

APPLICATION OF ION CHROMATOGRAPHY IN OILFIELD WATER ANALYSIS

TATJANA TOMIĆ, NADA UZORINAC NASIPAK

INA – Industrija nafte d.d., Zagreb, Croatia

e-mail: tatjana.tomic@ina.hr

Ion chromatography is a powerful tool for oilfield water sample analysis. Replacement of the classic analytical methods leads to the use of smaller sample content, faster analysis and getting multiple informations in a single analysis. In oil industry we can find numerous ion chromatography uses, some of which are connected to oil investigations and some to ecological demands and sustainable development. Oilfield waters are complex matrices with lots of artificial added substances and every sample demands specific approach. By combining anion separation and detection with proper sample preparation, determination of usual (F^- , Cl^- , NO_2^- , NO_3^- , Br^- , SO_4^{2-} , PO_4^{3-}) anions in oilfield water samples can be achieved.

Key words: ion chromatography, oilfield water, anion analysis.

Primjena ionske kromatografije u analizi voda prisutnih pri proizvodnji nafte. Ionska je kromatografija moćna tehnika pri analizi voda prisutnih pri proizvodnji nafte. Zamjenom klasičnih analitičkih metoda potrebna je manja količina uzorka za analizu, analize su brže, a pri jednoj analizi se dobivaju višestruki podaci. U naftnoj industriji mogu se naći brojne primjene ionske kromatografije, od koji su neke povezane s naftnim istraživanjima, a neke s ekološkim zahtjevima i održivim razvojem. Vode koje se javljaju pri proizvodnji nafte su kompleksni uzorci s mnoštvom umjetno dodanih komponenti te stoga svaki uzorak zahtjeva poseban pristup. Kombinacijom razdvajanja i detektiranja aniona s odgovarajućom pripremom uzorka može se postići određivanje uobičajenih aniona (F^- , Cl^- , NO_2^- , NO_3^- , Br^- , SO_4^{2-} , PO_4^{3-}) u uzorcima voda prisutnih pri proizvodnji nafte.

Ključne riječi; ionska kromatografija, vode prisutne pri proizvodnji nafte, analiza aniona.

INTRODUCTION

In oil wells water can origin from different sources: it can be inherent like a part of oil production layer, can be present in discrete horizontal sediment or can penetrate in a rock from outside. [1] When pressure is not high enough for production in oil producing well, secondary methods are used in order to increase recovery from an oil bed. In order to do so water is injected into a reservoir to pressurize and displace hydrocarbons to producing wells. [2]

Oilfield water investigation is done for two main reasons [3]:

1. qualitative determination of some or few ions in water, which geologists can use in identifying mineral constitution because oilfield water samples like crude oil are typical for their corresponding geological formation
2. quantitative determination of particular ion concentration aimed at classifying the water sample

Oilfield water samples can be divided in next categories:

- formation water – water that occurs naturally within the pores of a rock
- connate water – water trapped in the pores of a rock as it was formed. The chemistry of connate water can change in terms of composition throughout the history of the rock. Connate water can be dense and saline compared with seawater. Formation water in contrast is simply water found in the pore spaces of a rock and might not have been present when the rock was formed. Connate water is also described as fossil water
- sedimentary water – used as injection water in order to increase recovery from an oil bed. Composition is similar to formation water but with oilfield chemicals included
- brine – saline liquid usually used in completion operations and, increasingly, when penetrating a pay zone. Brines are preferred because they have higher densities than fresh water. Classes of brines include chloride brines (calcium and sodium), bromides and formates
- injection water – water injected into a reservoir to pressurize and displace hydrocarbons to producing wells. Injection water is also used in water-storage operations in offshore and remote locations with economic and environmental constraints. Sedimentary water is used usually as injection water in order to increase recovery from an oil bed

The significance of oilfield water analyses is characterization of water produced together with oil, quality check of injection water, prediction of corrosion rate, prediction of scale formation rate, monitoring of chemicals used for the water treatment, analytical backup for projects in oil industry and ecological demands [4].

For single anion analysis various classical analytical methods (volumetry, gravimetry) have been used [5]. Recently ion chromatography has been used as an alternative method for both anion [6] and cation determination [7].

Benefit of ion chromatography is simultaneous determination of all main anions and cations, small sample volume, short analysis time, fast and reproducible quantification and low consumption of chemicals and energy.

Main analytical problems in IC oilfield water analysis are the following: high chloride contents, separation of chloride and nitrate, presence of organics – hydrocarbons, oils and fats and interference of artificial added compounds.

Solutions to these problems are sample filtration to remove insoluble particles (e.g. 0.45 μm cellulose filters), dilution to bring analytes into working range, multiple analysis to cover all important ion determinations, use of OnGuard Ag/H cartridges to easily remove chloride, bromide and iodide from concentrated matrices or OnGuard II P cartridges to remove organic matter.

In this paper IC anion analysis of oilfield water samples under specific conditions is presented. Each sample was treated separately under specific working conditions. Detection has been performed by conductivity detector.

EXPERIMENTAL

Chemicals and standards

In ion chromatography analyses the mobile phases are set by eluent generator cartridge filled with potassium hydroxide (KOH) and with deionised water (18 M Ω) obtained from TKA Pacific/Gen Pure water purification system (TKA Water Purification Systems GmbH, Germany). The mobile phase ion strength is set by the computer program. A commercial standard solution of 7 anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻, Br⁻, SO₄²⁻, PO₄³⁻) was used as a stock solution for calibration.

IC procedure

IC measurements were performed on Dionex ICS 3000 modular ion chromatography system comprising high pressure pump, eluent generator module filled with KOH cartridge, IonPac AG 19 guard column and IonPac AS 19 analytical column, suppressor and conductivity detector. Flow rate was set on 1.0 mL/min, temperature of column department was set at 30 °C and of detector department was set at 20 °C. For data processing Chromeleon software from Dionex was used.

RESULTS AND DISCUSSION

In this paper analysis of oilfield water samples (formation and sediment water) and surface water samples near oil production well is described. Before chromatographic analysis of oilfield water it is essential to know water origin and possible contaminant substances (eg. organics, additives) because that strongly affects on sample preparation for analysis.

Calibration

Method calibration was performed by external standard method and for calibration stock standard solution was diluted to appropriate concentrations. The calibration graphs were constructed with six calibration points. All calibration curve should have regression coefficient above 0,99.

Sample preparation

All samples were filtered through a 0,45 μ m regenerated cellulose membrane filter and their conductivities were measured to check if it is necessary to dilute them with deionised water (18 M Ω). By sample dilution expected analyte concentration was within the calibration range. Sometimes, multiple analyses are needed to cover all important ion determinations. To prevent column contamination by hydrocarbons, samples were filtered through OnGuard RP cartridge before injection. If sample has high chloride content, it can be filtered through the OnGuard Ag/H cartridges which easily remove chloride, bromide and iodide from concentrated matrices. All those ions can be later determined in non filtered sample.

Formation water analysis

By formation water analyses both qualitative and quantitative data were observed. By qualitative analysis some conclusion about mineral rock constitution from which water originates can be made and by quantitative analysis ion concentration can be determinate in order to classify water sample. Chromatographic analysis must be optimized to achieve

optimal run time, good selectivity and resolution. Here, a great problem is the complex matrix especially if it is the case of sea oil well formation water which has great

amount of chloride (Figure 1.). Multiple injections must be performed to make determination of all important ions possible.

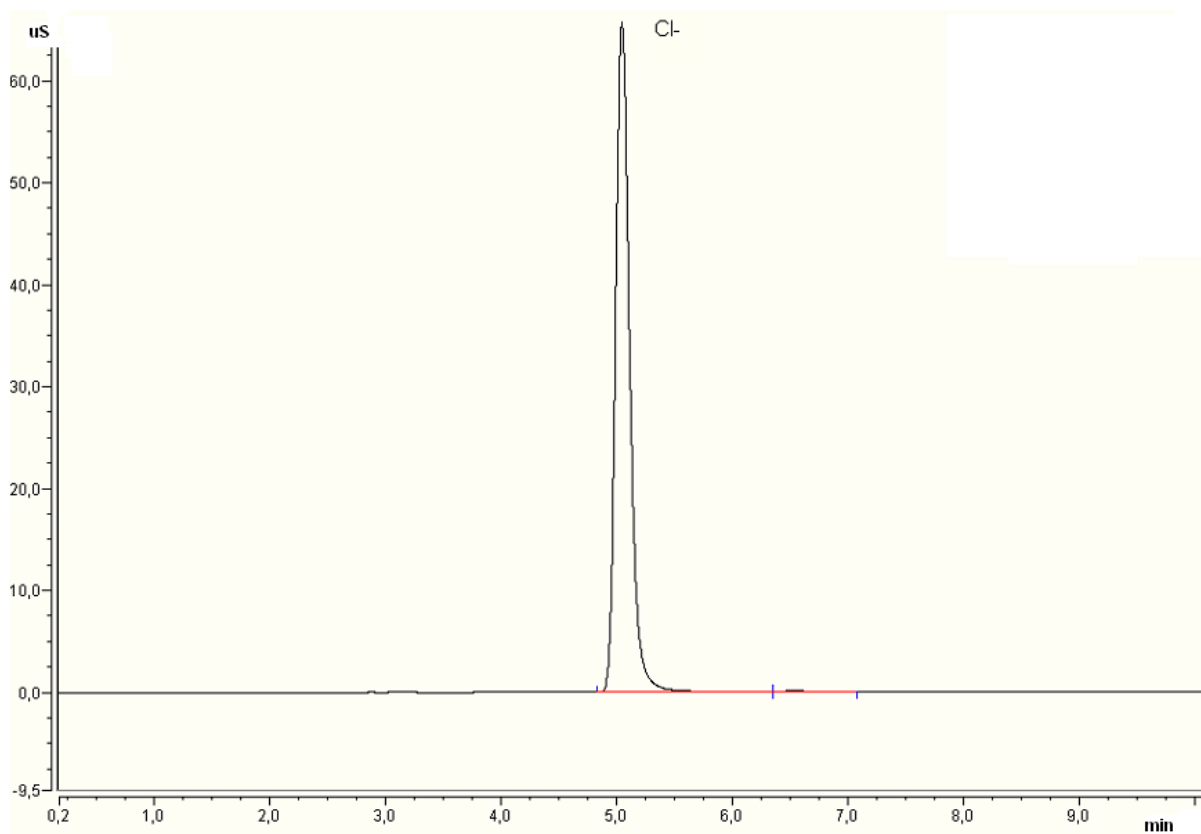


Figure 1. Separation of anions in sea oil well formation water

Slika 1. Razdvajanje aniona u formacijskoj vodi iz morske naftne bušotine

Formation water sample was first diluted 1000 times because sample has very high conductivity and injected without removing chloride ions. In this analysis all

other present ions were in field of baseline and they couldn't be detected. To remove chloride ions, sample was filtered through the OnGuard Ag/H cartridge (Figure 2).

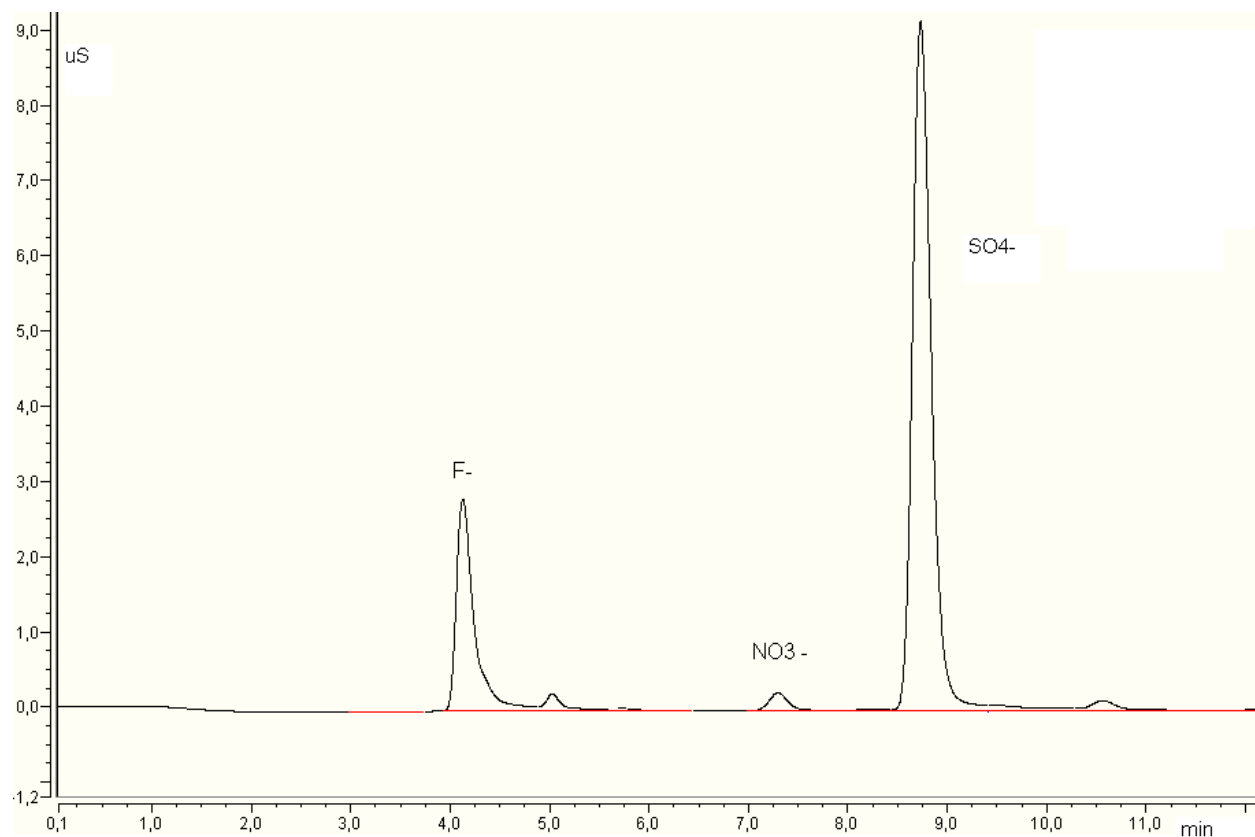


Figure 2. Separation of anions in sea oil well formation water, chloride ions removed
Slika 2. Razdvajanje aniona u formacijskoj vodi iz morske naftne bušotine, kloridni ioni uklonjeni

By removing chloride ions fluoride, nitrate and sulphate anions were detected

and by quantification following results were observed (Table 1):

Table 1. Anion determination in formation water

Tablica 1. Određivanje aniona u formacijskoj vodi

ion	Concentration (mg/L)
F ⁻	10,5
Cl ⁻	10421
NO ₃ ⁻	48,0
SO ₄ ²⁻	161

Sedimentary water analysis

Sedimentary water samples didn't have such a great amount of chloride comparing to other ions but still had high conductivity and was diluted. It contained artificial added compounds such as corrosion and scale inhibitors, well treatment

chemicals and residues from drilling fluids, so before injection, sample was filtered through OnGuard RP cartridge.

To make analysis time shorter and to keep good resolution, gradient elution was used. By that, we achieved good separation between chloride and nitrite anions (Figure 3).

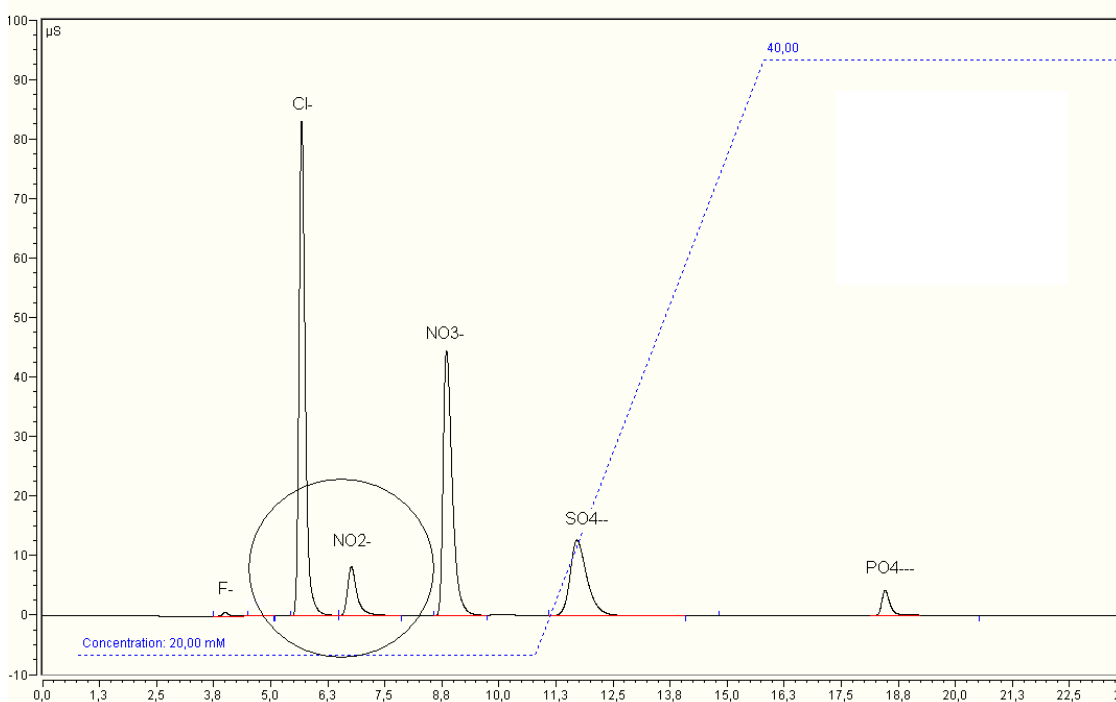


Figure 3. Separation of anions in sedimentary water

Slika 3. Razdvajanje aniona u sedimentnoj vodi

Surface water analysis

Near oil wells there are systems placed for collecting, shipping and transporting of oil and gas. All parts of oil production and transporting are possible pollutants and care must be taken to prevent both land and water contamination. One of the ways to prevent pollution is controlling

of surface waters near oil wells [8]. For that purpose analysis of different surface waters near oil wells from five locations in Croatia were performed (Figure 4.). It is necessary to perform analysis in as short time after sampling as possible to avoid sample decomposition. Anion analysis was performed by isocratic elution with 22 mM KOH.

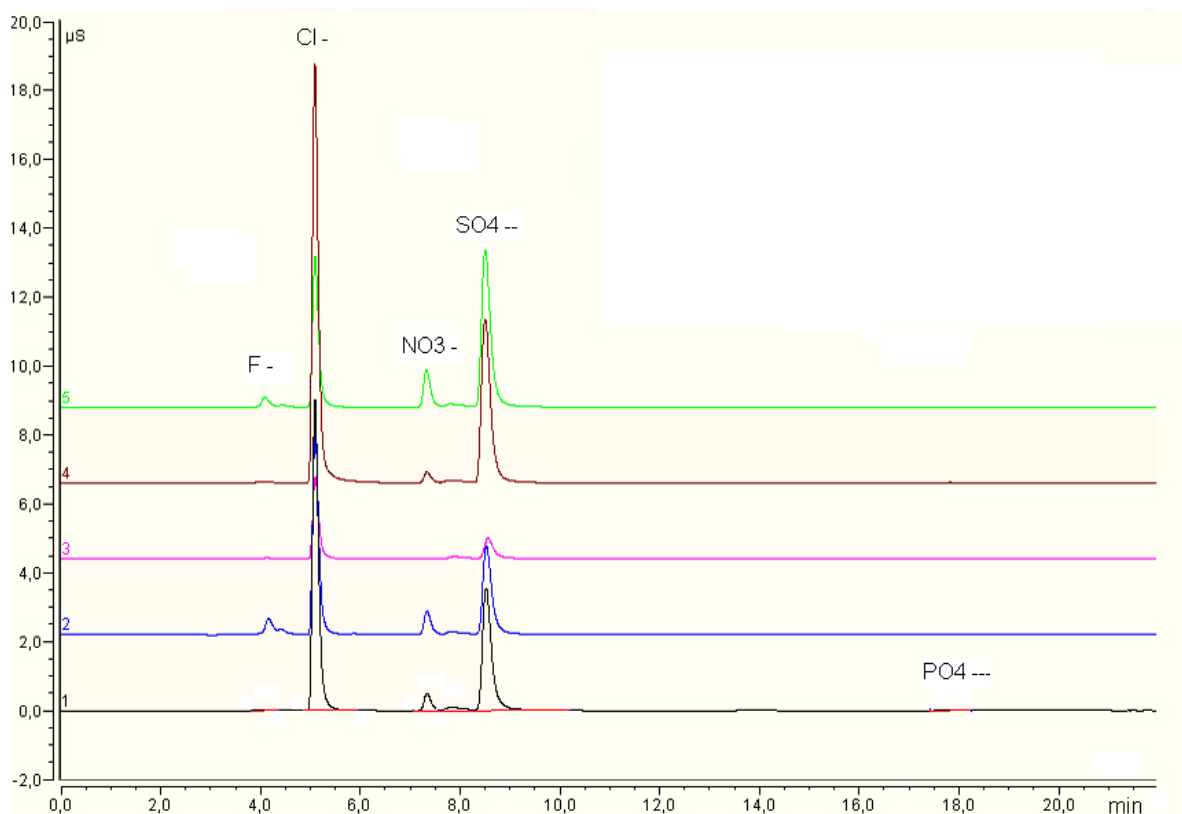


Figure 4. Anion analysis in 5 surface water samples
Slika 4. Analiza aniona u 5 uzoraka površinskih voda

CONCLUSION

This paper described ion chromatography method which is suitable for determination of chloride, nitrite, nitrate, sulfate and phosphate in oilfield waters and surface waters near oil wells. Anion separation was performed on IonPac AS19 (Dionex) column and with potassium hydroxide as eluent. With an optimized system good separation between chloride and nitrite ions was possible. To achieve optimal sample characterisation it is

necessary to know some data like sample conductivity and possible artificial added compounds.

If chloride content in sample is high by comparison with other present anions it should be removed from sample and determined separately. Gradient elution can be performed to shorten the analysis time. Weak point of method is sample instability because of bacterial activities and adsorption processes.

REFERENCES

1. M. Killer, Nafta 1(1951)11
2. E. Cerić, Nafta procesi i proizvodi, Zagreb, 2006
3. M. Killer, Nafta 7(1954)187
4. R. Kadnar, J. Rieder, J. Chromatogr. A 706(1995)301
5. P. E. Jackson, Ion chromatography in Environmental Analysis, Encyclopedia of Analytical Chemistry, 2779
6. HRN EN ISO 10304-1, Kakvoća vode - Određivanje otopljenih aniona ionskom tekućinskom kromatografijom-1. dio : Određivanje bromida, klorida, fluorida, nitrata, nitrita, fosfata i sulfata
7. HRN EN ISO 14911, Kakvoća vode - Određivanje otopljenih Li⁺, Na⁺, NH₄⁺, K⁺, Mn²⁺, Mg²⁺, Ca²⁺, Sr²⁺ i Ba²⁺ ionskom kromatografijom - Metoda za vode i otpadne vode
8. S. Radionov, D. Doležal, Međunarodni znanstveno-stručni skup o naftnom rudarstvu, Zadar, 30.09.-03.10.2003.; Knjiga sažetaka