Ion Chromatography ICP-Q-MS for the Detection of As Species in Apple Juice

Daniel Kutscher1, Shona McSheehy-Ducos1, Julian Wills1, Detlef Jensen2; 1Thermo Fisher Scientific, Bremen, Germany; 2Thermo Fisher Scientific, Olten, Switzerland

Overview

Purpose: This paper describes and assesses the coupling of the Thermo Scientific Dionex ICS-2000 ion chromatography system to the Thermo XSERIES II ICP Q-MS for the determination of inorganic arsenic species in apple juice.

Methods: Anion-exchange chromatography coupled to the XSERIES II ICP-Q-MS was used. The Thermo Scientific Dionex ICS-2000 system was used for preconcentration and separation of the arsenic species into a narrow peak. The low flow rate of 0.3 mL/min helps to reduce sample and mobile phase consumption.

Results: A synthetic mixture containing 10 ng/g of six As species (inorganic AsF3, arsenate (As5+), arsenite (As3+), MMA, DMA, and As) was analyzed using the Dionex ICS-2000 system. The chromatography results are shown in Figure 1. The detection limits were calculated based on three times the standard deviation of peak area. The chromatographic peak widths are listed in Table 3.

Determination of Spike Recovery

In a separate study, one of the resulting chromatographs is shown in Figure 4. The arsenic was identified as its inorganic (toxic) species As3+ and As5+ and as the MMA and DMA organic forms. In the second juice sample, the arsenic was found only as the inorganic arsenic species. The results of the speciation specific quantifications are shown in Table 2 together with the total arsenic concentration determined precisely. Each juice sample was spiked to be 10 ng/g.

Conclusions

• The combination of the Dionex ICS-2000 ion chromatography system with the XSERIES II ICP-Q-MS provides a highly sensitive, routine IC-ICP-Q-MS technique for the determination of trace species. The results for the arsenic speciation analysis and total arsenic analysis are in agreement. Other arsenic species being present in concentrations below the LOD found in apple juices were not detected. No further separation of arsenic species was necessary because all arsenic species existed in the juice samples in one or in the total arsenic species. The lower limit of 0.3 ng/g helps to reduce both sample and mobile phase consumption.

References

2. Letters from the FDA to the Dr. Olten Street Regarding Apple Juice and Arsenic http://www.fda.gov/forengineers/031160.html

FIGURE 4. Chromatogram of an apple juice sample showing peaks for As3+ and As5+.

One of the resulting chromatograms is shown in Figure 4. The arsenic was identified as its inorganic (toxic) species As3+ and As5+, and as the MMA and DMA organic forms. In the second juice sample, the arsenic was found only as the inorganic arsenic species.

The results of the speciation specific quantifications are shown in Table 2 together with the total arsenic concentration determined precisely. Each juice sample was spiked to be 10 ng/g.

Methods

Four different apple juices were purchased in a local supermarket. Allots of each sample were dialyzed and digested, and the arsenic content was determined using method of standard additions on the Dionex ICS-2000 system. One sample in each group was spiked in order to determine the recovery of arsenic species from apple juices. The dialysis rates were determined based on three times the standard deviation of peak area. The chromatographic peak widths are listed in Table 3.

Liquid Chromatography

Chromatographic Separations were carried out using the Dionex ICS-2000 ion chromatography system, Thermos Scientific Dionex anion-exchange column supervisor were used. Conditions can be found in Table 1.

TABLE 1. Chromatographic Separations of As species

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>Dionex AS94H™+ 7i 250 mm x 4.6 micrometer</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>A: 25mM Ammonium carbonate, pH 6.0 (250 mL/min) B: 250 mM Ammonium carbonate, pH 6.0 (Gradient from 0 to 100% B in 15 min)</td>
</tr>
<tr>
<td>Injection volume</td>
<td>50 µL</td>
</tr>
<tr>
<td>Detector</td>
<td>248 nm column conditioning</td>
</tr>
</tbody>
</table>

Results

Speciation of As in Apple Juice

An isocratic mixture containing 10 ng/g of six As species (inorganic AsF3, arsenate (As5+), arsenite (As3+), MMA, DMA, and methyl arsenite (AsMMA)) was analyzed using the Dionex ICS-2000 system. The chromatography results are shown in Figure 1. The detection limits were calculated based on three times the standard deviation of peak area. The chromatographic peak widths are listed in Table 3.

Although DNA and Arsenic were able to retain retention times (K) in a different about 10 and 40 m, respectively, which resulted in a peak overlap as shown in Figure 1. The retention times are listed in Table 3. The average recovery values for arsenic species were determined by standard addition experiments. The results for the arsenic speciation analysis and total arsenic analysis are in agreement. Other arsenic species being present in concentrations below the LOD found in apple juices were not detected. No further separation of arsenic species was necessary because all arsenic species existed in the juice samples in one or in its toxic inorganic species.