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Determination of alkali and alkaline earth metals in oilfield waters by ion chromatography

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Abstract

Inherent with the production of crude oil and natural gas, large amounts of water are also produced. This water has to be analyzed to deduce the correct geological formation. Extensive analyses of these highly saline waters are also necessary in connection with water flooding projects or in solving problems of scaling or corrosion. The main interest is often the analysis of anions or cations. Cation analysis is focused on alkali and alkaline-earth ions, plus ammonium. Columns for the simultaneous separation of mono- and divalent cations in one run by ion chromatography (IC) are now available. In analyzing high salinity produced water, one of the problems is the very different concentration ranges of the different analytes. For example, the concentration of lithium or barium is in the low ppm range while the concentration of sodium can be 10 000 ppm or higher. In recent years, we have tested two different separation columns (IonPac CS10 and CS12A) in our laboratory to study the possibility of an alternate IC-based method for the determination of the cations mentioned above. © 1998 Elsevier Science B.V.

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1. Introduction

Formation water normally is a highly saline brine of a composition typical for each geological formation. The major component is sodium chloride, mostly at concentrations higher than 10 000 ppm. To characterise these water samples a lot of different anions and cations have to be analyzed. Anions of interest are sulfate, bromide and iodide which can be measured by ion chromatography (IC) in a single run [1], and also chloride and hydrogencarbonate.

Cations of interest are alkali and alkaline earth ions, ammonium and iron. These ions are normally determined by flame atomic absorption spectrometry (AAS) in our laboratory; higher contents of calcium and magnesium being determined by complexomet-

ric titration. For the determination of ammonium, several colorimetric methods can be used or an acid–base titration is performed after a steam distillation.

A few years ago a column for amine separation (IonPac CS10) was tested in our laboratory. This column is also useful for the separation of mono- and divalent cations [2] using hydrochloric acid (HCl) or combinations of hydrochloric acid and DL-2,3-diaminopropionic acid (DAP) as eluent. This prompted us to start some investigations as to whether IC could offer an alternative to our standard laboratory methods. Later we extended our experiments using the IonPac CS12A separation column which offers the possibility of separating the mentioned cations (without iron) using sulfuric acid (H₂SO₄) or methanesulfonic acid (MSA) as eluent [3].

2. Experimental

2.1. Instrumentation

The equipment used for this work was a DX-300 gradient IC system (Dionex, Sunnyvale, CA, USA). The separated components were detected by suppressed conductivity using pulsed electrochemical detection (PED) in the conductivity mode. A micro membrane suppressor system CMMS-II was used for chemical suppression. The CMMS-II was continuously regenerated by 100 mM tetrabutylammonium hydroxide (TBAOH) solution at a flow-rate of 8–10 ml/min. Later, a cation self-regenerating suppressor, CSRS-I, was used in the autosuppression recycle mode. Integration was performed by an HP 3396A integrator (Hewlett–Packard) or by AI-450 software (Dionex). Method specific equipment and chromatographic conditions are summarized in Table 1. Columns used for separation were IonPac CS10 and CS12A (250×4 mm) separator columns with IonPac CG10 and CG12A (50×4 mm) guard columns.

2.2. Reagents

All reagents used were of analytical reagent grade from Merck, Darmstadt, Germany; TBAOH solution 40% from Riedel-de Haen, Seelze, Germany; DAP

from Fluka, Buchs, Switzerland. Deionized water (18 MΩ) obtained from a Milli-Q water purification system (Millipore) was employed throughout.

2.3. Calibration standards

Stock standard solutions (1 g l⁻¹) were either from Merck, or were prepared separately for each cation by dissolving salts in deionized water. Cation working standard mixtures for calibration were prepared every month from the stock standard solutions.

Evaluation was carried out by calibration curves up to concentrations of 3 ppm for lithium and 15 ppm for the other cations.

2.4. Ion chromatographic conditions

Injection volume was 25 μl. Method specific conditions are listed in Table 1.

2.5. Sample preparation

All samples were filtered through 0.45 μm filters and diluted with deionized water (18 MΩ), so analyte concentrations were within the calibration range. To prevent column contamination by liquid hydrocarbons, diluted samples were filtered through OnGuard RP cartridges before injection.

Table 1
Method specific equipment and chromatographic conditions

Parameter	Method 1	Method 2	Method 3	Method 4
IC System	DX-300 gradient chromatography system (Dionex)			
Detector	Pulsed electrochemical detector used in the conductivity mode			
Injection volume	25 μl			
Separation column	CS10	CS10	CS10	CS12A
Guard column	CG10	CG10	CG10	CG12A
Eluent	40 mM HCl	40 mM HCl 4 mM DAP	22 mM H ₂ SO ₄	11 mM H ₂ SO ₄
Eluent flow-rate (ml min ⁻¹)	1	0.9	1	1
Background Conductivity (μS)	<3		<2	
System Pressure (p.s.i.)	1200–1400			
Suppressor	CMMS-II		CSRS-I	
Regeneration	100 mM TBAOH		Autosuppression recycle mode	
Regenerant flow Rate (ml/min)	8–10	10		
Integration	HP 3396A Integrator		AI-450 software	

Table 2
Determination of ammonium in water samples

Sample	TDS (mg l ⁻¹)	Na:NH ₄ ratio	NH ₄ (titration) (mg l ⁻¹)	NH ₄ (IC-CS10) (mg l ⁻¹)
DST sample 1	185 000	400	147.3	152.6
DST sample 2	185 000	400	147.1	145.3
Formation water 1	26 000	120	83.2	81.4
Formation water 2	18 000	140	51.3	55.4
Formation water 3	21 000	130	62.8	64.3
Water treatment plant inlet	22 500	125	65.2	66.0
Water treatment plant outlet	22 500	125	68.1	66.0

3. Results and discussion

3.1. Method 1

Initial experiments have shown that it is possible to achieve good separation of the monovalent cations lithium, sodium, ammonium and potassium in water samples using IonPac CS10 as the separation column and hydrochloric acid as eluent. The separation was very good even where the ratio of sodium to ammonium was 100:1 or higher. Quantification is possible within short analysis times. The results are comparable to those of our standard laboratory methods. Some results are summarized in Table 2 (ammonium) and Table 3 (potassium).

Fig. 1 shows the chromatograms of two liquid samples from a drill stem test (DST) and the corresponding standard cation solution. DST sample 1 was a reservoir brine containing 5.5 ppm lithium, 58 170 ppm sodium, 147 ppm ammonium and 1353 ppm potassium. DST sample 2 consists of reservoir brine and potassium chloride-based drilling mud which contains 3.2 ppm lithium, 33 570 ppm sodium, 65 ppm ammonium and 7980 ppm potassium.

An eluent flow-rate of 1.5 ml min⁻¹ was initially employed. After reducing the flow-rate to 0.9–1 ml min⁻¹ it was easier to suppress conductivity and to obtain a more stable baseline. Alkaline earth metals were not eluted by hydrochloric acid.

3.2. Method 2

Following the installation manual of the IonPac CS10 we tried to use mixtures of hydrochloric acid and diaminopropionic acid as eluent for the elution of alkali, ammonium and alkaline earth ions in one

Table 3
Determination of potassium in water samples

Sample	TDS (mg l ⁻¹)	Na:K ratio	K (AAS) (mg l ⁻¹)	K (IC-CS10) (mg l ⁻¹)
Formation water 1	26 500	160	61.8	63.7
Formation water 2	18 000	150	46.8	47.9
Formation water 3	21 000	150	53.1	55.3
Injection water 1	22 500	100	84.8	83.7
Injection water 2	22 500	100	84.7	83.8
Injection water 3	22 500	100	84.3	83.1

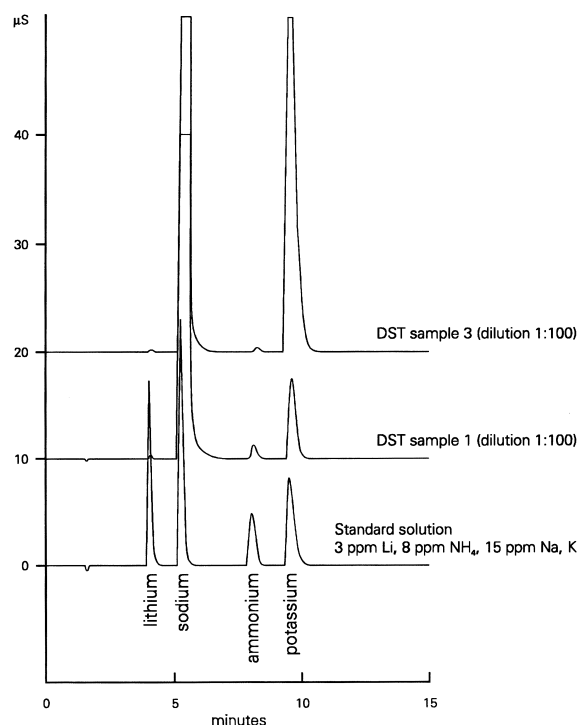


Fig. 1. Separation of alkali ions in water samples by IonPac CS10+CG10 with 40 mM HCl as eluent (Method 1).

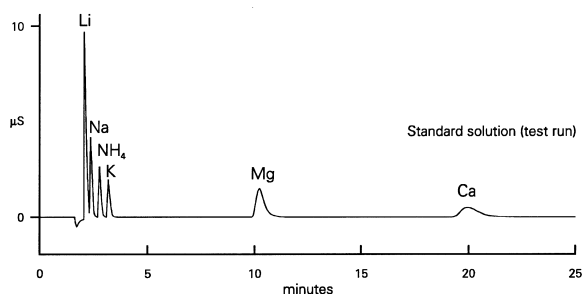


Fig. 2. Separation of alkali and alkaline earth ions by IonPac CS10+CG10 with 40 mM HCl–4 mM DAP as eluent (Method 2).

isocratic run. This method allowed the determination of calcium and magnesium, but analysis time was very high and the resolution of alkali ions was poor when compared to method 1. The method was therefore not useful for brines. Fig. 2 shows the test run of a standard cation solution.

The following experiments were performed with gradient programs. Using TBAOH for the regeneration of the CMMS-II it was not possible to get a constant baseline or to reduce background conductivity to the expected value. Experiments were deemed unsuccessful and stopped.

3.3. Method 3

After the expansion of our system with a PC and the AI-450 software and the substitution of our CMMS-II by a CSRS-I, a new series of experiments for the separation of cations was started. Method 3 is a modification of method 1, using the mentioned equipment and sulfuric acid as eluent as it is recommended to use no HCl-containing eluents in combination with the CSRS-I in the autosuppression recycle mode [4]. Separation is comparable to method 1, but the peak form shows more tailing. Fig. 3 is a test chromatogram of a standard cation solution.

3.4. Method 4

The separation column IonPac CS12A can be used with H_2SO_4 or MSA as eluent. We started experiments with H_2SO_4 in various concentrations which resulted in method 4. With this method it is possible to separate alkali and alkaline earth ions, ammonium and manganese in one single isocratic run. If the analyte concentrations are in the same range, no

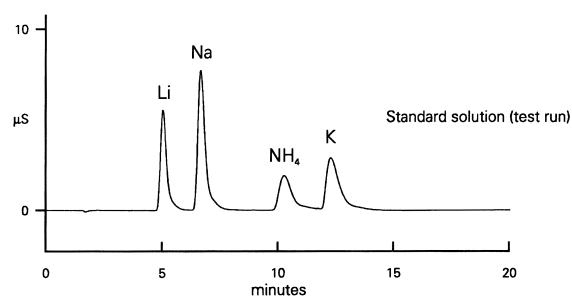


Fig. 3. Separation of alkali ions by IonPac CS10+CG10 with 22 mM H_2SO_4 as eluent (Method 3).

problems are expected and quantification is easy.

The analysis of highly saline brines can cause some problems. The high excess of sodium leads to insufficient resolution of sodium and ammonium which complicates the evaluation of the chromatograms. It is necessary to prepare matrix matched calibration standard solutions to get correct results, especially for ammonium. The very different concentration range of the analytes requires the performance of analytical runs from various dilutions of each sample. Thus, quantification was a time-consuming process. The results for lithium, potassium, strontium and barium are comparable to those from flame AAS. The results for sodium, magnesium and calcium were not reproducible. Depending on the sodium excess, the quantification of ammonium is nearly impossible.

Fig. 4 shows chromatograms of different dilutions of a formation water sample which contains 1.0 ppm lithium, 9 700 ppm sodium, 98 ppm ammonium, 63 ppm potassium, 85 ppm magnesium, 152 ppm calcium, 17.6 ppm strontium, 1.0 ppm barium, and a standard cation solution.

On the other hand the method is very useful for a quick semi-quantitative cation screening which is helpful e.g. for classification of aqueous samples from exploration or production wells or other water samples.

The brochure 'Dionex Solutions for Increased Productivity', Ref. [5], describes the gradient separation of cations in oilfield waters using the IonPac CS12A separation column. In the future, it will need to be verified if gradient programs in combination with this column can offer a better resolution of sodium and ammonium without characteristic increase of analysis time.

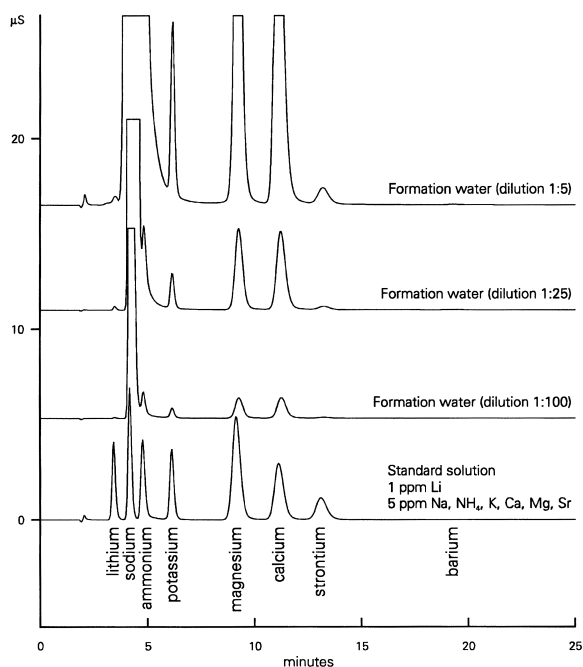


Fig. 4. Separation of alkali and alkaline earth ions in water samples by IonPac CS12A+CG12A with 11 mM H_2SO_4 as eluent (Method 4).

4. Conclusions

Alkali ions and ammonium can be analyzed with the IonPac CS10 separation column using HCl or H_2SO_4 as eluent in brines as well as in any other

kind of water. The results are comparable with results from other methods.

The experiments with DAP-containing eluents and gradient programs (to make separation of alkali and alkaline earth ions possible in one run) were not successful.

IC can be used as an alternative method for the determination of alkali and alkaline earth ions, using an IonPac CS12A as the separation column and H_2SO_4 as eluent, if the analytes are in the same concentration range.

The analysis of highly saline brines is possible but time consuming. Quantification of NH_4 is difficult at high sodium excess.

On the other hand the method is very useful for a quick semi-quantitative cation screening. Gradient separation of cations in oilfield waters requires further investigations.

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