Comparing IC and HPLC Systems for Speciation Analysis – A Case Study

Daniel Kutscher¹, Carl A. Fisher², John Schmelzer³


ABSTRACT

Speciation analysis is a widely accepted tool for the quantitative determination of different chemical forms of an element. For most critical elements, ion chromatography (IC) is the separation method of choice, as dedicated IC systems are specifically tailored to detect, quantify and compare benefits and drawbacks related to the different methods. It will also critically assess the use of IC systems for ion exchange chromatography for the separation of both elements.

INTRODUCTION

Two of the primary examples for the need to perform speciation analysis are chromium and arsenic, as both elements may appear in different chemical forms (e.g. Cr (III) vs. Cr (VI) or toxic vs. organic arsenic), each with different toxicity and thus, potential related hazards. The different species of arsenic are typically detected depending on the pH, so that in cation exchange chromatography is the preferred way for separation. In most cases, arsenic chromatography using an exchange matrix carbonate based eluant completes separation with narrow peak shapes and thus improved signal to noise ratio. For chromium, the two relevant species are charged differently, so that a fully mode mode resin is used, containing separation capacity for both cations and arsenic species. However, methods also basis on, for example, liquid chromatography have been applied. As this chromatographic method depends on the use of complexing agents such as EDTA and organic modifiers, significant interference will be created affecting the main ion speciation, chromium.

MATERIALS AND METHODS

A Thermoscientific™ SpectrAA™ RQ ICP-MS was used for analysis of background levels in different eluents. The instrument was turned on each measurement day in order to achieve best sensitivity across the mass range and effective suppression of occurring interference. For ion chromatography, a Thermoscientific™ Dionex™ ICS-3000 HPLC system was used, whereas for high performance liquid chromatography, a Thermoscientific™ Dionex™ Ultimate 3000 HPLC system was used. The time dependent evaluation indicates the transient nature of contamination as background volumes online or offline (fraction collection) using different chromatographic systems. The Thermoscientific™ Dionex™ ICS-3000 HPLC system was coupled to a fraction collector in order to collect the eluent in a frequency of every 15 minutes for quantitative evaluation using ICP-MS. The Ultimate 3000 HPLC system was coupled online to the ICP-MS and data acquired over a period of 15 minutes was averaged for comparison. In order to avoid any bias in the results, no column was connected during the experiment. Instead, a pressure coil was placed in the flow path to assure real-time monitoring of higher resolution columns that yield excellent peak separation and short elution time. The choice of the right separation method for a given analytical problem often determines the most appropriate hardware (e.g. type of chromatography system, column nature and dimensions, stationary and mobile phase). Whereas most applications are based on based chromatography, there is a significant difference between IC and HPLC, although the various applications demand to be almost identical.

Ion Chromatography

Hardware does not use any parts made of metal containing components (e.g. stainless steel or titanium alloys). These results indicate therefore reduced background caused by the absence of metal leaching over time and assume compatibility with strong salts such as diluted acids or alkaline eluents, such as hydroxides or carbones.

To assure best compatibility with the ICP-MS sample inlet, eluents such as KOH can be neutralized by neutralization to the plasma source, using a suppressor. Modern IC systems allow working with elevated pressures (up to 6,000 psi) to permit use of higher resolution columns that yield excellent peak separation and short elution time.

High Performance Liquid Chromatography...

For some elements, a time-dependent behavior of elution was observed for the HPLC system under test in this study, leading to a reduction in the observed levels over time. This indicates that the transient source of contamination could be washed out over time as surfaces are cleaned by the eluent. However, in no case of the observed levels of these elements reach equilibrium to the levels observed with a dedicated IC system. As an example, the time-dependent elution of chromium is shown in figure 2.

RESULTS

In order to compare IC and HPLC systems for their suitability to speciation analysis, a direct comparison for the detectability and stoichiometry of contamination was done between a dedicated IC system and an ICP-MS system. The analyte selected was chromium, where the two main speciation (Cr (III) vs. Cr (VI)) should be separated on an ion exchange column with dilute nitric acid and using a column with exchange capacity for both cations as well as arsenic species. This method achieves consistent separation of the two species in less than three minutes and was monitored in a time-dependent manner and the results for key elements are shown in Table 2.

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Table 2. Time-dependent concentrations of different trace elements in the eluent collected from IC and HPLC hardware

Table: 1. Experiments conducted for comparison of IC vs. HPLC for speciation analysis of Chromium

<table>
<thead>
<tr>
<th>Element</th>
<th>Interference (mg·L⁻¹)</th>
<th>Eluent/Pare</th>
<th>Species</th>
<th>PackedColumn (every 15 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>8.7 0.6</td>
<td>8.7 0.8</td>
<td>8.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

As can be seen from the data, the observed levels of contamination are typically lower for main elements, such as As, etc. For chromium, a significant drop in eluent concentration is observed for HPLC and IC systems, as well as for Cd, Cu and Sr, comparable levels are observed for both systems. It has to be noted that the metal-free HPLC system is also showing elevated contamination from a formerly clean eluent. It cannot be excluded though that this contamination has been caused through the process of collection or from the sample containers used in this study. Further investigation will be needed to determine the origin of the observed background.

CONCLUSIONS

Eluent contamination with trace elements is significantly increased for a variety of elements on an HPLC system compared to a dedicated IC system. This is most likely caused by metal containing parts in the flow path of the mobile phase, such as e.g. the pump heads, connections and tubing. For some elements such as e.g. chromium or vanadium, a time-dependent behaviour of elution was observed in the first two hours of operation, however, equivalent background levels when the IC and HPLC system were not achieved.

Increased backgrounds after long term usage of an HPLC system with a typical eluent used for IC speciation were not subject to study here, but could potentially be observed.

Chemostatic methods based on ion-exchange chromatography are ideally run on a dedicated IC system rather than an HPLC system in order to avoid elevated backgrounds caused by leaching of metals from hardware components.

REFERENCES

1. Application Note 43357: Arsenic Speciation in human urine by hyphenated ion chromatography (IC) and high performance liquid chromatography (HPLC).


TRADEMARKS

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