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Determination of inorganic ions in oil field waters by single-column ion chromatography

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Abstract

A new method to determine inorganic ions in oil field water by single-column ion chromatography is presented. On an anion-bonded column, using a mixture of sodium benzoate (1.5 mM) and sodium citrate (0.1 mM) as eluent, the Cl^- , NO_3^- and SO_4^{2-} in oil field water can be determined. On a cation-bonded column, using 1.5 mM HNO_3 as eluent, the Na^+ and K^+ in oil field water can be determined. If a mixture of oxalic acid and ethylene diamine (both at 1.5 mM) is used as the eluent, then Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} can be determined. If the content of Cl^- and Na^+ is much higher than that of other inorganic ions, the sample may be diluted to allow the determination of these ions. The proposed method is characterized by its simplicity, rapidity and accuracy. The results match those obtained with the current procedures used in oil fields. © 1997 Elsevier Science B.V.

Keywords: Oil field waters; Inorganic ions

1. Introduction

Oil and gas reservoirs are often accompanied by formation water. In the exploration and development of oil and gas, the analysis of water samples (formation waters and injection waters) is very important. The composition and content of inorganic ions in formation water can furnish important information about the geological structure of the oil field. During the recovery of petroleum, control of the content of some ions (e.g. SO_4^{2-}) can prevent a chemical reaction between it and other ions (e.g. Sr^{2+} , Ba^{2+}) taking place in formation water and can also prevent the formation of precipitate, which causes the plugging of the oil-bearing stratum. In the process of surfactant flooding to enhance oil recovery, the existence of excess salts or polyvalent metal ions can

cause serious deterioration of the flooding system's properties [1].

In the past, for the determination of inorganic ions, gravimetric methods, photometry and atomic absorption spectrophotometry [2] were the common methods used. These methods can analyse only one species of ion per operation. Also, the water sample has to be pretreated to avoid the influence of other ions on the determination, so these methods are laborious and time-consuming. Small et al. [3] and Gjerde and Fritz [4] suggested the use of two column and single column ion chromatography, respectively, and their methods are an effective way of analysing inorganic ions in water samples. Recently, Kadnar and Rieder [5] studied the determination of anions in oil field water using two column ion chromatography. In this article, a single column ion chromatographic method for the determination of both anions and cations in oil field water is described.

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2. Experimental

2.1. Instrumentation

A Waters ILC-1 Ion Liquid Chromatograph, with a Model 590 programmable solvent delivery system and a Model 430 conductivity detector, was used in this work. The column (100×4.6 mm I.D.) was slurry packed with a laboratory-made silica-based chemical-bonded stationary phase (5 μm).

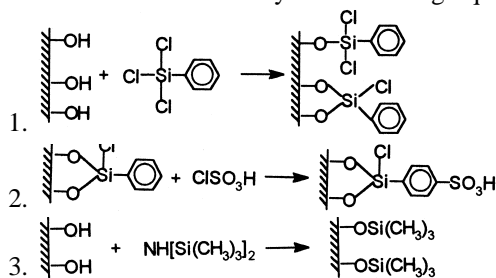
2.2. Reagents

Phenyl trichlorosilane, chemically pure, was from Chen Guang Chemical Plant (China) and chemically pure γ -chloropropyl triethoxy silane was from the Gai Xian Chemical Plant (China). Other chemicals were analytically pure reagents from the Shanghai Chemical Reagent Factory, China.

2.3. Preparation of stationary phases

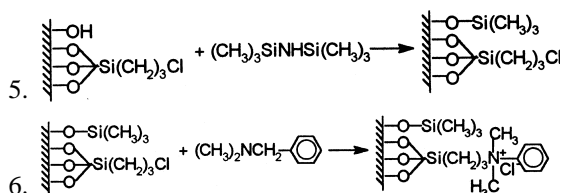
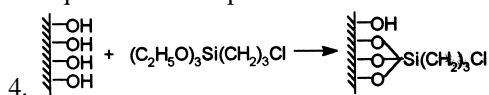
2.3.1. Cation stationary phase

Micro silica beads, phenyl trichlorosilane, chlorosulfonic acid and hexamethyl disilazane were used as the main materials. The required phase was synthesized through chemical bonding, sulfonation and deactivation as shown by the following equations:



2.3.2. Anion stationary phase

Micro silica beads, γ -chloropropyl triethoxy silane, hexamethyl disilazane and N,N-dimethyl benzylamine were used for the synthesis of the required phase. The chemical bonding, deactivation and quarternisation processes are as follows:



2.4. Ion chromatographic conditions

The injection volume was 25 μl. The eluent used for anion analysis was a mixture of sodium benzoate (0.1 mM) and sodium citrate (0.1 mM). The eluent for alkali earth metal separation was a mixture of oxalic acid and ethylene diamine (both 1.5 mM). Nitric acid (1.5 mM) was used for the separation of alkali metal ions. The flow-rate was 1.5 ml min⁻¹.

3. Results and discussion

3.1. Separation of standard sample

Standard anion solutions were prepared by dissolving sodium salts of different acids in deionized water, while standard cation solutions were prepared by dissolving their nitrates in deionized water.

Using selected chromatographic conditions, good separation of inorganic ions can be obtained. Using a mixture of sodium benzoate (0.5 mM) and sodium citrate (0.1 mM) as the eluent, six common inorganic anions (H₂PO₄⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻ and SO₄²⁻) were well separated within 15 min on an anion-exchange column. The theoretical plate number, as determined with SO₄²⁻, was 33 000/m. On the cation exchange column, the theoretical plate number, as determined with Ca²⁺, was 31 000/m. The complete separation of the alkali metal ions, Li⁺, Na⁺ and K⁺, was obtained within 12 min when 1.5 mM nitric acid was used as eluent. Very good separation of the alkali earth metal ions, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺, was achieved within 9 min when an aqueous solution of oxalic acid and ethylene diamine (both at 1.5 mM) was used as the eluent. These separations are shown in Fig. 1a–c and the detection limits of some ions are shown in Table 1.

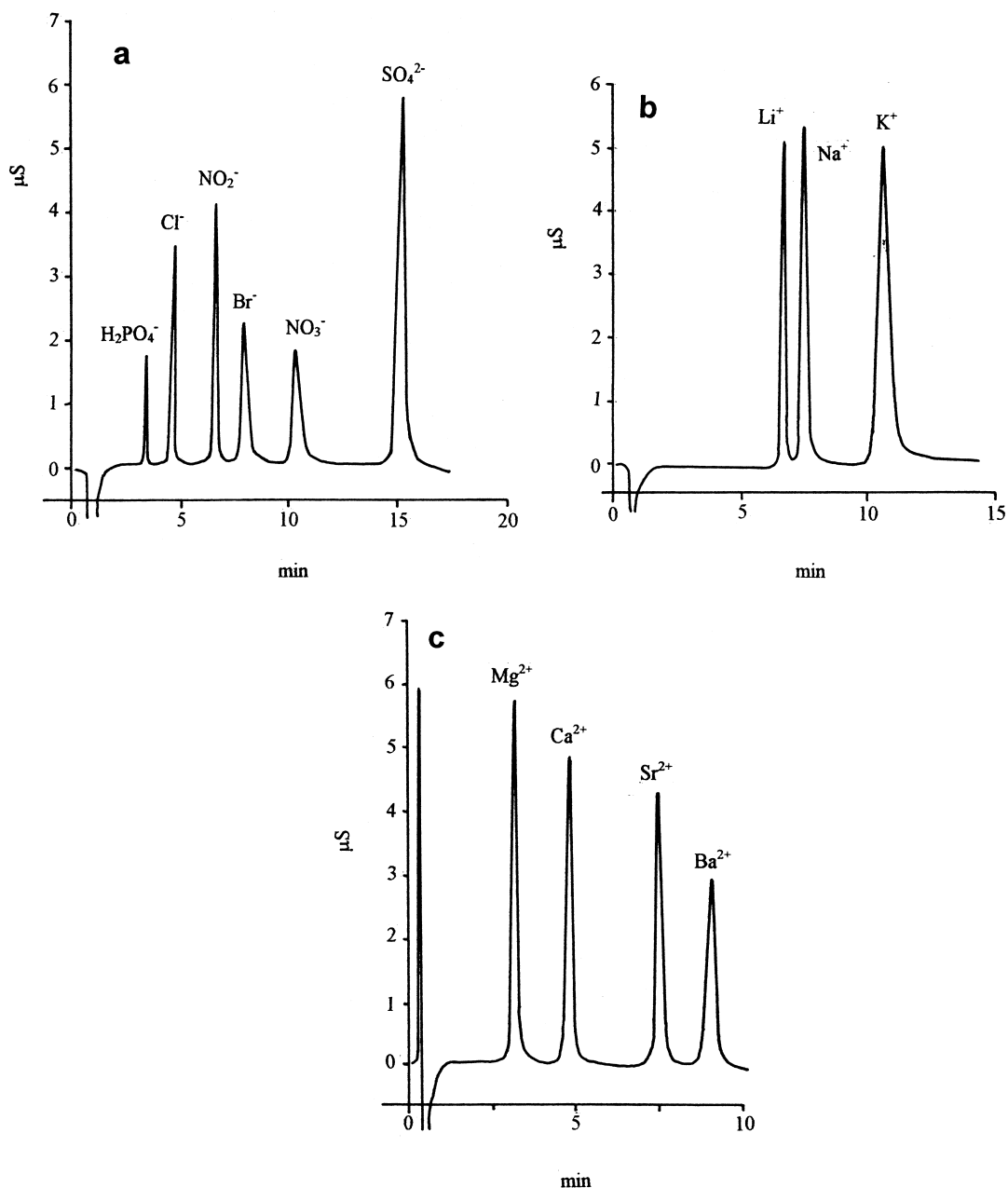


Fig. 1. Separation of inorganic ions in a standard mixture: (a) Anion separation. The eluent used was a mixture of sodium benzoate (0.5 mM) and sodium citrate (0.1 mM); (b) alkali metal ion separation. The eluent used was 0.1 mM HNO_3 ; (c) alkali earth metal separation. The eluent used was a mixture of oxalic acid and ethylene diamine (both at 1.5 mM).

3.2. Analysis of an actual sample

Fig. 2 shows the ion chromatogram of an oil field water sample. It can be seen from the chromatogram

that the Cl^- content in oil field water is much higher than that of other anions, also, the content of the alkali metal Na^+ is much higher than that of K^+ . This is the reason that a single operation cannot be

Table 1
Detection limit of some ions (ppm)

Ion	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Detection limit	0.5	2.0	1.0	2.0	3.0	0.1	0.2

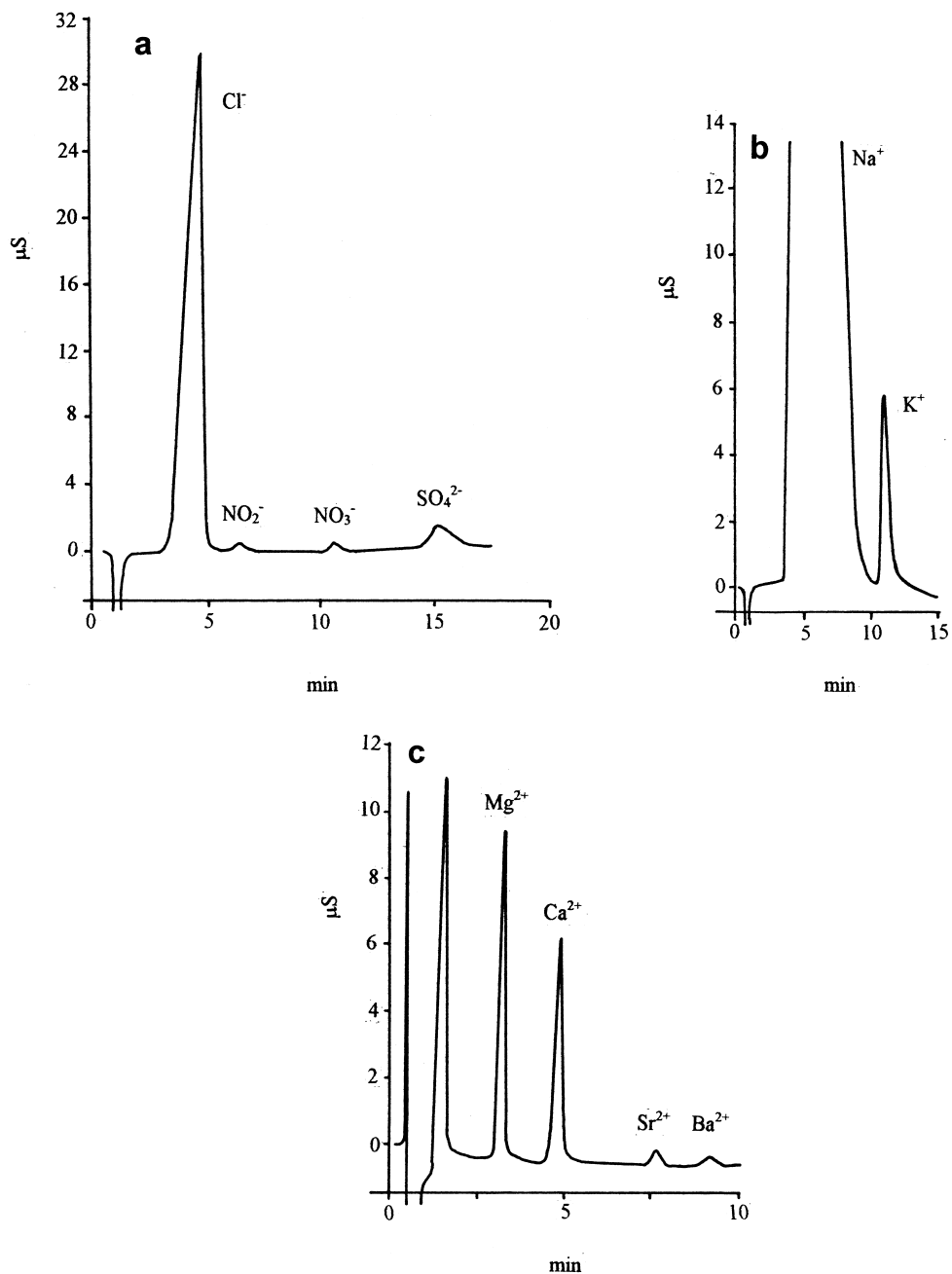


Fig. 2. Separation of inorganic ions in oil field water: (a) Anion separation; (b) alkali metal ion separation; (c) alkali earth metal ion separation. Chromatographic conditions: as in Fig. 1a–c, respectively.

Table 2
Analysis of the anion content in oil field water (ppm)^a

Water sample	Cl ⁻	NO ₃ ⁻	NO ₂ ⁻	SO ₄ ²⁻
K-13	1.93·10 ⁴ (1.89·10 ⁴)	1.90·10 ³	1.23·10 ³	2.43·10 ³ (2.35·10 ³)
P-2	9.68·10 ⁴ (9.34·10 ⁴)	1.25·10 ³	9.82·10 ²	1.67·10 ³ (1.66·10 ³)

^a Values in parentheses were determined by the volumetric method.

Table 3
Na⁺ and K⁺ content in oil field water (ppm)

Water sample	IC		Volumetric method
	Na ⁺	K ⁺	Na ⁺
G-185	2.25·10 ³	7.3	2.27·10 ³
G-406	3.75·10 ³	323	4.97·10 ³

used to separate and determine both inorganic anions and alkali metal ions. In order to solve this problem, a two-step operation is adopted to quantitatively determine anion and alkali metals in oil field water. At first, the original water sample is used to measure the anion of low content and K⁺, then the sample is diluted with deionized water for the determination of Cl⁻ and Na⁺. The expected result is obtained. Tables 2–4 show the analytical results obtained for inorganic anions and cations in the oil field water sample and from a few oil wells. The linear range and standard deviation ($n=5$) of some of the ions determined are as follows: Na⁺, 1–300 mg/l, 1.1%; K⁺, 3–400 mg/l; Mg²⁺, 4–400 mg/l; Ca²⁺, 0.5–400 mg/l, 3.0%; Cl⁻, 0.2–700 mg/l, 1.4%; NO₂⁻, 0.4–700 mg/l, 2.7%; NO₃⁻, 1.2–800 mg/l, 2.3% and SO₄²⁻, 1.0–800 mg/l, 1.1%. In order to check the reliability of our method, the inorganic ions in oil field water were determined using the volumetric analysis method that is used in the oil field from

Table 4
Analysis of alkali earth metals in oil field water (ppm)^a

Water sample	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
H-181	84 (80)	63 (60)	19 (17)	15 (14)
H-184	55 (50)	88 (89)	21 (20)	17 (16)

^a Values in parentheses were determined by the volumetric method.

which the water samples were taken. Results are also reported in Table 3 and in brackets in Tables 2 and 4. It can be seen that the results obtained using both methods are basically identical, showing the feasibility of using single column ion chromatography for the analysis of inorganic ions in oil field water.

4. Conclusion

The use of single column ion chromatography for the determination of inorganic ions in oil field water was established. Using this method, the content of Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ in oil field water was determined. The results obtained were fundamentally identical to that obtained using the methods in current use in oil fields. The proposed method has the advantage of being rapid, sensitive and selective. Its chief drawback is that the determination of CO₃²⁻ and HCO₃⁻, which have to be ascertained in oil field water, is still difficult.

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