, pH 9 Gradient from 20 to 200 mmol L ⁻¹ in 12 minutes
Injection vol.	20 µL
Duration	12 minutes + column conditioning



For Cr speciation, an isocratic method using 0.3 mol L⁻¹ nitric acid as eluent was employed. An anion exchange column (AS-7) was used. In contrast to comparable methods, no previous incubation of the samples in mobile phase is therefore required. Details on the method can be found in Table 2.

The proposed method for Cr speciation can also be carried out on other Thermo Scientific Dionex IC systems as e.g. the ICS-900.

Table 2. Conditions for Cr speciation analysis.

Parameter	Value
Column	Dionex AG7 (2 mm I.D., 50 mm length)
Elution	Isocratic elution (0.4 mL min ⁻¹)
Mobile phase	0.3 mol L ⁻¹ Nitric Acid
Injection vol.	20 µL
Duration	3 minutes

ICP Mass Spectrometry

An iCAP Qc ICP-MS was used throughout this study. The operation parameters are summarized in Table 3. For the detection of As and Cr, the collision cell was pressurized with He in order to remove the spectral interference from ⁴⁰Ar³⁵Cl at *m/z* 75 and potential interferences (e.g. ⁴⁰Ar¹²C) at *m/z* 52.

Table 3. Conditions for iCAP Qc ICP-MS analysis.

Parameter	Value
Forward power	1550 W
Nebulizer gas	0.80 L min ⁻¹
Injector	2 mm i.D.
Cell gas flow / KED voltage	4.8 mL min ⁻¹ He / 3V
Dwell time	100 ms

Results

Analysis of As in Organic Brown Rice Syrup (OBRS)

For the three samples analyzed in this study, the total As concentration was determined after microwave assisted acidic digestion. Table 4 shows the obtained results.

Table 4. Total As concentrations in OBRS.

Sample #	Total As concentration [ng g ⁻¹]
ORBS Sample #1	118 ± 7
ORBS Sample #2	136 ± 7
ORBS Sample #3	107 ± 11

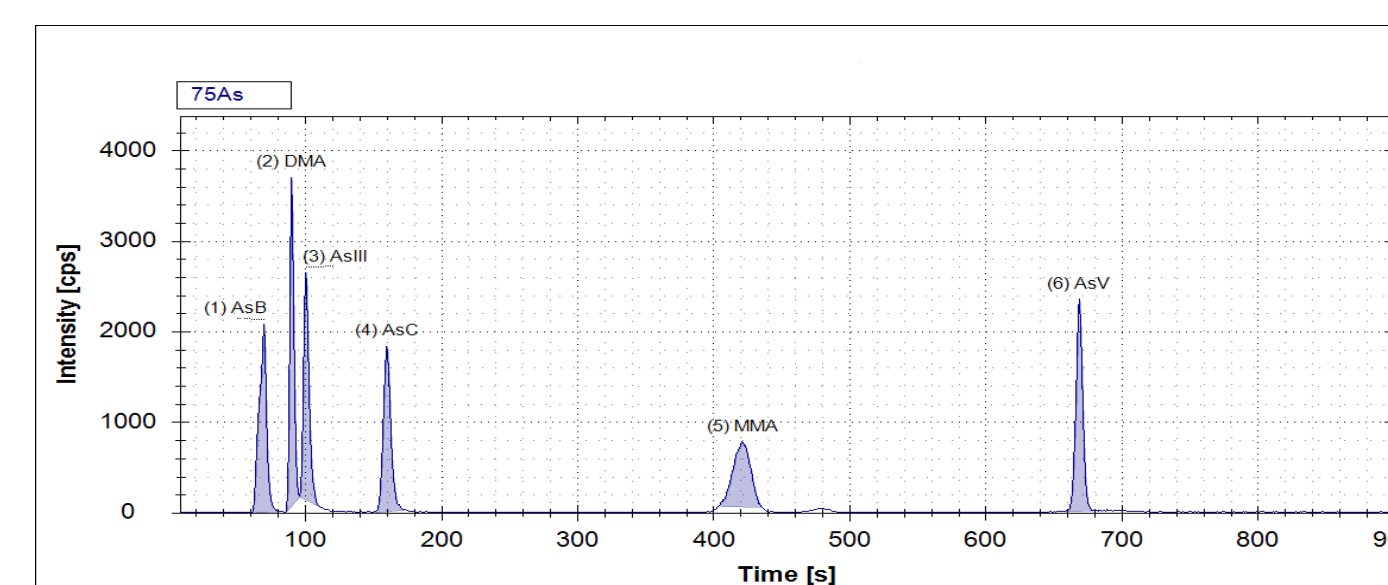
An instrumental detection limit (LoD) of 0.9 pg g⁻¹ with a background equivalent concentration (BEC) of 0.8 pg/g was achieved using a He KED analysis on the iCAP Qc ICP-MS. Taking into account the 160 fold dilution used, a method detection limit of 0.13 ng g⁻¹ was achieved.

As it can be seen from the table, all samples contained more than 100 ng g⁻¹. However, as there is no indication whether the amount of As found is toxic inorganic or rather harmless organic As, speciation analysis has to be carried out for the different samples.

Speciation of As in Organic Brown Rice Syrup

Based on a previously developed IC separation⁴, OBRS samples were analyzed for the presence of six As species: As (III) and (V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB) and arsenocholine (AsC). A model chromatogram containing each of the species in a concentration of 0.5 ng g⁻¹ is shown in figure 1.

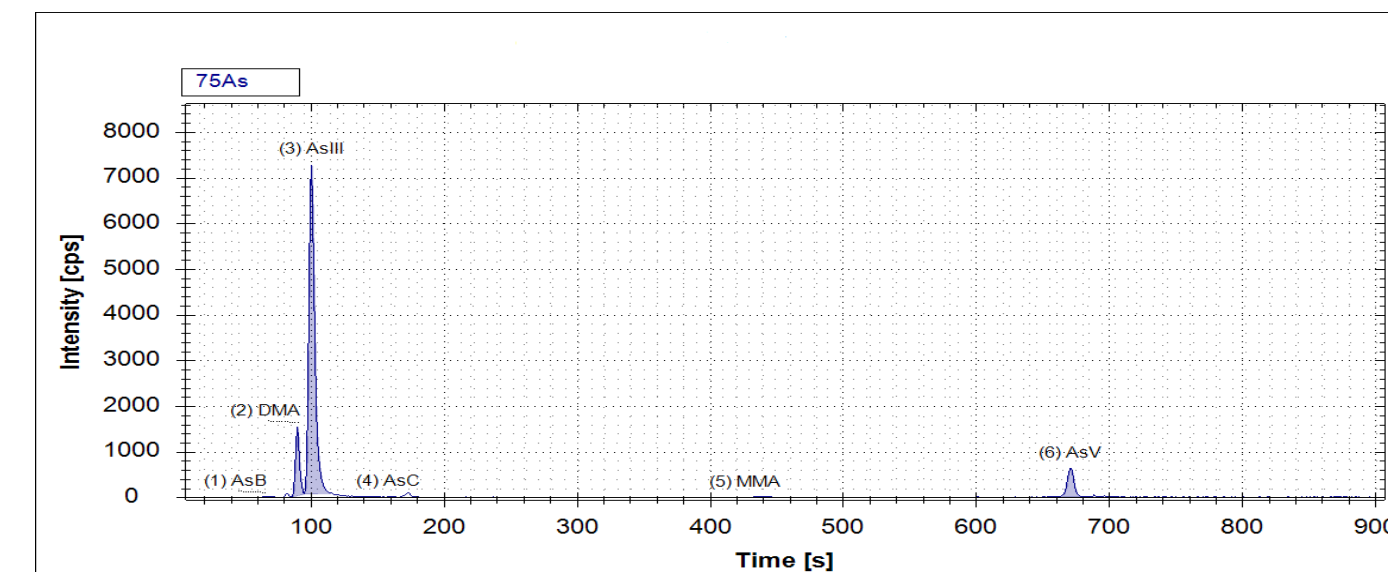
Figure 1. Separation of six As species using IC-ICP-MS.



Evaluation of peak areas and generation of compound specific calibration curves was accomplished using the tQuant module of the Qtegra™ software.

Figure 2 shows a chromatogram for one of the OBRS samples investigated in this study.

Figure 2. Separation of six As species using IC-ICP-MS.



It can be seen that the most abundant As species found in OBRS are indeed the toxic, inorganic forms, predominately As (III). The less toxic species DMA is also found. Table 4 gives an overview on the species distribution in the different samples. Based on the single species quantification also the extraction efficiency was calculated. Each sample was analyzed in triplicate.

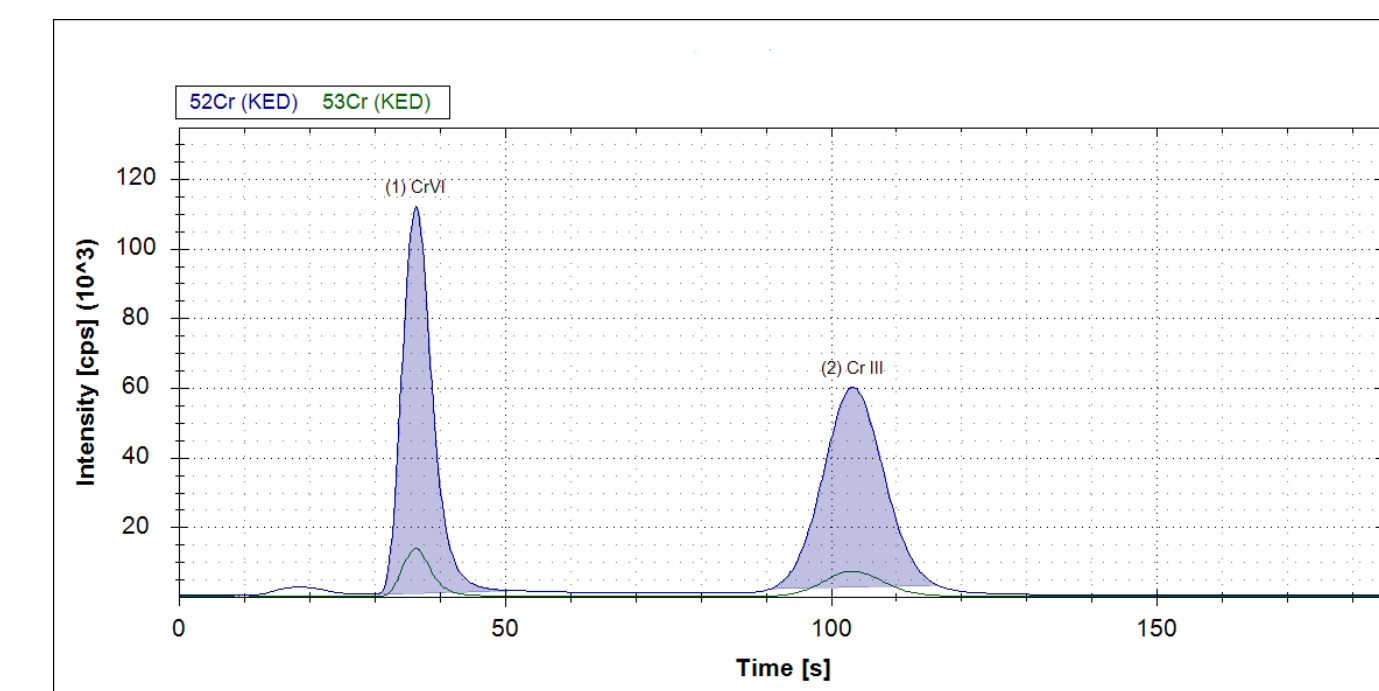
Table 5. Overview on the observed species distribution of As in OBRS and extraction efficiency.

Sample #	DMA [%]	As (III) [%]	As (V) [%]	Efficiency [%]
ORBS Sample #1	12 ± 0.3	82 ± 0.5	6 ± 1	78
ORBS Sample #2	12 ± 0.6	83 ± 0.3	5 ± 1	74
ORBS Sample #3	10 ± 0.5	85 ± 0.4	4 ± 1	76

Speciation of Cr in Drinking Water

Due to the routine monitoring of Cr in environmental samples, short analysis times and high sample throughput are desirable for Cr speciation analyses. As can be seen in the chromatogram in Figure 4 (5 ng g⁻¹ of each species), elution of both species can be accomplished in less than 3 minutes. As this method is based on ion chromatography only, no prior incubation with complexing agents (such as EDTA) is required. This improves sample throughput significantly.

Figure 3. Chromatographic separation of Cr (VI) and Cr (III).



Detection limits of 0.20 pg g⁻¹ for Cr (VI) and 0.38 pg g⁻¹ for Cr (III) were determined.

In order to investigate whether species conversion might occur during the chromatographic separation, different mixtures of both species were analyzed to determine the spike recovery. The results are shown in Table 5.

Table 6. Spike recovery results for Cr (VI) and Cr (III).

Concentration [ng g ⁻¹]	Found Cr (VI) [ng g ⁻¹]	Recovery [%]	Found Cr (III) [ng g ⁻¹]	Recovery [%]
2.34 each	2.31 ± 0.01	99 ± 1	2.35 ± 0.02	100 ± 1
6.03 Cr (VI); 1.90 Cr (III)	6.01 ± 0.02	100 ± 1	2.00 ± 0.008	105 ± 1
1.87 Cr (VI); 6.20 Cr (III)	1.85 ± 0.01	99 ± 1	6.15 ± 0.03	99 ± 1

Figure 5. Species distribution of Cr in local potable water.

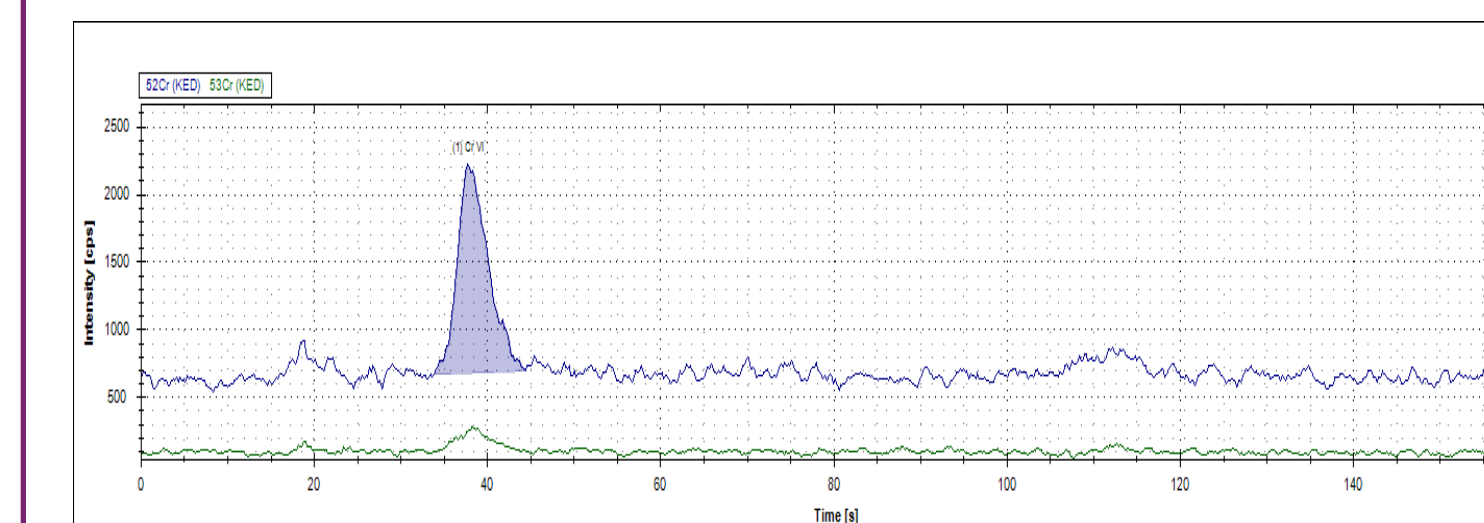


Figure 5 shows the resulting chromatogram for the analysis of a potable water sample. A single peak, Cr (VI), was detected. After external calibration, its amount was determined to be 42.5 ± 1 pg g⁻¹.

Conclusion

- The combination of the Thermo Scientific Dionex ICS-5000 ion chromatography system with the iCAP Qc ICP-MS provides a highly sensitive, routine technique for the determination of trace metal species.
- A highly sensitive and specific method for the speciation analysis of As in OBRS samples has been developed and applied to the analysis of different samples. The results indicate that legislation for As in foodstuffs need to be established.
- A fast and accurate method based on ion chromatography for the speciation of Cr in water samples has been developed.
- The AS7 and AG7 anion exchange columns used were not only able to efficiently separate different elemental species, but also helped to improve detection sensitivity as the separated species eluted with as narrow signals. The low flow rate of 0.3 - 0.4 mL min⁻¹ helps to reduce both sample and mobile phase consumption.

References

- Thermo Scientific Dionex homepage (<http://www.dionex.com/en-us/products/columns/ic-rfc/specialty-packed/ionpac-as7/lp-73274.html>)
- Brian P. Jackson *et al.*, Arsenic, Organic Foods, and Brown Rice Syrup; Environmental Health Perspectives, 2012, <http://dx.doi.org/10.1289/ehp1104619>
- Huang *et al.*, Quantitative Chemical Extraction for Arsenic Speciation in Rice Grains, J. Anal. At. Spectrom. 25 (2010),800-802
- Thermo Fisher Scientific Application Note 43099

All trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others.

Published at 19th International Conference on Mass Spectrometry, Kyoto, Japan, September 2012.