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Journal of Chromatography A, 804 (1998) 289–294

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Determination by ion chromatography of selected organic and inorganic acids in rainwater at Maracaibo, Venezuela

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Abstract

Chemically suppressed ion chromatography with a Dionex Model 2000i/sp, IonPac AS11, IonPac AG11, ASRS-I system was used for the analysis of major organic and inorganic acids in precipitation samples collected in the city of Maracaibo during a one-year period. Two different isocratic methods were used. First, inorganic (sulfuric, nitric and hydrochloric) acids were adequately determined by using 21 mM NaOH as eluent. Second, organic (formic and acetic) and hydrofluoric acids were determined by using 0.5 mM NaOH as eluent; however, occasional poor resolution of acetic and hydrofluoric acid peaks were obtained. The methods showed good reproducibility (R.S.D. ca. 5%) for primary inorganic anions plus formate and relatively poor reproducibility (R.S.D. ca. 15%) for fluoride plus acetate. In the Maracaibo rainwater system, the concentrations of the typical urban pollutants (SO_4^* , NO_3^- , Cl^* , H^+) are significantly larger than those found in Caracas precipitation, suggesting that Maracaibo is affected to a greater extent by air pollution. NO_3^- and Cl^- dominated the anionic composition. About 92% (as SO_4^*) and 50% (as Cl^*) of the total each ion concentration was represented by non-marine-derived species. Organic and inorganic anion balances showed that potential acid rain (volume-weighted average pH=5.35) in Maracaibo is mainly caused (ca. 90%) by sulfuric, nitric and hydrochloric acids. Only about 4% of the original acidity of the rainwater was found to be free acidity, indicating a high degree of neutralization in the Maracaibo precipitation. © 1998 Elsevier Science B.V.

Keywords: Water analysis; Environmental analysis; Acids; Inorganic anions

1. Introduction

Rainfall plays an important role in scavenging soluble compounds from the atmosphere. A useful index, therefore, for the pollution level of a site and the cycling of material through the atmosphere would be the chemical composition of its rainwater. Such studies have been carried out in India and relate to the estimation of major cations and inorganic anions for use in assessing air quality. At present,

anthropogenic, deposition (mainly sulfuric and nitric acids) and ecosystem acidification are two of the most serious environmental problems that industrialized nations are facing [1].

It is well known that the main cause of the increasing acidity of natural precipitation is the high emission levels of sulfur and nitrogen oxides, which are converted under atmospheric conditions into sulfuric and nitric acids. Additional anionic contributions to atmospheric pollution in the form of fluoride and chloride come from different industrial processes [2].

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Venezuelan rural areas are almost unaffected by regional air pollution; ‘natural’ acid rain (volume-weighted average pH values around or below 5.0) occur throughout Venezuela, and preliminary results have indicated that the acidity is due largely (>60%) to compounds (formic and acetic acids) other than sulfuric or nitric acids [3,4]. However, a serious potential drawback has recently arisen as a result of the intensive petroleum and petrochemical activities carried out in the Lake Maracaibo basin (Zulia State) in Venezuela. As a result, studies on the environmental impact of these activities are now in course, with special attention paid to the acidity of precipitation [5].

In the literature there are several reports on the use of ion chromatography (IC) in the determination of common anions such as Cl^- , NO_3^- , H_2PO_4^- , SO_4^{2-} , HCOO^- and CH_3COO^- in rainwater samples [2,6–9]. With high volume sample loops, the presence of a ‘water dip’ can interfere with the fluoride peak. So, to cover adequately all the common acids, a combination of gradient and isocratic methods has been developed [8].

The acids commonly found in precipitation-related samples as reported in the literature are sulfuric, nitric, hydrochloric, hydrofluoric, formic and acetic acids, in addition to propionic, lactic, glycolic, butyric, methane sulfonic, oxalic, hydroxymethylsulfonic, and nitrous. In this paper, the major organic and inorganic acids (formic, acetic, nitric, sulfuric, hydrochloric and hydrofluoric) in Maracaibo precipitation samples, were determined in isocratic conditions by chemically suppressed IC.

2. Experimental

2.1. Sampling

Rainfall samples ($n=44$) were collected manually and strictly by events using polyethylene bottles with wide polyethylene funnels from October 1995 to November 1996 at Maracaibo city. The collection system was kept completely closed (free from contamination) and was opened only at the beginning of a rainfall event. A fraction of the rain samples was immediately preserved with HPLC-grade CHCl_3 (3:500, v/v) in polyethylene bottles and cooled to

4°C after the rainfall to avoid biological degradation that could change the chemical composition of the rainwater. Rainwater pH was measured the same day of the rainfall event with a Fisher pH meter calibrated with standard buffer solutions (Fisher) of pH 4.01 and pH 7.41 before and after each measurement.

Maracaibo, the capital of Zulia State and the second largest city (≈ 1.8 million inhabitants), with medium-size industries such as a cement factory and an oil-fired electrical power plant, is located 10°34' N, 71°50' W, at 66 m altitude. The city is located on the west-shorelake of the strait of Maracaibo Lake and is relatively near to the industrial petrochemical complex El Tablazo, with large ammonia and chlorine plants. The annual mean precipitation is ≈ 490 mm (based on 30 years' data). The driest months are between December to March, with <6% of the total amount of rainfall. The climate is semi-arid and the annual mean temperature is $\approx 30^\circ\text{C}$.

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. Standard solutions of the organic acids (formic and acetic) were prepared from their sodium salts (certified A.C.S.; Fisher Scientific). Also the inorganic standard solutions were prepared using sodium salts of chloride (Riedel–De Haën, Seelze–Hannover, Germany), nitrate (Merck) and sulfate (Merck). A sodium fluoride standard $0.1000 \pm 0.0005 \text{ mol l}^{-1}$ per liter (NBS, Orion Research) was used. A stock solution of 1000 mg l^{-1} was prepared for each anion, and organic anions (formate and acetate) were preserved with HPLC-grade CHCl_3 (3:500, v/v). All calibration standards and samples were preserved likewise.

2.3. Instrumentation and procedure

All analysis were conducted on a Dionex 2000i/SP ion chromatography equipment (Dionex, Sunnyvale, CA, USA), consisting of an isocratic pump, two eluent switches (E_1 and E_2), an anion pre-column (Dionex AG11, 4-mm), an anion separator column

Table 1
Program for the separation of formate, acetate and fluoride

Time (min)	Event or action
0	Eluent run out (0.5 mM NaOH). Equilibration.
1	Load sample
1.5	Injection sample
6.5	Eluent change (42 mM NaOH) and data acquisition
15.5	Eluent change (0.5 mM NaOH). Re-equilibration.
30	End run and next injection sample

(Dionex AS11, 4-mm) coupled with an anion self-regenerating suppressor (ASRS-I, 4-mm), a Dionex 4400 integrator and a conductivity detector.

Two different isocratic methods were used. First: sulfuric, nitric and hydrochloric acids were adequately determined by using 21 mM NaOH as eluent (flow-rate 1 ml min⁻¹). Second: formic, acetic and hydrofluoric acids were determined by using 0.5 mM NaOH as eluent (flow-rate 1 ml min⁻¹). An eluent step change (using the switch E₂ of eluent 2) with 42 mM NaOH was used to quickly purge retained matrix components from the column; detailed program is shown in Table 1. An injection volume of 10 µl was used.

3. Results and discussion

3.1. Identification and quantification

The resolution of chloride, nitrate and sulfate using a first isocratic method with 21 mM NaOH as eluent and the analysis time for a mixed standard solution and a sample of rainfall are shown in Fig. 1. As can be seen, the standard and unknown rain sample exhibit a well defined resolution and symmetrical peaks (not broadened) giving results in less than 10 min (including column clean-up). However, fluoride, acetate and formate are co-eluted in peak 4. Chromatograms of a standard solution (fluoride, acetate and formate) and a rainwater sample using a second isocratic method with 0.5 mM NaOH as eluent are shown in Fig. 2. The results show a good resolution for formate, however fluoride and acetate are not always well resolved. Furthermore, using 0.1 and 0.2 mM NaOH as eluents, resulted in fluoride–acetate co-elution, a slight change in eluent concentration (0.5 mM NaOH) was

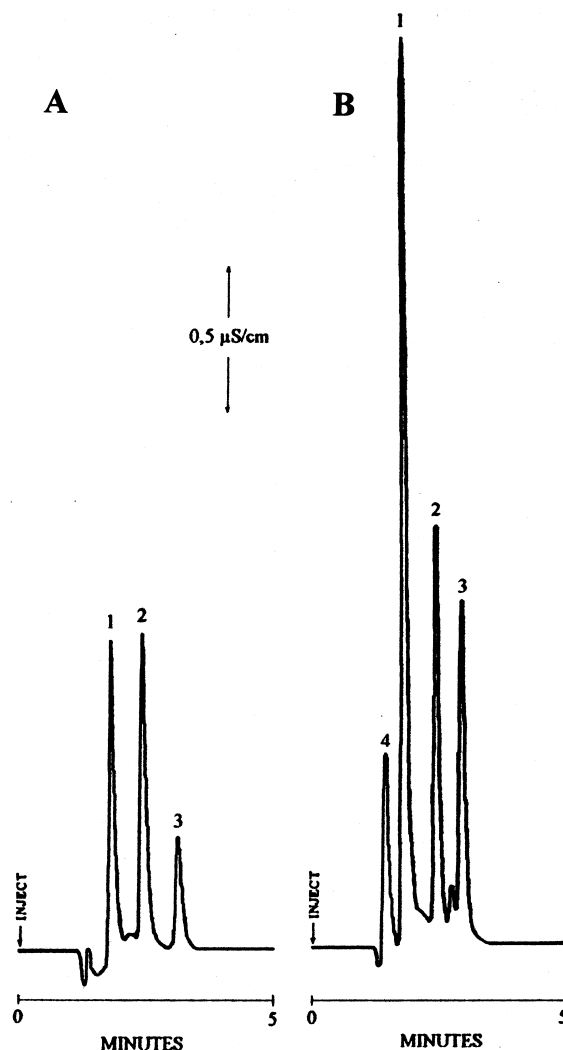


Fig. 1. Separation of hydrochloric, nitric and sulfuric acids on a Dionex IonPac AS11 column. Injection volume was 10 µl. (A) Standard solution; peaks: 1=chloride (0.5 mg l⁻¹), 2=nitrate (0.5 mg l⁻¹) and 3=sulfate (1.0 mg l⁻¹). (B) Rainfall sample; peak 4=Co-elution of fluoride, acetate and formate.

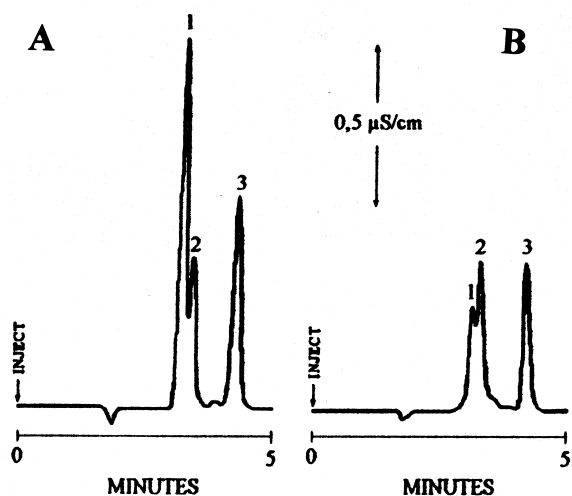


Fig. 2. Separation of hydrofluoric, acetic and formic acids on a Dionex IonPac AS11 column. Injection volume was 10 μl . (A) Standard solution; peaks: 1=fluoride (0.1 ppm), 2=acetate (0.5 ppm) and 3=formate (0.5 ppm). (B) Rainfall sample.

necessary to achieve a better resolution. Peaks identification was based on resolution times and standard addition.

A set of calibration graphs for mixed standards with different concentration ranges (0.2–6 ppm) with a good linear regression was used: Cl^- : $y = 95\,127x + 6\,193$ ($R^2 = 0.9996$); SO_4^{2-} : $y = 66\,166x - 10\,146$ ($R^2 = 0.9998$); NO_3^- : $y = 39\,648x - 1582$ ($R^2 = 0.9999$), where y =peak height (response counts) and x =concentration (ppm). The relative standard deviations ($n=6$) obtained for four rain samples and four standard solutions showed good reproducibility (R.S.D. \approx 5%) for primary chloride, nitrate, sulfate and formate and relatively poor reproducibility (R.S.D. \approx 15%) for fluoride plus acetate. The calculated detection limits for SO_4^{2-} , NO_3^- and Cl^- were lower than 1 μM ; HCOO^- (ca. 0.2 μM) and for CH_3COO^- and F^- the value was estimated at ca. 0.2 μM and ca. 0.05 μM , respectively.

3.2. Acidity-related anion concentrations

Solute concentrations generally are inversely related to the volume of rainwater falling during a storm. Computing volume-weighted average concentrations (VWACs) homogenizes the light rains, having relatively high concentrations, and heavy

rains, in which the constituents are more dilute. Volume-weighted average concentrations were calculated by [10]: $\text{VWAC}(x)_i = (\sum P_{ij}[x]_i)(\sum P_i)^{-1}$, where $[x]_i$ =concentration (μM) for the j th constituent in i th rain event and P_i =amount of rainfall i (mm). The volume-weighted average pH value was computed by converting each precipitation pH value to H^+ equivalents, entering these values into C_{ij} to obtain a volume-weighted average H^+ and converting to pH.

Non-marine or 'excess' sulfate and chloride (SO_4^* and Cl^*) concentrations were calculated, using Na^+ as reference and ratios of 0.12 and 1.17 (in μM) for $\text{SO}_4^{2-}/\text{Na}^+$ and Cl^-/Na^+ for the sea water composition respectively, by the formula [11]: $[x^*] = [x]_p - ([\text{Na}^+]_p)([x]/[\text{Na}^+]_{\text{sea water}})$, where the subscript p refers to precipitation concentration.

Volume-weighted mean concentrations and observed concentration ranges for major anions responsible for acidity of the rain are shown in Table 2. In general, the results indicate that Maracaibo precipitation is relatively concentrated in its anionic content. The relative contributions of the major anionic species show that NO_3^- and Cl^- dominated the anionic composition, comprising ca. 35% each on an equivalent basis. Sulfate (ca. 22%) follows as the next most abundant anion, while CH_3COO^- , HCOO^- and F^- appears only as trace constituents. Fluoride was the anion with lowest contribution (\approx 0.5%). Excess concentrations indicate that 92% (SO_4^*) and 50% (Cl^*) of the total of each anion concentration in Maracaibo rainfall was represented by non-marine-derived species (based on Na^+).

A comparison of our results with those obtained in

Table 2
Volume-weighted average concentrations (VWAC (μM))

	Range	VWAC (μM)
pH	(3.7–6.8)	5.3
H^+	(0.2–218.8)	4.5
SO_4^{2-}	(4.2–342.3)	28.3
SO_4^*	(1.0–337.7)	26.2
Cl^-	(5.9–256.8)	41.9
Cl^*	(<0–164.6)	21.4
NO_3^-	(2.7–506.6)	42.8
CH_3COO^-	(1.0–60.8)	7.7
HCOO^-	(0.003–21.4)	1.2
F^-	(0–4.7)	<0.7

$n=44$ event rains.

Caracas [12] (the capital of Venezuela with a high car density and very few industries compared with Maracaibo) and in Pasadena [13] (a zone highly contaminated in the Los Angeles Basin) is presented in Table 3. In the Maracaibo rainwater system, the concentrations of the typical urban pollutants (SO_4^* , NO_3^- , Cl^* and H^+) are significantly larger than in Caracas precipitation, suggesting that Maracaibo is more highly affected by air pollution. Cl^* concentrations found in Maracaibo rains are related to the emissions of Cl_2 from a chlorine plant located upwind at the El Tablazo Petrochemical Complex. Excess $[\text{SO}_4^{2-}]$ probably arises in precipitation by two processes: (1) oil fields, and anthropogenic combustion of fossil fuels containing sulfur, and (2) biogenic emissions of sulfur compounds. On the other hand, the excess $[\text{SO}_4^{2-}]$ may be attributable to long-range transport of sulfur pollutants (possibly from the Cardon–Amuay and Aruba–Curacao refineries). Maracaibo rainwater anion concentrations are lower than those found in Pasadena, where a high concentration of secondary pollutants is produced during photochemical smog formation.

3.3. Precipitation acidity

The observed pH of precipitation ranged between 3.7 and 6.8, i.e. acidic to \approx neutral (Table 2). The mean volume-weighted pH, 5.35, is well within the pH considered normal for rainfall. Original acidity of the rain is defined as: H_2SO_4 (SO_4^*/Σ Anions), HCl (Cl^*/Σ Anions), HNO_3 (NO_3^-/Σ Anions), HCOOH (HCOO^-/Σ Anions) and CH_3COOH ($\text{CH}_3\text{COO}^-/\Sigma$ Anions), where Σ Anions = $\text{SO}_4^* + \text{Cl}^* + \text{NO}_3^- + \text{HCOO}^- + \text{CH}_3\text{COO}^-$.

Table 4 summarizes the potential contributions of organic and inorganic acids to the free acidity. It is

Table 4

Organic and inorganic acids contribution to potential acidity of the Maracaibo rainfall

	HNO_3	H_2SO_4	HCl	CH_3COOH	HCOOH
%	42.8	26.2	21.9	7.7	1.4

observed that the maximum contribution of the inorganic acids is about 90%, mainly by HNO_3 (43%). The potential contribution of HCl (22%) to the free acidity is relatively high, gaseous HCl can be released to the atmosphere from marine NaCl aerosols after reaction with H_2SO_4 and/or HNO_3 . The $\text{H}^+ / (\text{NO}_3^- + \text{SO}_4^* + \text{Cl}^* + \text{HCOO}^- + \text{CH}_3\text{COO}^-)$ ratio equal to 0.037 indicates that in the Maracaibo rainfall, about 96% of the original acids have been neutralized by alkaline species. The emissions of NH_3 from the ammonia plant located at the El Tablazo Petrochemical Complex, and the alkalinity due to soil dust and cement plant emissions (metal carbonates and oxides) are the more important bases in the Maracaibo atmosphere.

Acknowledgements

The Council for Human and Scientific Development (CONDES) of the University of Zulia is thanked for its financial support; also we want to thank the Dionex Corporation for their help in carrying out this study. We thank Johan Mesa for experimental assistance during the work.

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Table 3

Weighted average anion concentrations and comparison with Caracas and Pasadena urban sites

	Maracaibo (μM)	Caracas (μM)	Pasadena (μM)
H^+	4.5	1.2	87.0
SO_4^*	26.2	11.1	57.0
Cl^*	21.9	1.8	0.1
NO_3^-	42.8	13.6	75.0
CH_3COO^-	7.7	8.5	–
HCOO^-	1.2	9.3	–

*=Non-marine concentration.

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