Ion Chromatography in Water Analysis

Application in Analysis of Anions in Water and Waste Water

Since the 1980’s, Ion Chromatography was developed into a powerful and sensitive tool for Ion Analysis. Nowadays, anion- and cation-chromatography is a well-established technique and used for the determination of a large number of ions in different matrices. As the presentation of an overview of the wide field of Ion Chromatography (IC) is clearly beyond the scope of this short paper, the book of Joachim Weiss [1] is strongly recommended. This paper focuses on the analysis of anions in water and waste water and aims to motivate to use this technique.

Since ion chromatography found its way into water laboratories the routine analysis of nitrate and sulfate presented one of the major problems in water analysis. The determination of nitrate in water by photometric analysis required the use of high concentrated sulfuric acid to nitrify an aromatic compound. The analysis of sulfate was time consuming and labor intensive. Instead, ion chromatography was a fast and easy method to determine nitrate and sulfate in a large number of samples. Thus, the determination of fluoride, chloride, nitrate and sulfate by ion chromatography was the first well established IC method in water analysis. The anions were detected by conductivity. In some cases UV-detection and inverse UV-detection were used. The suppressor systems, necessary for sensitive measurements using conductivity detection, were improving. Nowadays the measurement of concentrations in ppb-range is possible. Furthermore, the separation columns for anion determination are much more efficient in comparison to the beginnings of ion chromatography; a wide offer of different columns allows to solve nearly all separation problems in routine analysis.

Thus, it is possible to analyze bromide, chloride, fluoride, nitrate, nitrite, o-phosphate and sulfate in one run (method according to DIN EN ISO 10304-1). By following the routine of the standard DIN EN 10304-3 it is possible to analyze chromate, iodide, sulfite, thiocyanide and thiosulfate. Chlorite, chloride and chlorate are monitored according to DIN EN 10304-4 and bromate to EN ISO 15061, using separation columns with high capacity. With these columns it is possible to combine the standards to determine as many anions as possible in one
In cases where the analyte absorbs UV-light, an UV-detector is useful to ensure reliable results.

Interferences with chloride can be reduced by using silver cartridges, interferences with sulfate by barium cartridges. C18 columns are sometimes helpful if the matrix contains a high amount of organic substances.

**Special Methods**

Alongside the method for routine analysis, several special methods are applied in the laboratory of this article’s authors.

**Waste water:** Here, the specification is not a low determination limit but a wide linear working range. Thus, an Ion Chromatograph without a suppressor system is used, leading to linear working ranges for chloride from 0.1 to 200 mg/L, nitrate from 0.5 to 300 mg/L and sulfate from 1 to 600 mg/L. By using an eluent with a high concentration of acetone the lifetime of the column can be extended. No sample preparation with C18-cartridges is necessary, only filtration by a 0.45 µm membrane filter.

**Cyanide:** An easy way to measure cyanide is to deflate the cyanide and absorb it in an alkaline solution. This solution is injected in an IC-system with an alkaline eluent. Cyanide is quantified using amperometric detection with a silver working electrode (DIN 38406 Part 7).
Bromate: During water treatment by ozonization bromide can be oxidized to more toxic bromate. Due to the drinking water limit 10 µg/L and a quantification limit of 1 µg/L a very sensitive IC method is necessary here. As direct IC determination with conductivity detection is not sensitive enough, a post column reaction technique with UV-detection and a quantification limit of 0.5 µg/L is used (DIN EN ISO 11206).

Iodide: In some cases, the analysis of iodide in water and waste water samples is necessary. Due to its long retention time at room temperature the column temperature should be increased to higher temperatures (e.g. 55°C), so that iodide elutes much earlier and moves in front of sulfite and sulfate. An interfering peak can appear in waste water samples; thus, the iodide results which are achieved by conductivity detection have to be confirmed by UV-detection (at 226 nm).

Perchlorate: To monitor perchlorate in swimming pool water, river water or tap water a very sensitive IC method is required. Very low quantification limits (lower than 1 µg/L) are reached by hyphenation of IC and mass spectrometry. When IC and conductivity detection is utilized, a large volume injection should be possible and a separation column with a high capacity should be used. When perchlorate has to be analyzed in waters with high matrix concentrations of chloride, nitrate and/or sulfate different techniques to reduce the matrix influence can be applied. The authors recommend Ag- or Ba-cartridges to reduce the matrix concentration of chloride and sulfate respectively, the column cut technique, or the reinjection technique. It is also possible to use the mathematical method and to calculate and subtract the baseline resulting from the interfering peak.

Trifluoroacetic Acid: Like perchlorate, the trifluoroacetic acid peak eluates in the shoulder of a matrix peak. Thus, in the case of high matrix concentrations and a corresponding interfering peak the reinjection technique to eliminate the interference is used. This allows for quantification limits in the range of 1 µg/L. The results of this technique are comparable to those that have been achieved by high resolution LC-MSMS.

Chromium(VI): When the sample contains higher concentrations of Chromium(VI) (> 100 µg/L), it can be determined using IC with UV-detection, based on the yellow color of chromate. In very low concentrations Chromium(VI) can be identified highly sensitive by post column reaction with 1,5-diphenylcarbazide (Draft: DIN 38405-D52), where quantification limits of 20 ng/L can be achieved. The same quantification limits can be reached by hyphenating IC with ICP-MS. Theoretically, this technique enables a Chromium(VI) – Chromium(III) speciation using EDTA as complexing agent for Chromium(III). However in “real” samples the concentrations of calcium-, magnesium- or iron-ions are too high to allow for a stable Cr(III)-EDTA
complex.

**Sum Parameters**

IC is also used to monitor sum parameters:

Total Nitrogen (TN$_b$): Normally the TN$_b$ is determined by high temperature burning of the sample and quantified by fluorescent measurement. An alternative is the alkaline microwave digestion of the sample with the addition of potassium persulfate. During microwave digestion all nitrogen (inorganic and organically bound nitrogen) is transformed to nitrate, which can be quantified by IC (EN ISO 11905-1). The potassium persulfate causes a high sulfate content; thus, a column and eluent have to be selected which permits a good separation of Nitrate and Sulfate.

AOX, AOF, AOCI, AOBr, AOI: The increasing sensitivity of the IC system facilitates the determination of organic bound halogens. Organic bound halogens are enriched on activated carbon, burned in a wet stream of oxygen, absorbed in water (or water with hydrogen peroxide) and measured using an IC-system (Combustion IC/CIC). When a natural activated carbon containing sulfur is used, ultrapure water is sufficient to absorb the halogenes as halogenides. When a synthetic charcoal with a very low sulfur content is used, is the risk exists that the organic bound iodide is transformed to iodine (I$_2$) and escapes. In this case an absorption solution containing hydrogen peroxide in necessary. Routine measurements of the AOI demonstrate that inorganic iodide is also adsorbed on activated carbon and measured as AOI. Thus, the content of inorganic iodide should be controlled by an additional direct IC measurement of the sample. If the concentration of inorganic iodide is > 10 µg/L, a sample pretreatment by solid phase absorption is essential. Furthermore, it was found that inorganic fluoride is also enriched on activated carbon (acid absorption, acid washing as AOX) in the cases of sample concentrations higher than 0.2 mg/L. If the adsorption is accomplished under neutral conditions inorganic fluoride < 10 mg/L is tolerable. The CIC determination of the AOX yielded values comparable to the standard method (DIN EN ISO 9562). By applying CIC instead of the classical AOX determination, more detailed information about organic bound chlorides, bromides and iodides can be gained. Last but not least, the parallel use of conductivity and UV detection allows for reliable results and excludes interfering peaks like those of fluoride and iodate.

**Conclusion**

Nowadays the ion chromatographic determination of anions is a well-established method in analytical chemistry. IC can be used for separation, sample preparation
and quantification. IC is a reliable and sensitive method with a good reproducibility, is fully automated and moderate in costs. IC can be used with different detectors (from conductivity to mass spectrometry) and many different separation columns are available. IC solves many problems of daily lab work.

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