Short communication

Determination of chloride, sulfate and nitrate in groundwater samples by ion chromatography

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Abstract

Groundwater is a significant source of water for both domestic and agricultural use in some regions of the Maracaibo lake basin in Venezuela. Chemically suppressed ion chromatography with a Dionex Model 2000i/sp, Ionpac AS11, ASRS-I system was used for the analysis of major inorganic anions in groundwater samples. About 50 samples of groundwater, taken over several months in three different locations, were analyzed after filtration and sometimes dilution. In all the samples, the separation between the peaks of chloride, nitrate and sulfate showed good resolution (symmetrical peaks, not broadened), even when the chloride concentration was as high as 850 mg l^{-1} and reproducibility (RSD) was ~2%. No other peaks (i.e. fluoride, nitrite and phosphate) were observed at selected experimental conditions. With the chosen parameters, the method is well-suited for the routine determination of these anions in groundwater samples, giving results in less than 10 min (including column clean-up). With an appropriate combination of detector output ranges (300 and 1000 μS), only one set of calibration solutions was needed for all samples. In the Sierra Maestra location, the groundwater samples, were significantly different in total anion levels. Mean total chloride plus sulfate concentrations (~525 mg l^{-1}) were about 100 times higher than in the other sites. Some water quality implications of these groundwater samples are also discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rain and snowmelt percolating down through the soil are the sources of groundwater. Water can move through rock formations like sandstone or through cracks in rocks; an area that holds a lot of water, is called an aquifer. Groundwater usually is in motion, flowing from upland areas of recharge to lower areas where it may discharge to a spring, a stream or other body of surface water. Water passing through the soil dissolves large amounts of carbon dioxide generated by soil microorganisms decomposing organic matter.

This carbon dioxide dissolves in soil moisture, producing carbonic acid solution that attacks carbonate and silicate minerals of calcium, magnesium, potassium and sodium, causing their solution. Groundwater stays in long contact with the surrounding rocks, which allows more time for chemical reactions to occur.

The normal components of clean groundwater may include: major constituents (i.e. chloride, calcium, magnesium, sodium, hydrogencarbonate, sulfate), greater than 5 mg l^{-1}; minor constituents (i.e. nitrate, potassium, fluoride, iron) in the interval 0.01–10.0 mg l^{-1}; and trace constituents (i.e. aluminium, arsenic, bromide, cadmium, chromium, copper, lead, manganese, nickel, . . .), in less than 0.1 mg l^{-1}. The

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levels of any specific chemicals considered objectionable depend on the use of the water. The drinking water standards have smaller recommended concentrations than the standard for agricultural water. Water with concentrations exceeding these limits would be considered polluted for that use.

Groundwater is contaminated by the movement of pollutants through an aquifer recharge zone into the aquifer. Pollutants percolate through a recharge zone which usually includes a soil layer. Although groundwater moves slowly, contaminants may travel long distances over long periods of time since little degradation or dilution takes place in the anaerobic groundwater environment. Some contaminant problems due to geography, geology or industrial location are unique to specific parts of the country. Principal sources of groundwater contamination are: industrial wastes, municipal landfills, agricultural chemicals, septic system and cesspool effluents, leaks from petroleum pipelines and storage tanks, animal wastes, acid mine drainage, oil field brines, saltwater intrusion and irrigation return flow.

About 40 million people in the USA depend on septic tanks or cesspools, and this same population relies on groundwater for drinking water; groundwater comprises 75–80% of the water used for agricultural irrigation [1]. In Venezuela, groundwater is a significant source of water for domestic, livestock and agricultural use inside some regions of the Maracaibo lake basin.

Although a wide variety of methods have been proposed for determination of anions in natural waters, few are rapid, sensitive, precise and relatively free of interferences, having lengthy procedures. Traditional methods used for the determination of nitrate, chloride and sulfate are either based on colorimetric methods which are subject to interferences from a variety of ions, require reductions and destillation, or require special analytical skill. Ion chromatography (IC) is becoming more and more popular for the analysis of environmental samples (i.e. [2–7]) and because of its high accuracy and reliability, chemically suppressed IC has recently been recognized by the US Environmental Protection Agency (EPA) as the method of choice for the determination of anions in natural waters.

In this paper the major inorganic anions (chloride, sulfate and nitrate) in groundwater samples of Maracaibo lake basin, were determinated in isocratic conditions by chemically suppressed IC. Some water quality implications are also discussed.

2. Experimental

2.1. Sampling

The groundwater samples were obtained during a year period, from three monitoring networks: one urban (Sierra Maestra), located within the city of Maracaibo (the capital of Zulia State with ~1.8 million inhabitants) and two rurals, located about 80 km (Pompey) and 115 km (Viateca) southwest of Maracaibo. An even areal distribution of the sampling positions has been aimed at. Water was pumped from the test wells with an all teflon pumping system. About 50 specimens were collected over several months in 1-l polyethylene bottles and immediately preserved with HPLC-grade $CHCl_3$ (3:500, v/v) after filtration and cooled to 4°C, in order to minimize biological degradation of the samples. Also, the same day of taken samples, groundwater pH was measured with a Fisher pHmeter calibrated with standard buffer solutions (Fisher) of pH 4.01 and pH 7.41 before and after each measurement.

2.2. Reagents

High-purity reagents were used throughout together with Milli-Q purified water, deionized and then filtered through a 0.2 μm Whatman membrane. Anion standard solutions were prepared using sodium salts of chloride (Riedel-De Haën, Seelze–Hannover, Germany), nitrate (Merck) and sulfate (Merck). All calibration standards and samples were preserved like wise.

2.3. Instrumentation and experimental conditions

All analyses were conducted on Dionex 2000i/sp ion chromatography equipment (Dionex, Sunnyvale, CA, USA), consisting of an isocratic pump, an anion pre-column (Dionex AG11, 4 mm), an anion separator column (Dionex AS11, 4 mm) coupled with an anion self-regenerating suppressor (ASRS-I,

4 mm), a Dionex 4400 integrator and a conductivity detector.

3. Results and discussion

3.1. Identification and quantification

The resolution of chloride, sulfate and nitrate using isocratic conditions with 21 m*M* NaOH as eluent and the analysis time for a mixed standard solution (peaks B and C) and a sample of ground-water (peak A) are shown in Fig. 1. As can be seen, the standard and unknown groundwater samples exhibit a well defined resolution and symmetrical peaks (not broadened) giving results in less than 10 min (including column clean-up). Peaks identification was based on retention times and standard

Fig. 1. Separation of chloride, nitrate and sulfate on a Dionex IonPac AS11 column. Injection volume was 10 μl and 21 m*M* NaOH as eluent. (A) Groundwater sample. Detector output range=300 μS. (B) Standard solution; peaks: 1=chloride (10 mg l^{-1}), 2=sulfate (5 mg l^{-1}) and 3=nitrate (5 mg l^{-1}). Detector output range=300 μS. (C) Standard solution. Same concentrations as in (B), but using a detector output range of 1000 μS.

addition, and no other peaks (i.e. F^-, NO_2^- and $H_2PO_4^-$) were observed at selected experimental conditions. Under the described conditions and using a mixed standard solution, a well resolution was obtained for fluoride and phosphate (see a very small first peak in the chromatogram A (groundwater sample), Fig. 1). Nitrite is not well resolved; however, it was possible to make an estimation of the minimum detectable concentration of this anion. The retention times for F^-, Cl^-, NO_2^-, SO_4^{-2}, NO_3^- and $H_2PO_4^-$ were: 1.71; 1.93; 2.06; 2.23; 2.55 and 3.54 respectively.

A set of calibration graphs for mixed standards with different concentration ranges (0.1–10 ppm) with a good linear regression (R^2=0.9996–1.0000) were used. The detection signal was registered as peak height (response counts). The chromatography calibration was obtained using four concentration levels of each anion. One of these was at a concentration near, but above, the minimum detectable concentration, and the other concentrations were as near as possible to the expected range of values found in real samples. The working calibration curve was verified daily by the measurement of the 5 ppm (SO_4^{2-}, NO_3^-) and 10 ppm (Cl^-) calibration standards. The minimum detectable concentration of an anion is a function of the sample injection size and the conductivity scale used. In this work, with a scale of 300 μS and a 10 μl sample loop, the minimum detectable concentration for Cl^-, SO_4^{2-} and NO_3^- was lower than 0.1 ppm, and lower than 0.1; 0.05 and 0.01 ppm for $H_2PO_4^-$, F^- and NO_2^- respectively. The detection limits were estimated based on three times standard deviation of peak height from ten determinations of lower standard solution used for each anion. The relative standard deviations (*n*=6) obtained for four groundwater samples and four standard solutions showed good reproducibility (RSD≈2%) for the analyzed anions.

In order to improve the performance of the ion chromatographic analysis, an appropriate combination of detector output ranges (300 and 1000 μS) was proved. Using a standard solution, it was found that the peak heights relationships (H_1/H_2) are equals to output ranges relationships ($\mu S_2/\mu S_1$) (see Table 1 and Fig. 1), with a relative error percentage less than 1%. The results show that the same concentrations obtained by suitable output ranges
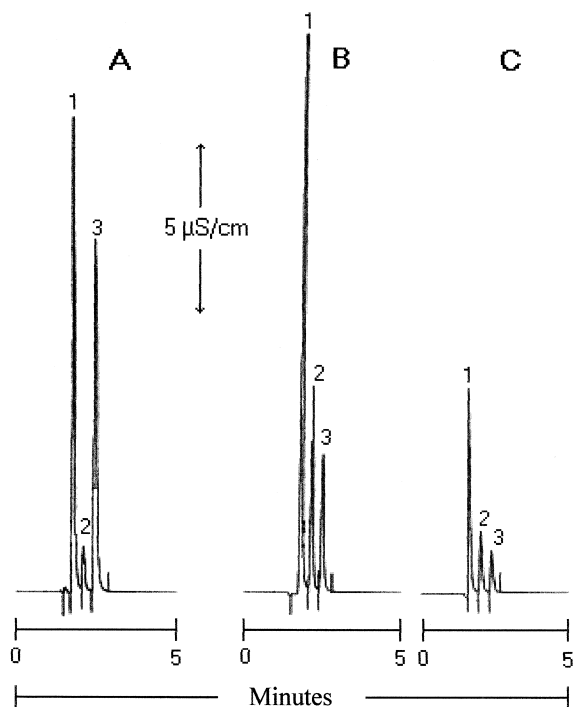
Table 1
Experimental conditions used for the successful ion chromatographic analysis of groundwater samples

Peak heights (H, counts) and concentration (C, mg l^{-1})			
	Cl^-	SO_4^{-2}	NO_3^-
Detector output ranges			
300 μS_1	303 947 (H_1)	91 789 (H_1)	60 933 (H_1)
	10 (C_1)[a]	5 (C_1)	5 (C_1)
1000 μS_2	909 891 (H_2)	27 709 (H_2)	18 421 (H_2)
	2.98 (C_2)[a]	1.51 (C_2)	1.52 (C_2)
H_1/H_2	3.34	3.31	3.31
$\mu S_2/\mu S_1$	3.33	3.33	3.33
$(\mu S_2/\mu S_1)/xC_2$ [b]	9.92	5.03	5.06

[a] C_1=standard solution used for check the working calibration curve with a scale of 300 μS. C_2=chromatogram registering concentration when a scale of 1000 μS is used.

[b] The equation $(\mu S_2/\mu S_1)/xC_2 = 3.33xC_2$ was used for the calculation of anion concentrations when the scale was 1000 μS.

give a similar relative error percentage (see Table 1). So, the analysis of major anions in the groundwater samples was much simpler and only one set of calibration solutions (The Dionex 4400 integrator was programmed using the working calibration curves and 300 μS as detector output range) was needed for all samples. The samples taken at Sierra Maestra always showed a higher salinity, owing to the proximity of the Lake Maracaibo, and they were always analyzed diluted (1:10 or 1:100).

3.2. Distribution of parameters

In order to evaluate the quality of groundwaters, an inorganic basic chemical analysis was done and the results are summarized in Table 2. Basic inorganic chemical analysis which is more widely spread than extended chemical analysis, includes only the main ions. However, trace constituents such as aluminium, arsenic, lead, iron, cadmium, ... are important to analyze. Only the anionic parameters were determined by ion chromatography.

At Sierra Maestra, the total ion concentrations (~1500 ppm) were about 100 times higher than in the other sites. It is often assumed that chloride in groundwater is dominantly derived from marine salts, either via (a) salts in precipitation, (b) leaching of fossil salts from the aquifer, or (c) intrusion of current (or fossil) sea water. The spatial distribution of chloride in groundwater (Table 2) shows a dominant importance of marine salts with the highest concentrations of several thousand mg l^{-1} occurring

in Sierra Maestra coastal location due to direct sea-water intrusion. In some way, the higher pH values observed at Sierra Maestra groundwaters are related to marine salts being leached out of overlying marine deposits, or to fossil (entrapped) sea-water in the bedrock aquifer.

Inland typical chloride concentrations (~6 ppm) were observed at Pompey and Viateca sites. At Sierra Maestra, the Cl/Na ratio was greater (~3 times) than sea-water ratio, suggesting possible lithological sources of Cl in this site.

At Pompey, it was found that Cl^-, NO_3^- and Na^+ exhibit a similar seasonal trend of concentrations with the highest values in the rainfall peak months of October–November and May. No similar trends were observed at the other sites. Studies done in Venezuela have found that significantly higher non-seasalt SO_4^{2-}, non-sea-salt Cl^-, NO_3^-, NH_4^+ and hydronium concentrations are deposited by precipitation in western Maracaibo lake [8,9]. Regional studies concerns the potential impact of acid rain deposition on groundwater resources are needed. In contrast, SO_4^{2-} concentrations and pH values not showed seasonal variation, probably reflecting rapid fixation of SO_4^{2-} by soil material and resultant low mobility down through the soil profile; and indicating a pH buffering mechanism within the aquifer.

3.3. Water quality implications

Table 2 summarizes the numbers of parameters exceed accepted Venezuelan drinking water norms. It

Table 2
Summary of basic chemical analysis of the groundwater samples and Venezuelan drinking water norms for some parameters of health-related or other significance[a]

Parameter	Mean concentrations (mg l^{-1} except where otherwise stated)[b]			
	Sierra Maestra ($n=13$)	Pompey ($n=16$)	Viateca ($n=16$)	Norm [10]
pH	6.97 (6.4–7.4)	4.93 (4.3–5.3)	5.31 (5.0–5.7)	6.5–8.5
Conductivity ($\mu S\ cm^{-1}$)	3037.2 (61–68)	34.1 (11–144)	37.6 (8–68)	
NO_3^- (IC)	24.2 (16–42)	5.6 (1.1–33.3)	2.9 (1.5–10.5)	45
NO_2^- (IC)	<0.01	<0.01	<0.01	0.03
Cl^- (IC)	821.6 (747–877)	4.9 (3.4–11.4)	7.5 (0.8–9.9)	250–300
SO_4^{-2} (IC)	100.9 (98–107)	1.1 (0.9–1.7)	0.5 (0.2–2.3)	250–500
$H_2PO_4^-$ (IC)	<0.1	<0.1	<0.1	
F^- (IC)	<0.05	<0.05	<0.05	0.8 1.5[d]
NH_4^+	0.2 (0.04–0.25)	0.1 (0.03–0.18)	0.1 (0.01–0.24)	
Na^+	151.6 (33–200)	2.3 (1.1–3.9)	4.1 (2.6–7.2)	200 (20–150)[d]
K^+	34.5 (18–58)	0.8 (0.2–3.0)	0.3 (0.2–1.0)	<12[d]
Ca^{+2}	187.5 (25–382)	1.0 (0.2–5.0)	0.7 (0.3–1.6)	15–25[d]
Mg^{+2}	145.5 (86–359)	0.6 (0.2–3.0)	0.3 (0.2–0.4)	<20[d]
Hardness ($CaCO_3$)	1075	5.0	3.0	250–500
Total dissolved solids[c]	1822	20.5	22.6	600–1000 (700–3000)[e] (3000–7000)[f]
SAR	2.0	0.5	1.0	(10–18)[e]

[a] IC, determined by ion chromatography; NH_4 (Selective electrode); Na and K (Atomic emission spectrometry); Ca and Mg (Atomic absorption spectrometry). SAR=Sodium adsorption ratio calculated using the equation: $SAR=Na/[(Ca+Mg)/2]^{1/2}$ where concentrations are given in equivalents per million. n=Number of samples.

[b] () values=Minimum and maximum values.

[c] Calculated using the equation: Conductivity×0.6.

[d] Norwegian drinking water norms [11].

[e] Irrigation crops recommended limits [10,12].

[f] Livestock recommended limits [10,12].

will immediately be seen that in all groundwater samples, no violations of norms for nitrate, fluoride, sulfate and sodium occur. None of the samples of groundwater from Viateca and Pompey aquifers exceeds maximum drinking water norms with respect to chloride, potassium, calcium, magnesium, hardness and total dissolved solids. These six parameters are known to exceed maximum norms in Sierra Maestra samples. Viateca and Pompey samples violate norms solely on the basis of pH with respect to Table 2 parameters.

According to recommended concentration limits for water used for livestock and irrigation crop production, none of the groundwater samples from the three aquifers violate the recommended limits established on the basis of total dissolved solids. The

very low values of sodium adsorption ratio (SAR) indicate that these groundwaters could to have an agricultural use non-representing a problem by sodium excess in the soil.

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