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## Determination of organic acids by ion chromatography in rain water in the State of Zulia, Venezuela

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Ion-exchange chromatography with a Dionex Model QIC system was used to identify and determine formic and acetic acid in event rains collected at the La Esperanza site (Zulia, Venezuela). Pyruvic acid was observed infrequently and always at very low concentrations. The method can be adapted for the routine determination of these acids, giving results in less than 12 min (only the chromatogram without column clean-up). A set of calibration graphs for mixed standards with different concentration ranges (0.5–80  $\mu\text{M}$ ) with a good linear regression ( $R^2 = 0.9992\text{--}1.0000$ ) were used. The estimated limit of quantification was  $<0.2 \mu\text{M}$  for both acids. Replicate analyses of four different fractions of a certain sample taken and preserved with chloroform showed relatively good reproducibility (R.S.D. *ca.* 7%) for both acids, and the results were well within acceptable data quality limits. Both the absolute organic acid concentrations and the ratio of organic acid concentrations to inorganic acid concentrations were significantly lower in La Esperanza than those reported at other rural Venezuelan sites. Organic and inorganic anion balances revealed a low potential contribution (*ca.* 7%) of formic and acetic acid to the acidity of the rain (volume-weighted average pH = 4.1). In other rural Venezuelan sites these acids contributed over 60% to the free acidity.

### 1. Introduction

Organic acids have been observed in precipitation from both polluted and remote regions of the world. These acids may be emitted by stationary and/or mobile sources and are also formed in polluted air by chemical reactions including the reaction of ozone with olefins [1]. Biogenic emissions from vegetative sources have been suggested as important natural sources for formic and acetic acid [2].

Ion chromatography (IC) has been applied in

the analysis of environmental samples [3] and, because of its high accuracy and reliability, chemically suppressed IC has recently been specified by the US Environmental Protection Agency (EPA) as the method of choice for the determination of ion composition in rainfall samples. There are numerous organic and inorganic acids present in precipitation samples and both acid types need to be determined accurately for proper accounting of atmospheric chemistry processes and precipitation ionic balances. The natural tendency is to develop a single method that can determine all the acids. However, to cover adequately all the common acids, the best

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solution is to use a combination of gradient, isocratic and ion-exclusion methods [4] or with the use of capillary ion chromatographic analysis.

This paper describes an ion chromatographic method for the determination of organic acids in event rains, and reports the contribution of formic and acetic acid to the acidity of rain in a rural site of Zulia State, Venezuela.

## 2. Experimental

### 2.1. Sampling

Event rains ( $n = 41$ ) were collected from November 1988 to November 1989 in a rural site (La Esperanza) located at the Lake Maracaibo Basin (Zulia State), ca. 100 km south and downwind of the El Tablazo Petrochemical complex and the city of Maracaibo.

The sample collector unit consisted of a large, square Plexiglas funnel, with a collecting area of 0.25 m<sup>2</sup>, mounted 2 m away from the surface, and a 20-l polyethylene bottle. The 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 preserved with HPLC-grade CHCl<sub>3</sub> (3:500, v/v) in polyethylene bottles and cooled to 4°C immediately after the rainfall to avoid biological degradation of organic acids. After each sampling, the container and funnel were thoroughly rinsed with distilled, deionized water. The conductivity of the final rinse was checked to ensure that all the sample was removed.

### 2.2. Reagents

High-purity reagents were used throughout together with Milli-Q-purified Water, deionized and then filtered through a 0.2- $\mu$ m Whatman membrane. Standard solutions of the organic acids (formic, acetic and pyruvic) were prepared from their sodium salts (analytical-reagent grade; Fisher Scientific). A mixed 100 mM stock standard solution was prepared for each organic anion and preserved with CHCl<sub>3</sub>. Calibration

standards were prepared from a 1 mM mixed standard solution using a series of dilutions, and always with preservation with CHCl<sub>3</sub>.

### 2.3. Equipment and operating conditions

The IC equipment used was a Dionex Model QIC equipped with an APM analytical pump, HPIC-AS4A separator and AMMS suppressor columns, a conductivity detector and a data processing system using a double-channel recorder to measure peak height. The APM continuously pumps the eluent through the whole system. High-performance ion chromatographic (HPIC) guard columns are used primarily to protect analytical columns. These columns filter particulate matter from the eluent and sample aliquots. The fibre suppressor contains a tubular cation-exchange membrane. Eluent passes through the inside of the membrane and dilute acid (5.0 mM H<sub>2</sub>SO<sub>4</sub>) regenerant solution flows counter-current to the eluent on the outside of the membrane. This type of suppressor can be operated continuously and does not require periodic regeneration. The suppressor column chemically converts the highly conductive species of the eluent (1.5 mM Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) into the significantly less conductive, weakly ionized species H<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (the background conductivity of the eluent can be reduced to a negligible level), resulting in increased detection sensitivity for the analytes.

After the system reaches equilibrium, a test sample is loaded and injected into the path of the eluent, which carries the sample into the highest efficiency separator column (S<sub>4</sub>); here the anions are separated according to factors such as pK<sub>a</sub>, eluent pH and resin type. The resin based consists of poly(styrene-divinylbenzene) copolymer and involves the use of low-capacity pellicular ion exchange on the bead surface.

The eluent anion (B<sub>4</sub>O<sub>7</sub><sup>2-</sup>) competes with the sample anions for the exchange sites of the resin. This causes the sample anions to move down the column at different rates and leave the column as separated peaks, and be detected by a conductivity detector. The detection signal is registered as peak height.

### 3. Results and discussion

#### 3.1. Qualitative and quantitative analysis

The IC technique does not distinguish between undissociated and dissociated forms of organic acids and the values obtained correspond to the total undissociated and dissociated compounds ( $AH + A^-$ ):



$$[A]_{\text{total}} = [AH] + [A^-]$$

If the total concentrations of organic acids, their  $pK$  values and the  $pH$  of the sample are known, the levels of concentration of dissociated and undissociated acids can be calculated.

The organic acids commonly found in precipitation-related samples as reported in the literature are formic, acetic, propionic, lactic, pyruvic, etc. [4,5]. The resolution of analytes 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 sample exhibit well defined resolution and symmetrical peaks (not broadened), giving results in less than 12 min. Peak identification was based on retention times.

Formic and acetic acid were the major organic acids found in the rainfall. Pyruvic acid was always observed at very low concentrations, and therefore the conditions were optimized for the determination of formic and acetic acid. A set of calibration graphs for mixed standards with different concentration ranges ( $0.5\text{--}80 \mu M$ ) with a good linear regression ( $R^2 = 0.9992\text{--}1.0000$ ) were used (Table 1). When, in an 8-h period, the standards were injected at 30-min intervals, no significant changes in gain (R.S.D. < 2%) were observed, and therefore it was not necessary to run standards at frequent intervals.

In order to calculate the experimental error in the determination of the organic acids, in the rain event  $E_{41}$  four fractions were taken and preserved with chloroform. The analysis of these fractions showed relatively good reproducibility (R.S.D.  $\approx 7\%$ ) for both organic acids, and there-

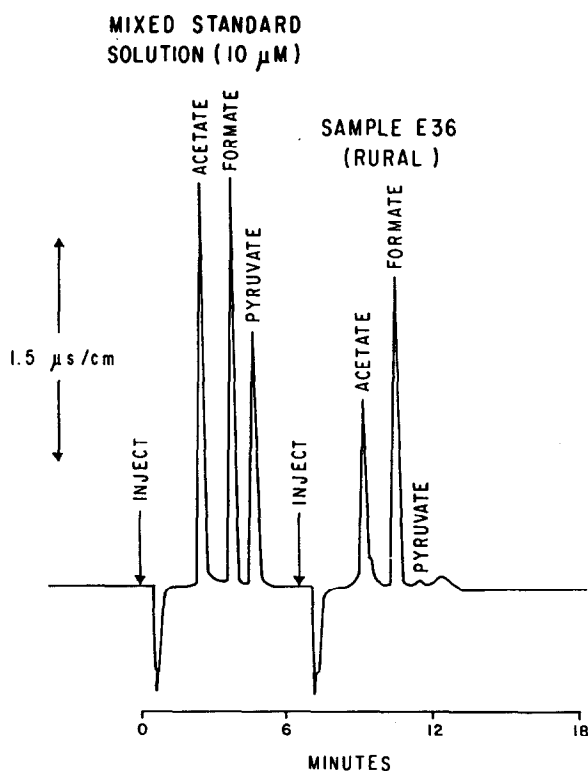


Fig. 1. Chromatogram of organic acids for a sample of precipitation from La Esperanza, Venezuela, and for a standard solution.

fore the results were well within acceptable data quality limits. The calculated limit of quantification was  $<0.2 \mu M$  for both acids.

Table 1  
Calibration graphs (formate + acetate)

Standard solution ( $\mu M$ )	Formate	Acetate
0.5; 1; 3; 5; 10 (scale: 1 $\mu s$ )	$y = 23.2x - 2.8$ ( $R^2 = 1.0000$ )	$y = 22.3x + 5.9$ ( $R^2 = 0.9998$ )
10; 15; 20; 30 (scale: 3 $\mu s$ )	$y = 7.1x + 0.8$ ( $R^2 = 1.0000$ )	$y = 6.6x + 8.5$ ( $R^2 = 0.9997$ )
30; 40; 60; 80 (scale: 10 $\mu s$ )	$y = 1.8x + 8.0$ ( $R^2 = 0.9994$ )	$y = 1.2x + 14.5$ ( $R^2 = 0.9992$ )

$y$  = Peak height (mm);  $x$  = concentration ( $\mu M$ ).

### 3.2. Organic acid concentrations

In general, the ionic concentration in rainfall is inversely proportional to the volume. The volume-weighted average concentration (VWAC) homogenizes the low-precipitation events with high ionic concentrations and the high-precipitation events with dilute concentrations. The equation used for calculating the VWAC is

$$\text{VWAC (x)}_i = \frac{\sum_{i=1}^n P_i [x]_i}{\sum_{i=1}^n P_i}$$

where  $[x]_i$  = ionic concentration of the event rain  $i$  ( $\mu\text{M}$ ) and  $P_i$  = amount of rainfall  $i$  (mm).

The VWACs of formic and acetic acid in rain water at the La Esperanza site were lower than those reported at other Venezuelan rural sites (Table 2). The highest levels (up to 34.4  $\mu\text{M}$  for acetic and 24.4  $\mu\text{M}$  for formic acid) were obtained at the beginning of the rainy season (April and May) when the vegetation is beginning to grow and flower. This may indicate a possible biological source of these acids in the atmosphere. Organic and inorganic anion balances revealed a low contribution (ca. 7%) of these acids to the acidity of the rain (93% is due to inorganic acids [6], and the volume-weighted average pH is 4.1). In other rural sites these organic acids contributed over 60% to the free acidity [7].

It seems clear that, in La Esperanza, the

Table 2  
Volume-weighted average concentrations of formic and acetic acid in Venezuela rural rains

Location	Formic acid ( $\mu\text{M}$ )	Acetic acid ( $\mu\text{M}$ )
La Esperanza <sup>a</sup>	4.4	5.5
Guri [7]	6.6	4.3
Chaguaramas [7]	8.5	7.8
La Paragua [7]	9.3	9.5

<sup>a</sup> This work ( $n = 41$ ).

higher contributions of inorganic acids, mainly  $\text{H}_2\text{SO}_4$  [6], can be attributed in part to anthropogenic activities. The monitoring site is downwind of potentially important  $\text{SO}_2$  and  $\text{NO}_x$  sources: the Cardon–Amuay and probably Aruba–Curacao refineries, the El Tablazo Petrochemical complex and the city of Maracaibo (ca.  $2 \cdot 10^6$  inhabitants). In contrast, the eastern Venezuelan savannah region is virtually unaffected by anthropogenic emissions, natural sources being responsible for the acidity of its rains. Comparisons between precipitation in impacted and remote regions indicate that, although possibly important near large population and industrial centres, anthropogenic emissions are probably not major sources for organic acids in precipitation over broad geographic regions [2].

### 4. Acknowledgements

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