Determination of Anions in High-Purity Water by Ion Chromatography

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Summary. The determination of the concentration of some different anions in high-purity water (µg/l-level) using ion chromatography after concentration on pre-columns is described. The detection is made by a conductivity cell after passing an anion fiber-suppressor (AFS). Two different separator columns (AS-4 and AS-5) and some different separator systems were tested. In all cases linearity is given for the determined anions. The concentration of the anions was determined not directly but by addition of a standard solution and subsequent graphic extrapolation of the calibration diagram. The determination levels are below 1 µg/l. The AS-5 column gives better results than the AS-4 column.

1. Introduction
The production of semi-conductors sets special standards also for the purity of the water. The electrical conductivity gives a general information about the ionic content of the water, but much better information can be obtained by the individual determination of cations and anions. This report describes the determination of anions in high-purity making use of ion chromatography (HPIC).

This method with different modifications is used very frequently since it has been introduced in 1975 by Small et al. [1]. We utilized a chromatograph made by the Dionex corporation. The standard conditions proposed by the manufacturer and some authors [1–4] make it possible to determine the anions in the range of mg/l, but they cannot be used in the range of µg/l because of a strong disturbance of the Cl⁻- and NO₂⁻-peak by the “water-dip”¹.

To solve these problems it was necessary to find out the most suitable parameters of elution, to improve the concentration technique and to elaborate the best methods for the production of the standard solutions and the handling of the samples. Our aim was to determine chloride and nitrite together with other anions like sulfate without any disturbance by the “water-dip” in one analysis.

2. Experimental

2.1 Apparatus, Columns and Chemicals
Ion Chromatograph IC 2020 i, Dionex Corp., Sunnyvale, CA, USA with two internal concentrator columns.
Integrators: 3390 A. Hewlett Packard, C-R2AX Shimadzu.

Columns:

- separator columns
- concentrator columns
(anion separator — AS) (anion guard — AG)
HPIC™ AS-4 (3 x 250 mm) AG4 (3 x 50 mm)
HPIC™ AS-5 (5 x 250 mm) AG 5 (5 x 50 mm)

Both types of columns are packed with the same resins (either 4 or 5). These types of resins are distinguished from one another by other ammonium groups, other hydrophobicity and different size of the latex particles.

Hollow anion-fiber suppressor (AFS), regenerated by 0.0125 mmol/l H₂SO₄ at a flow rate of 2.4 ml/min.
Milton Roy high pressure pump for concentration
All chemicals were of “p.a.” quality (Merck, Darmstadt, FRG); Argon “pure” to degas CO₂ out of the samples.
The high-purity water was in addition purified by a Millipore-Super-Q installation (“Super Q-Water”).

2.2 Procedure
The volume of concentration was 15 ml for all experiments. The samples were taken in PE-bottles out of the pure water circuit [5] or they were inserted directly into the concentrator columns via a Teflon connection. Remote loading of the concentrator columns might be a source of errors [5].

¹ “Water-dip” is a big negative peak (“dead volume”) disturbing or overlapping the peaks of chloride and nitrite.
Table 1. Experimental conditions and results

<table>
<thead>
<tr>
<th>System column</th>
<th>Eluent (mmol/l)</th>
<th>Flow rate (ml/min)</th>
<th>Anions</th>
<th>Retention time (min⁻¹)</th>
<th>Limit of detection (µg/l)</th>
<th>Result for &quot;Super-Q-Water&quot; (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard conditions (amplification 30 µs)</td>
<td>2.8 NaHCO₃</td>
<td>2.0</td>
<td>Cl⁻</td>
<td>1.6</td>
<td>100 µg - 10 µg/l</td>
<td>no results because of overlapping peaks</td>
</tr>
<tr>
<td>AS-4 Column</td>
<td>2.4 Na₂CO₃</td>
<td>1.9</td>
<td>NO₂⁻</td>
<td>according to the manufacturer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>System 1 (amplification 1 µs)</td>
<td>1.2 NaHCO₃</td>
<td>1.5</td>
<td>Cl⁻</td>
<td>4.0</td>
<td>0.5</td>
<td>0.25 ± 4.5%</td>
</tr>
<tr>
<td>System 2 (amplification 1 µs)</td>
<td>2.4 NaHCO₃</td>
<td>1.4</td>
<td>Cl⁻</td>
<td>2.8</td>
<td>0.4</td>
<td>0.5 ± 2.8%</td>
</tr>
<tr>
<td>AS-4 Column</td>
<td>1.44 Na₂CO₃</td>
<td>3.2</td>
<td>NO₂⁻</td>
<td>n.n.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>System 3 (amplification 1 µs)</td>
<td>8 NaOH</td>
<td>2.0</td>
<td>Cl⁻</td>
<td>2.0</td>
<td>0.2</td>
<td>0.2 ± 4.0%</td>
</tr>
<tr>
<td>AS-5 Column</td>
<td>0.09 Na₂CO₃</td>
<td>2.4</td>
<td>NO₂⁻</td>
<td>≤ 0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* See chapter 3.2

The standard solutions were prepared in three steps of dilution from 1,000 mg/l over 1 - 10 mg/l to 0.2 - 1 µg/l in a "clean bench". Reproducible results were obtained if the most diluted solutions are prepared day by day [7].

3. Results and Discussion

3.1 Summary of the Results

Table 1 gives a short summary of all the different experimental conditions and the results obtained with the two different column systems.

3.2 Experiments with the AS-4 Columns

Tests with NaOH- and Na₂B₄O₇-solutions as eluents were not successful. Using system 1 the chloride peak was separated and not affected by the "water-dip". However, because of the very low ionic strength HPO₄²⁻, NO₃ and SO₄²⁻ were not eluted. This system isst specially appropriate for very accurate determinations of Cl⁻ and NO₂ even if there are very different concentration ranges between them.

In system 2 with higher ionic strength all anions were eluted, however, the chloride peak is obviously overlapped by an unknown matter. These are not the HCO₃⁻ ions (the samples were degassed with argon) and the source must be within the concentrator columns.

The shape of the Cl⁻-peak is very bad and it is too broad. This overlapping is the reason for the big differences between the results for chloride in system 1 and 2.

3.3 Experiments with the AS-5 Columns

No reproducible results could be obtained with different mixtures of CO₃²⁻ and HCO₃ solutions and a NaOH-solution alone. By adding small amounts of carbonate to the NaOH-solution the force of elution was increased sufficiently without losing the advantage of the NaOH-solution: smaller background conductivity and therefore a smaller "water-dip". However, phosphate is not eluted in this system because at the pH value of 11.75 there are trivalent PO₄³⁻-ions.

In this system there was a small peak at the retention time of nitrite. This was no electronic interfering signal and increased with growing volume of concentration. The content of nitrite is in the range ≤ 0.1 µg/l.

By adding 2 Vol.-% acetonitrile and 0.08 mmol/l 4-hydroxybenzonitrile the time of retention of SO₄²⁻ was halved, however Cl⁻ was again overlapped by the "water-dip" and on the other side PO₄³⁻ was not yet eluted.

3.4 Evaluation

An accurate comparison of 10 measured values confirmed the statement of Roberts [6], that the application of the peak height instead of the peak area for computation gives better results with smaller standard deviations (e.g. chloride: ± 2.8% peak height ± 9.7% peak area).

Two different methods were used to examine the linearity:

a) constant volume of concentration with varying concentration of standards,

b) varying volume of concentration with concentration of standards.

In both cases and for all detectable anions the correlation coefficients for a linear least squares fit were between 0.9918 and 0.9989.

The responses of the anions in "Super-Q-Water" were in part very small and of bad shape hence we did not determine the content of the anions directly. We added in stages standard solutions, calculated the calibration curves and read the content of the anions at the points of intersection with the axis of the abscissa.

This method makes it possible to calculate the contents of the anions even below their chromatographic detection limits. (Compare the limits of detection and the results for "Super-Q-Water" in Table 1.)