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# Determination of anions in oilfield waters by ion chromatography

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## Abstract

For the characterization of oilfield waters (formation waters, injection waters, filtrates of drilling mud, etc.) the minor components bromide, iodide and sulfate are very important among the major components chloride and hydrogencarbonate. The chloride content of these water samples is mostly higher than 1% (10 000 ppm), whereas the concentration of the minor components is in the lower ppm range. The proposed method permits the determination of the above three minor components in one ion chromatographic (IC) run. For separation an IonPac AS9-SC analytical column is used with sodium carbonate as eluent. Detection is performed by suppressed conductivity. Chloride will be titrated because of its high concentration. In principle it is also possible to determine chloride by IC if the sample is diluted to an appropriate concentration.

## 1. Introduction

In exploration and production of crude oil and natural gas, the analysis of water samples is also very important. Oil and gas reservoirs are often accompanied by formation water. This is normally a highly saline brine of a composition typical for each geological formation. Formation waters in Austria differ widely in salinity and composition. The major component is sodium chloride, mostly at concentrations higher than 10 000 ppm (up to 70 000 ppm). Formation waters contain, compared with sea water, higher concentrations of the biogenic elements bromine, iodine and nitrogen and lower concentrations of sulfate and magnesium. For classification of water samples, the contents of bromide, sulfate and iodide are of interest in addition to the contents of chloride

and hydrogencarbonate. In some instances a knowledge of the contents of nitrate, phosphate, fluoride, thiocyanate or organic acids is of interest.

Typical applications are the analyses of liquid samples taken from exploration wells (filtrates of drilling mud, water samples from tests) to see if there is any influx of formation water, analyses of water produced together with oil or gas to characterize the original formation water, quality check of injection water used for improved oil recovery projects and tracer studies to observe the influence of injection water or drilling mud on formation water.

In the past, various gravimetric, volumetric and photometric methods have been used to determine the mentioned anions [1, 2]. In the last few years, ion chromatography (IC) has been used as an alternative possibility for the determination of anions in aqueous solutions.

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The main problem for the IC determination of anions in formation water is the large excess of chloride (from 100:1 up to 1000:1) compared with the minor components. Our aim was to find a method for the separation and determination of bromide, sulfate and iodide (concentrations mostly <100 ppm) in presence of chloride at concentrations of 10 000 ppm and higher. If possible, the determination should be performed in a single IC run with only one detector.

A Dionex Application Note [3] describes the determination of the relevant anions, but it is necessary to use two different columns (HPIC-AS2 and HPIC-AS5) for separation. Weiss [4] described some useful methods for the separation of bromide, nitrate and sulfate on IonPac AS1, AS2, AS3, AS4, AS4A, AS5, AS5A and AS9 analytical columns. Iodide and thiocyanate can be separated on an IonPac AS4, AS5 or CS5 column [4]. In this paper, a method for the separation of bromide, sulfate and iodide in brines using an IonPac AS9-SC analytical column with Na<sub>2</sub>CO<sub>3</sub> as eluent in a single run is described.

## 2. Experimental

The installation manual of the IonPac AS9-SC column [5] describes several different eluents for the separation of inorganic anions. For this work we tested various mixtures of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> as eluents to separate chloride, bromide, sulfate and iodide. Tests were performed on new and used ("aged") columns.

### 2.1. Instrumentation

The equipment used for this work was a DX-300 gradient ion chromatographic system (Dionex, Sunnyvale, CA, USA). The separated components were detected by a pulsed electrochemical detector (PED) in the conductivity mode (10  $\mu$ S range). An AMMS-II micro membrane suppressor system was used for chemical suppression. The AMMS-II was continuously regenerated with 12.5 mM sulfuric acid at a flow-rate of 4–6 ml/min. Integration was per-

formed by an HP 3396A integrator (Hewlett-Packard) and by CLAS/2000 (Chromatography Laboratory Automation Software, Perkin-Elmer). Columns used for separation were an AS9-SC analytical column (250  $\times$  4 mm I.D.) and an AG9-SC guard column (50  $\times$  4 mm I.D.). The AS9-SC analytical column has selectivity and performance identical with those of the AS9 but with added features to improve efficiency and solvent compatibility, and has an ion-exchange capacity of ca. 30  $\mu$ equiv. per column [5].

### 2.2. Reagents

All reagents were of analytical-reagent grade (Merck, Darmstadt, Germany). Deionized water (18 M $\Omega$ ) from a Milli-Q water-purification system (Millipore) was employed throughout.

### 2.3. Calibration standards

Stock standard solutions were prepared for each anion separately by dissolving salts in deionized water. Mixed anion working standard solutions for calibration were prepared every month from the stock standard solutions. Calibration graphs were constructed for analyte concentrations up to 10 ppm of bromide, sulfate and iodide. The ratio of chloride to bromide was 130:1 in all calibration standard solutions.

### 2.4. Ion chromatographic conditions

The injection volume was 25  $\mu$ l. The eluent used for separation was 3 mM Na<sub>2</sub>CO<sub>3</sub> at a flow-rate of 2 ml/min. The expected background conductivity was 13–15  $\mu$ S and the system pressure was normally 1200–1400 p.s.i.

### 2.5. Sample preparation

All samples were filtered through a 0.45- $\mu$ m filter and diluted with deionized water (18 M $\Omega$ ) so that the expected analyte concentrations were within the calibration range. To prevent column contamination by liquid hydrocarbons, the di-

luted samples were filtered through OnGuard RP cartridges before injection.

### 3. Results and discussion

Experiments have shown that it is possible to achieve good separations of chloride–bromide and sulfate–iodide using new columns. As eluents we tested  $\text{Na}_2\text{CO}_3$  and various combinations of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ .

One of the weak points of the column is the rapid decrease in capacity of the AS9-SC (decrease in retention times with time). Maybe this is caused by components of the water samples, which cannot be removed by column clean-up procedures (the use of the AS9-SC column is possible only in the pH range 2–11, so strong acidic or basic clean-up solutions cannot be used).

With  $\text{Na}_2\text{CO}_3$  as eluent it is possible to achieve a good separation of sulfate–iodide with “aged” columns and the separation of chloride–bromide is acceptable. Fig. 1 shows the chromatograms of an anion standard solution containing 1000 ppm chloride, 7.7 ppm bromide, 4.9 ppm sulfate and 9.1 ppm iodide, separated on a new and an “aged” column. Between the two runs shown in Fig. 1 ca. 300 analytical runs were carried out, representing the “ageing”. As the decrease in retention times proceeds (when the retention time of iodide reaches <40% of the initial value), the determination of bromide is only possible when there is no large excess of chloride. Hence eventually the column becomes unusable for our application.

With  $\text{Na}_2\text{CO}_3$ – $\text{NaHCO}_3$  mixtures as eluent it is not always possible to separate sulfate–iodide satisfactorily, depending on the eluent and the column condition. In the worst case the two anions cannot be separated at all. Fig. 2 shows the separation of an anion standard solution on an “aged” AS9-SC column (after ca. 200 analytical runs) using different eluents (the concentrations of anions in the standard solution were the same as in Fig. 1).

Fig. 3 shows two chromatograms of liquid samples taken during an open hole test at an

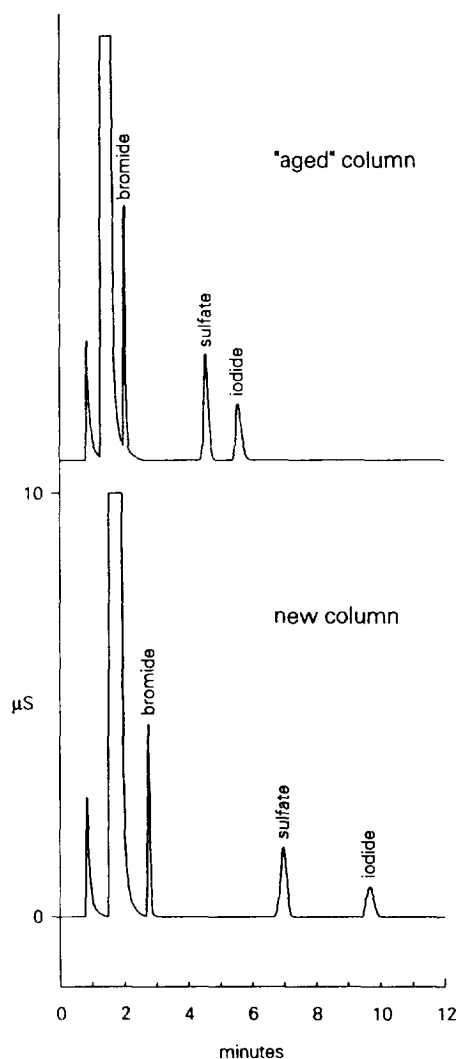


Fig. 1. Separation of anions in a standard solution (chloride to bromide ratio = 130:1) using the IonPac AS9-SC and AG9-SC columns with 3 mM  $\text{Na}_2\text{CO}_3$  as eluent, with new and “aged” columns.

exploration well. The filtrate of the drilling mud contains organic acids and chloride as major anions and the concentration of bromide and iodide is <2 ppm. The water sample shows, compared with the analysed drilling mud filtrate, a lower content of organic acids and an enhanced chloride content; the concentrations of the analytes are 68.2 ppm bromide and 23.4 ppm iodide. The sample was diluted 1:20.

Fig. 4 shows the chromatogram of a water

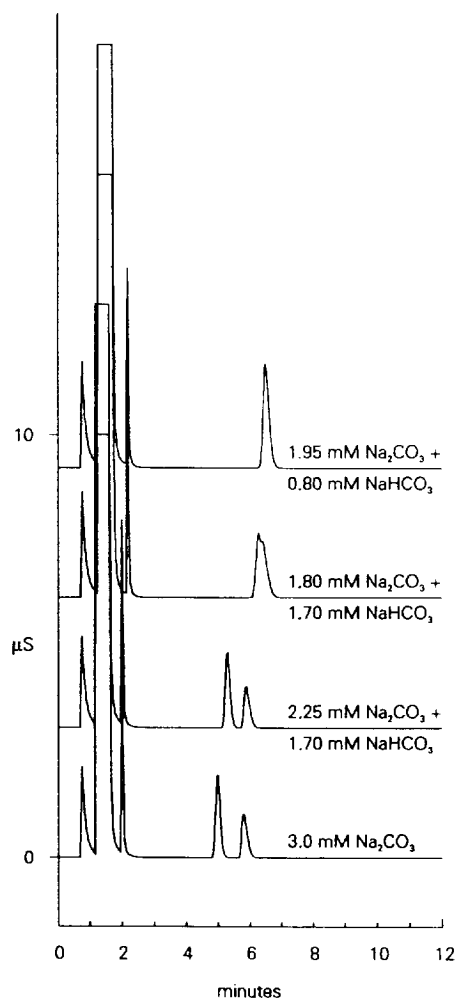


Fig. 2. Separation of anions in a standard solution (chloride to bromide ratio = 130:1) using "aged" IonPac AS9-SC and AG9-SC columns with various mixtures of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  as eluent.

sample from a gas well containing 17 650 ppm chloride, 28.1 ppm bromide, 590 ppm sulfate and 15.1 ppm iodide. The sample was diluted 1:25. The ratio of chloride to bromide is ca. 630:1.

Generally it is also possible to determine other anions in various aqueous solutions with our separation method. Depending on the sample matrix, quantification is not always easy. Fig. 5 shows a chromatogram of an anion standard solution, obtained with 3 mM  $\text{Na}_2\text{CO}_3$  as eluent. The analyte concentrations in this solution were

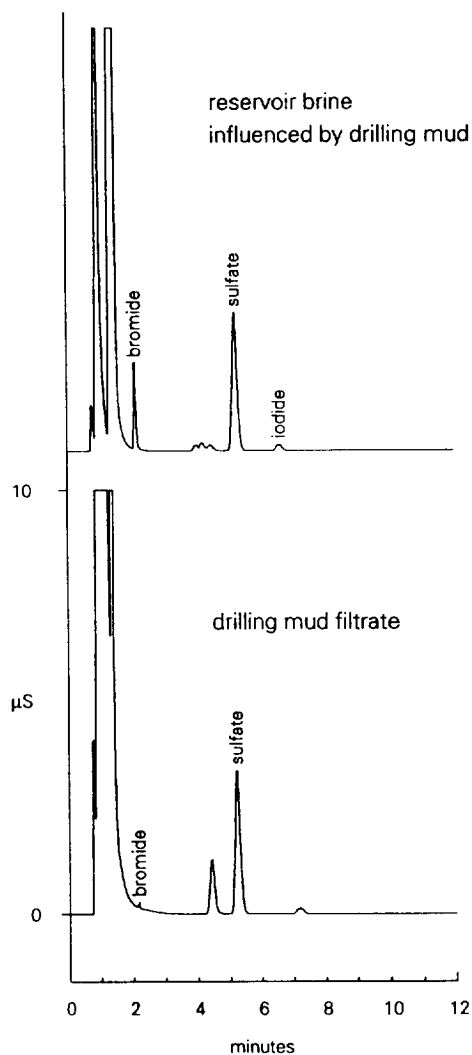


Fig. 3. Separation of anions in aqueous samples from an open hole test using the IonPac AS9-SC and AG9-SC columns with 3 mM  $\text{Na}_2\text{CO}_3$  as eluent.

1.9 ppm fluoride, 3.2 ppm chloride, 3.5 ppm nitrite, 5.1 ppm bromide, 3.7 ppm nitrate, 3.5 ppm orthophosphate, 4.2 ppm sulfate, 10.0 ppm iodide, 6.6 ppm oxalate, 9.9 ppm thiocyanate and 5.2 ppm thiosulfate. For separation of phosphate–hydrogensulfide and sulfite–sulfate, a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  should be used as the result. The presence of tartrate in the water sample would enhance the sulfate content (co-elution of these two anions). Fluoride and

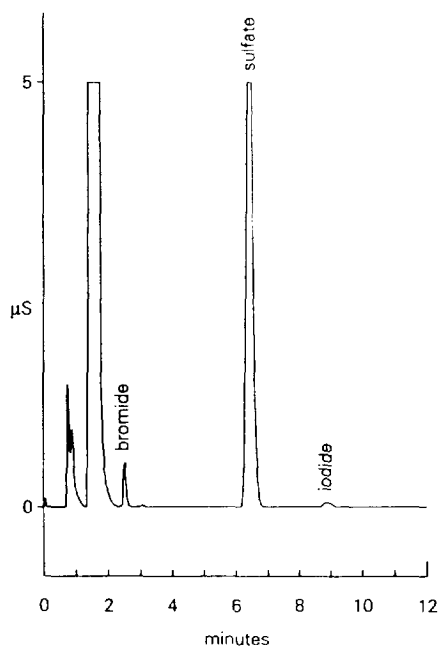


Fig. 4. Separation of anions in a water sample from a gas well (chloride to bromide ratio = 630:1) using the IonPac AS9-SC and AG9-SC columns with 3 mM  $\text{Na}_2\text{CO}_3$  as eluent.

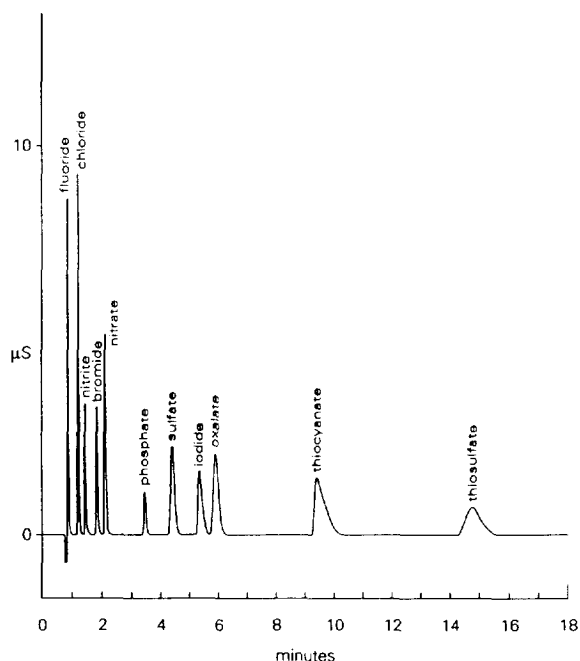


Fig. 5. Separation of anions in an anion standard solution using "aged" IonPac AS9-SC and AG9-SC columns with 3 mM  $\text{Na}_2\text{CO}_3$  as eluent.

small carboxylic acids (formate, acetate, propionate, butyrate) elute near the front and should not be determined using the AS9-SC column. The separation of these anions should be performed on an IonPac AS10 column with  $\text{Na}_2\text{B}_4\text{O}_7$  as eluent [6].

#### 4. Conclusion

The described method for the separation of anions on an IonPac AS9-SC column with 3 mM  $\text{NaCO}_3$  as eluent is useful for the determination of bromide, sulfate and iodide in oilfield waters and in other aqueous solutions. The detection limits are 0.1 ppm for bromide and sulfate and 0.2 ppm for iodide. With an optimized system the determination of bromide is possible even when the chloride to bromide ratio is up to 1000:1. The determination of sulfate and iodide is not dependent on the chloride excess and can be performed without analytical problems. Other anions, such as nitrate, oxalate, phthalate, thiocyanate and thiosulfate, can also be determined. Weak points of the method are the rapid loss of capacity, resulting in decreasing retention times and incomplete resolution of chloride–bromide, and the pH sensitivity of the AS9-SC column.

#### References

- [1] APHA. AWWA and WPCF, *Standard Methods for the Examination of Water and Waste Water*, American Public Health Association, Washington, DC, 12th ed., 1965.
- [2] *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung*, Verlag Chemie, Weinheim, 1960.
- [3] *Dionex Application Note 3: Determination of Tracer Ions in Oilfield Drilling Fluids and Geological Brines*, Dionex, Sunnyvale, CA, 1987.
- [4] J. Weiss, *Ionenchromatographie*, VCH, Weinheim, 2nd ed., 1991.
- [5] *Installation Instructions and Troubleshooting Guide for the IonPac AG9-SC Guard Column and the IonPac AS9-SC Analytical Column*, Dionex, Sunnyvale, CA, 1992.
- [6] R. Kadnar and J. Rieder, *J. Chromatogr.*, in press.