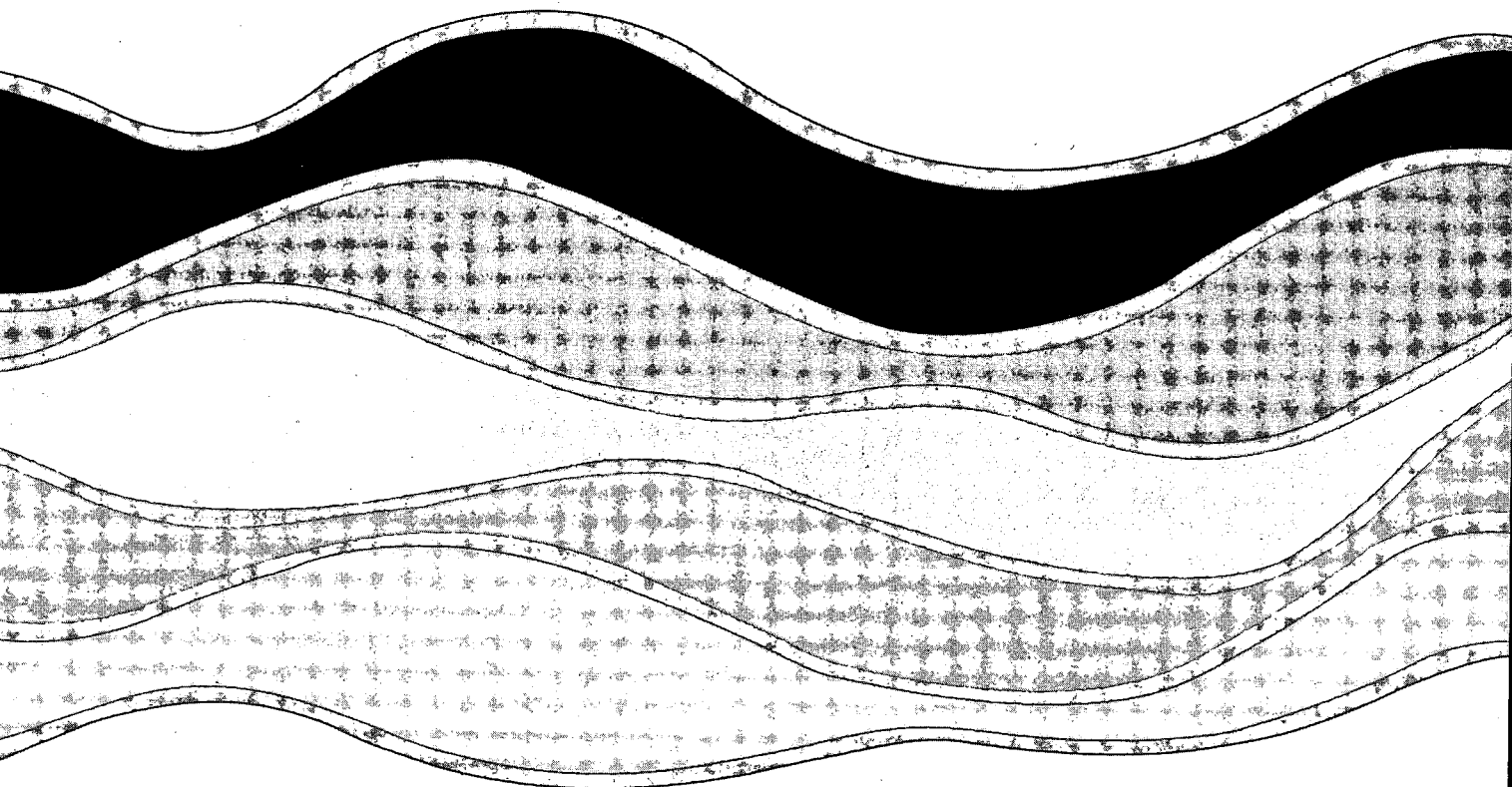


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**ION-EXCLUSION CHROMATOGRAPHIC DETERMINATION
OF ORGANIC ACIDS IN PRECIPITATION SAMPLES**

V. Cheam

NWRI CONTRIBUTION 90-145

MANAGEMENT PERSPECTIVE

Organic acids originate from both biogenic and anthropogenic sources and can account for up to 80% of total acidity in both cloud droplets and rainwater. The acids are present in significant quantity in the atmosphere and need to be determined accurately for proper accounting of atmospheric chemistry processes and precipitation ionic balances.

This report describes an ion - exclusion chromatographic method for simultaneous analysis of organic acids usually found in precipitation - related samples. The method "excludes" most strong inorganic acids and resolves most organic acids particularly lactic and acetic, which the powerful gradient method can not resolve. The analyzable acids are citric, hydrofluoric, lactic, glycolic, formic, acetic, propionic and butyric.

Dr. John Lawrence

Director

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PERSPECTIVE GESTION

Les acides organiques peuvent provenir autant de sources biologiques qu'anthropogènes et représenter jusqu'à 80 % de l'acidité totale dans les gouttelettes des nuages et dans l'eau de pluie. Comme il y en a des quantités significatives dans l'atmosphère, il faut pouvoir les doser avec exactitude pour rendre compte fidèlement de la chimie de l'atmosphère et des bilans ioniques des précipitations.

Dans ce rapport, on décrit une méthode de chromatographie à exclusion ionique permettant d'analyser simultanément les acides organiques qu'on retrouve habituellement dans les précipitations et autres milieux du même genre. Avec cette méthode, on "exclut" la plupart des acides inorganiques forts et l'on peut séparer la plupart des acides organiques, et plus particulièrement l'acide lactique et l'acide acétique, ce qui est impossible avec la méthode du gradient, même si elle est puissante. Avec la méthode présentée, on peut analyser les acides suivants : citrique, fluorhydrique, lactique, glycolique, formique, acétique, propionique et butyrique.

D^r John Lawrence

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ABSTRACT

This report describes an ion - exclusion chromatographic method for simultaneous analysis of organic acids usually found in precipitation - related samples. The method "excludes" most strong inorganic acids, i.e. elutes them in a narrow band (the void volume or water dip region), resolves most organic acids, and can determine eight acids; namely, citric, hydrofluoric, lactic, glycolic, formic, acetic, propionic and butyric. Although the number of analyzable analytes is less than that determined by the gradient method, lactic and acetic are well resolved, which is important in analysis of precipitation samples. (The gradient method can't resolve these two acids). The eluent HCL was used in spite of the somewhat noisy baseline and high background conductivity relative to actanesulfonic acid eluent, because the latter could give erroneous results for propionic acid determination. Two natural samples were used for recovery studies, which resulted in recoveries clustering around $100 \pm 5 \%$. The detection limit ranges from 0.1 to 0.4 ppm. The analysis of three rain samples showed presence of several organic acids notably formic and acetic acids, whose concentration ranged from 0.3 to 3.7 ppm.

RÉSUMÉ

Dans ce rapport, on décrit une méthode de chromatographie à exclusion d'ions qui permet d'analyser simultanément les acides organiques habituellement présents dans les précipitations et autres milieux du même genre. Avec cette méthode, on "exclut" la plupart des acides inorganiques forts, c'est-à-dire qu'ils sont élués en bande étroite (dans la région du volume vide ou du creux dû à l'eau), on sépare la plupart des acides organiques et l'on peut analyser les huit acides suivants : citrique, fluorhydrique, lactique, glycolique, formique, acétique, propionique et butyrique. Bien qu'on ne puisse pas analyser autant de substances qu'avec la méthode du gradient, l'acide lactique et l'acide acétique sont bien séparés, ce qui est important dans l'analyse des précipitations. (On ne peut pas séparer ces deux acides avec la méthode du gradient). On a utilisé du HCl comme éluant, même s'il donne un bruit de fond plutôt important dans la ligne de base et une forte conductivité d'arrière-plan par comparaison à l'acide acétonesulfonique, car avec ce dernier l'analyse de l'acide propionique peut donner des résultats erronés. On s'est servi de deux échantillons naturels pour l'étude de la récupération : celle-ci a donné des valeurs regroupées autour de 100 plus ou moins 5 %. La plage des limites de détection va de 0,1 à $0,4 \times 10^{-6}$. L'analyse de trois échantillons d'eau de pluie a révélé la présence de plusieurs acides organiques, notamment d'acide formique et d'acide acétique, à des concentrations variant de 0,3 à $3,7 \text{ p.} \times 10^{-6}$.

INTRODUCTION

Organic acids originate from both biogenic and anthropogenic sources. Sanhueza et.al.¹ and Likens et.al.² reported that over 60% of free acidity in a remote site of Venezuela and Australia is due to formic and acetic acids, which are mainly of biogenic origins. Also, it has been reported that in Northern Territory, Australia formic and acetic acids make up about 80% of total acidity in both cloud droplets and rainwater³. Grosjean^{4,5} indicated that motor vehicles are primary sources of organic acids, formic and acetic being major components (80-90%) of total organic acids and being present in greater quantity than nitric and hydrochloric acid combined. So organic acids are present in significant quantity in the atmosphere and need to be determined accurately for proper accounting of atmospheric chemistry processes and precipitation ionic balances⁶⁻¹⁰.

Organic acids are present in most samples, and are an integral part of the various processes forming the living environment. Yet organic acids are relatively unknown and not as frequently analysed as the inorganic acids. Partly it is because organic acids readily desintegrate, and therefore analysts can not usually detect them during analysis of unpreserved water samples. A method was recently developed for simultaneous determination of many organic and inorganic acids¹¹. Although it is a very powerful method, the eluents are not as stable as the standard carbonate/bicarbonate eluent and need to be frequently changed to prevent poor resolution

of some organic monoprotics. This report describes a method which excludes the strong inorganic ions (thus the name ion-exclusion) from the main elution process, allowing mostly the organic acids to be analytically separated.

EXPERIMENTAL

Chemicals

High-purity chemicals were used: HCl, Octanesulfonic acid (OSA), Milli-Q water (MQW, 18 M Ω), sodium and potassium salts: citrate, fluoride, glycolate, lactate, formate, acetate, propionate, and butyrate. A stock solution of 1000 ppm (mg/L) was prepared for each acid and was preserved with 0.2% HPLC grade CHCl₃. All standards and spiked samples were also preserved likewise.

Equipment and operation conditions

Figure 1 shows the equipment comprising Dionex's system 2020i with an analytical pump, columns, conductivity detector CDM-1, and autoion 400. The operating conditions are given in Table 1.

RESULTS AND DISCUSSION

Commonly reported acids

Although there are numerous acids present in precipitation samples, the major acids commonly cited are sulfuric, nitric, hydrochloric, hydrofluoric, formic and acetic, as well as propionic, lactic,

glycolic, butyric, methanesulfonic, hydroxymethanesulfonic, nitrous, oxalic, phosphoric, and citric as shown in Table 2¹¹.

Optimization

Either 1mM HCL or 1mM OSA can be used as eluent. Various flow rates ranging from 0.5 to 1.2 ml/min were tested. Any one of the rates could be used to resolve the acids but in our case the 0.8 ml/min seems to be the optimal choice -- not too long an analysis time and acceptable resolution for the 4 closely eluted peaks (HF, lactic, glycolic, and formic) in standard or spiked natural samples. Eight acids can be resolved satisfactorily: citric, HF, lactic, glycolic, formic, acetic, propionic, and butyric, whereas the inorganics, methanesulfonic, hydroxymethylsulfonic, and oxalic are co-elutants in peak 1 or elute in the water dip region (Fig.2). Although the number of analytes is less than that determined by the gradient method¹¹, lactic and acetic are well resolved, which is important in analysis of precipitation samples. (The gradient method can not resolve these 2 acids).

Choice of eluents

Octanesulfonic acid (OSA) and HCL eluents at 1mM concentration were tested. OSA produced better baseline (less noise) and better detection limit than HCL. However, with OSA there is a large unwanted peak coeluting with the propionic peak, which is unacceptable as propionic is one of the important acids. A run of a $\text{CO}_3^{2-}/\text{HCO}_3^-$ solution shows coelution of propionic and CO_3^{2-} peak in

both eluents but the peakheight with OSA is higher than that with HCL. Table 3 compares the peakheights generated by OSA and HCL for some samples, and seems to show that the unwanted peak is the $\text{CO}_3^{=}$ peak as also observed earlier by Franklin et al.¹². Furthermore, an analysis of the Milli-Q water, the standard, and the rain sample by a gradient method¹¹ shows agreement with the HCL runs, i.e. only a small amount of propionic acid is observed. Therefore, HCL eluent was chosen in spite of its noisier baseline and higher background conductivity of 99 μS (vs. 43 μS for OSA).

Sensitivity

Method sensitivity has been discussed at length recently¹¹. It is depicted in this report as the response in function of concentration (Fig. 3). Each point represents an average value of several (at least 3) analyses. For each acid at four to five low concentration levels, a line was manually drawn and the regression parameters were calculated and shown in the legend. If sensitivity is taken as the response per unit concentration, it may be equated to the slope of each line, and the sensitivities for the various acids can be easily compared as shown in Table 4 and Figure 3. Note that for citric acid, sensitivity is given at 3 concentration levels because the line is not linear. The non-linearity occurs because the early part of the citric elution is partly hidden in the void volume region and the baseline was drawn over the water dip to obtain peak height for citric (Figs. 2 & 4).

Performance characteristics

Two types of water were used: a rain sample from Sibley collected by the surveillance and monitoring group, and a Eulerian quality control sample (EU-ANI-1, a composite rain sample) prepared by the quality assurance group. Both samples were originally unpreserved as dictated by their protocol, but were preserved with 0.2% CHCl_3 when used in recovery studies. For each water and acid, six replicate or more analyses were made. Fig. 4 shows a representative chromatogram for a spiked water sample. The recovery data are presented in Tables 5 and 6 and indicate that the precisions are somewhat poor for HF, lactic, glycolic and formic. This is due to the fact that these acids elute very closely to each other.

Table 7 lists the detection limits of the acids. Each limit was equated to 3 times the standard deviation of 10 replicate analyses of a standard containing 2-5 times the estimated detection limit. The latter was the concentration giving a signal equal to 2-3 times that of the noise. If needed, the detection limits can be improved by increasing the size of sample loop or using concentrators.

Analysis of rain samples

Three rain samples from the Burlington area were collected and were immediately preserved with 0.2% CHCl_3 . Several organic acids were detected especially formic and acetic acids, whose concentration ranged from 0.3 to 3.7 ppm (Table 8).

CONCLUSION

An ion-exclusion method has been described for simultaneous analysis of organic acids usually found in precipitation samples. The method is capable of resolving lactic and acetic acids, which is very important in analysis of rain samples. In this way, the method adequately complements the powerful gradient method, which can not resolve the two acids but can separate 15 other organic and inorganic acids.

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Table 1. Operating Conditions

Eluent = 1 mM HCl

Suppressor = AMMS - ICE

Flow rate = 0.8 ml/min

Regenerent / flow rate = 5 mM TBAOH* / 2 ml min⁻¹

Sample loop = 50 μ L

Detector = conductivity, CDM-1

Separator = HPICE-AS1 (250 x 9 mm)

Analytes = citric, hydrofluoric, lactic, glycolic, formic,
acetic, propionic, butyric

*Tetrabutylammonium hydroxide

Table 2. Acids commonly reported in precipitation-related samples

<u>ACIDS</u>	<u>FORMULA</u>
Formic	HCOOH
Acetic	CH ₃ COOH
Oxalic	HOCCOOH
Glycolic	HOCH ₂ COOH
Propionic	CH ₃ CH ₂ COOH
Lactic	CH ₃ CHOHCOOH
Butyric	CH ₃ CH ₂ CH ₂ COOH
Succinic	HOOCCH ₂ CH ₂ COOH
Citric	HOOC(CH ₂ COOH) ₂ COOH
Methanesulfonic	CH ₃ SO ₃ H
Hydroxymethylsulfonic	HOCH ₂ SO ₃ H
Sulfuric	H ₂ SO ₄
Nitric	HNO ₃
Hydrochloric	HCl
Hydrofluoric	HF
Phosphoric	H ₃ PO ₄
Nitrous	HNO ₂

Table 3. Peakheight comparison between eluent OSA (octanesulfonic acid) and eluent HCL at propionic elution peak

<u>SAMPLE</u>	<u>RT(min.)</u>	----PEAK HEIGHT----	
		<u>OSA</u>	<u>HCL</u>
Eluent	-----	0	0
MQW	14.12	1.20×10^6	0
Standard	14.11	1.56×10^6	0.58×10^6
Rain sample	14.14	1.42×10^6	0.20×10^6

Table 4. Method sensitivity for the acids (response counts/ppm)

ACID	SENSITIVITY
HF	675
Formic	455
Citric	194 in .5-1 ppm region
Citric	320 in 1-2 ppm region
Citric	388 in 2-5 ppm region
Acetic	251
Glycolic	216
Lactic	179
Propionic	145
Butyric	74

Table 5. Spike recoveries for Sibley rain water (in ppm and in %)

ACIDS	RECOVERY± S.D. mg/L	%CV	%REC
Citric	1.06±0.06	5.9	106
Hydrofluoric	0.20±0.04	17.3	100
Lactic	0.50±0.07	12.9	101
Glycolic	0.52±0.10	20.0	103
Formic	0.49±0.08	16.4	97
Acetic	0.99±0.11	11.5	99
Propionic	1.03±0.15	14.6	103
Butyric	1.05±0.33	31.0	105

Table 6. Spike recoveries for a Eulerian quality control sample,
EU-ANI-1 (in ppm and in %)

ACIDS	RECOVERY± S.D. mg/L	%CV	%REC
Citric	1.06±0.09	8.2	106
Hydrofluoric	0.19±0.02	8.8	96
Lactic	0.61±0.14	23.4	122
Glycolic	0.51±0.07	13.8	102
Formic	0.43±0.06	13.1	86
Acetic	1.08±0.07	6.6	108
Propionic	1.05±0.09	8.4	105
Butyric	1.00±0.13	12.9	100

Table 7. Detection limit of the acids, in ppm

ACIDS	DETECTION LIMIT
Citric	0.4
Hydrofluoric	0.1
Lactic	0.3
Glycolic	0.2
Formic	0.4
Acetic	0.2
Propionic	0.3
Butyric	0.4

Table 8. Analysis of 3 rain samples from Burlington area

ACIDS	SAMPLE 1	SAMPLE 2	SAMPLE 3
Citric	---	0.56	---
Hydrofluoric	---	---	---
Lactic	0.28	0.42	---
Glycolic	---	---	---
Formic	0.64	3.70	0.55
Acetic	0.27	1.47	0.25
Propionic	0.41	0.59	---
Butyric	---	---	---

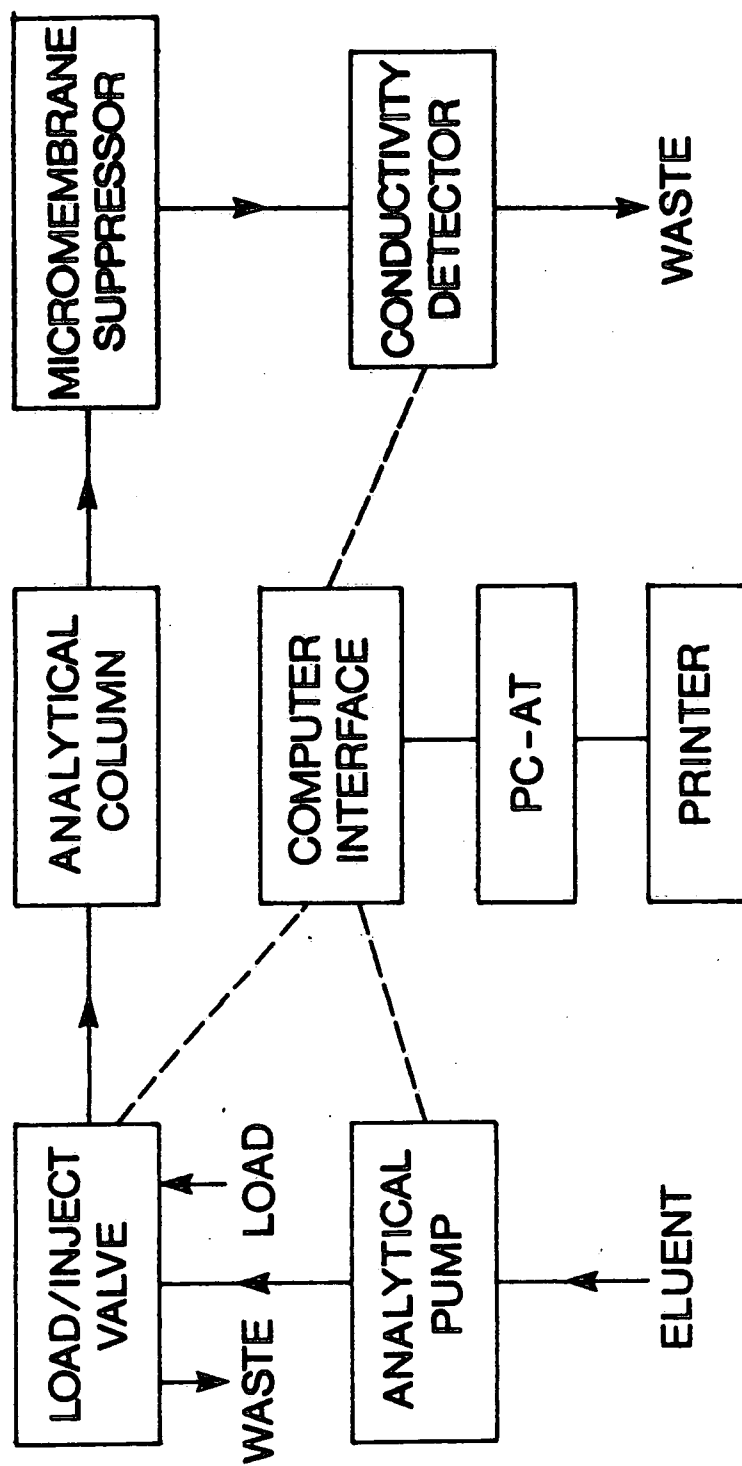


FIG. 1. SYSTEM SCHEMATIC

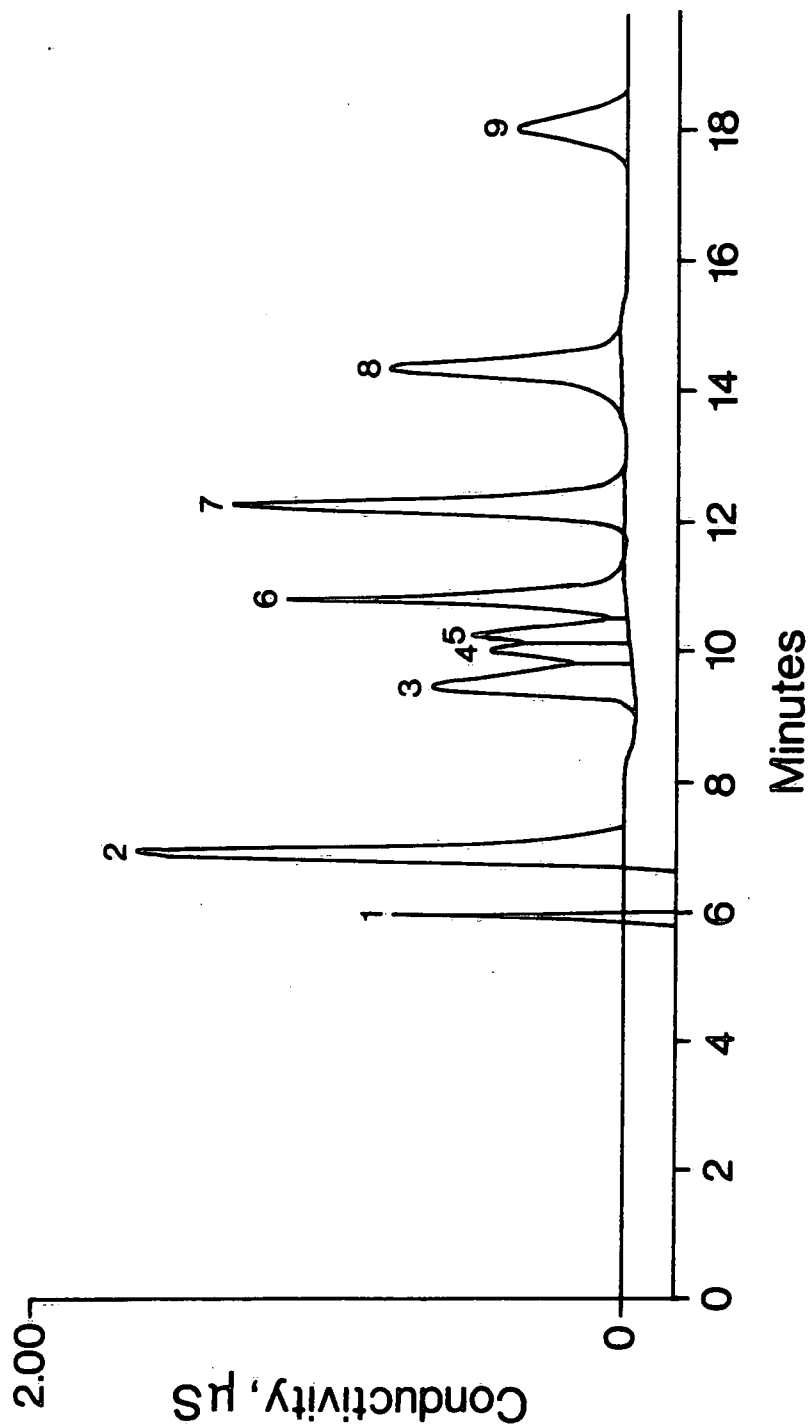


Fig. 2 Chromatogram of a standard: 1= Inorganics (HCl , H_2SO_4 , HNO_3 , HNO_2 , H_3PO_4), $\text{CH}_3\text{SO}_3\text{H}$, $\text{HOCH}_2\text{SO}_3\text{H}$, and Oxalic; 2= Citric 5 ppm; 3=HF 1 ppm; 4= Lactic 2.5 ppm; 5= Glycolic 2.5 ppm; 6= Formic 2.5 ppm; 7= Acetic 5 ppm; 8= Propionic 5 ppm; 9= Butyric 5 ppm.

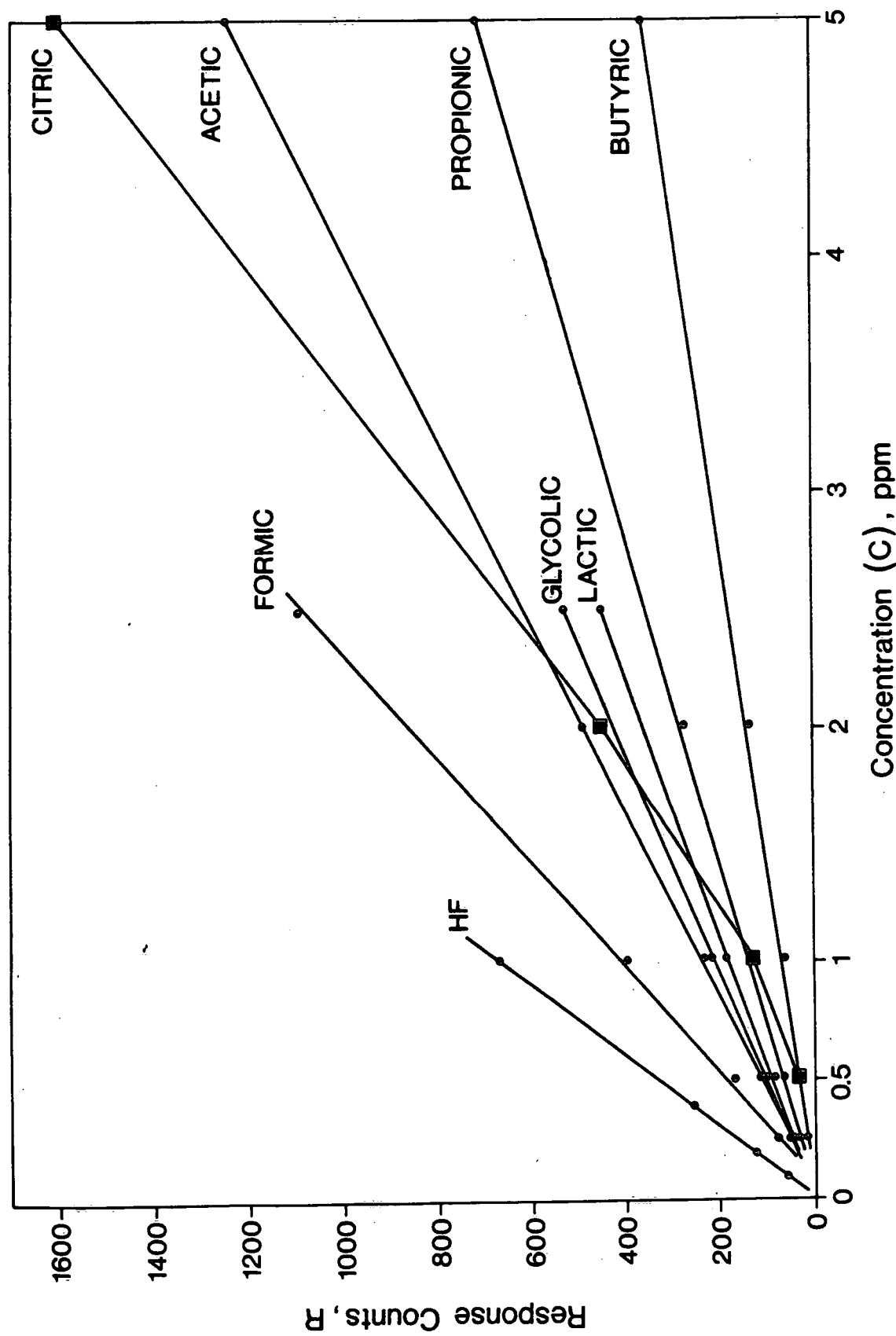


Fig. 3. Method sensitivity for the acids. Regression equations (r = correlation coefficient) are: HF = $0.013 + 0.00148 R$ ($r = 1.000$); Formic = $0.12 + 0.0022 R$ ($r = 1.000$); Citric = $0.43 + 3.82e^{-3} R - 6.12e^{-7} R^2$; Acetic = $0.054 + 0.00398 R$ ($r = 1.000$); Glycolic = $0.026 + 0.00463 R$ ($r = 1.000$); Lactic = $0.005 + 0.0056 R$ ($r = 1.000$); Propionic = $0.067 + 0.0069 R$ ($r = 1.000$); Butyric = $0.144 + 0.0135 R$ ($r = 1.000$).

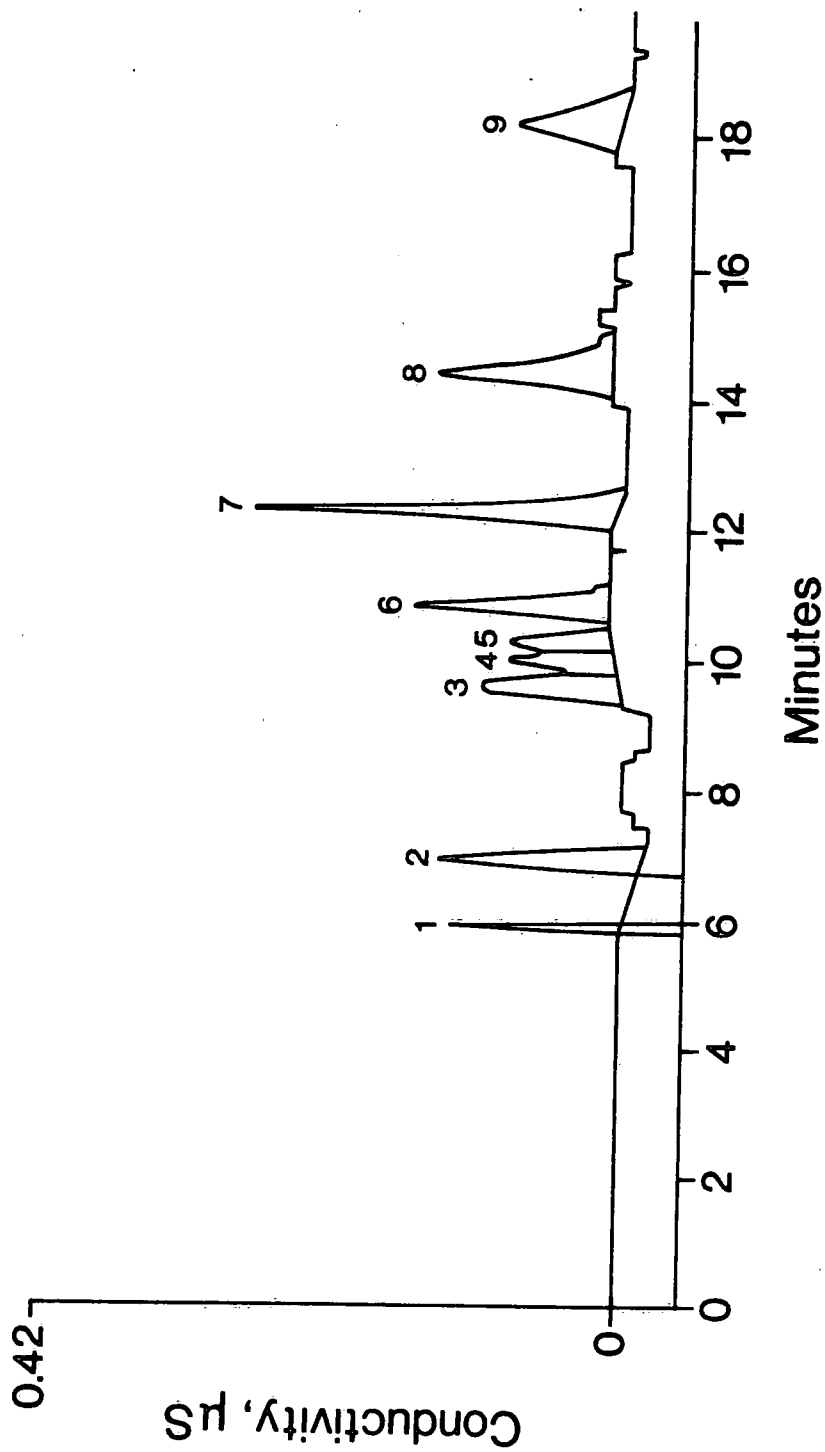
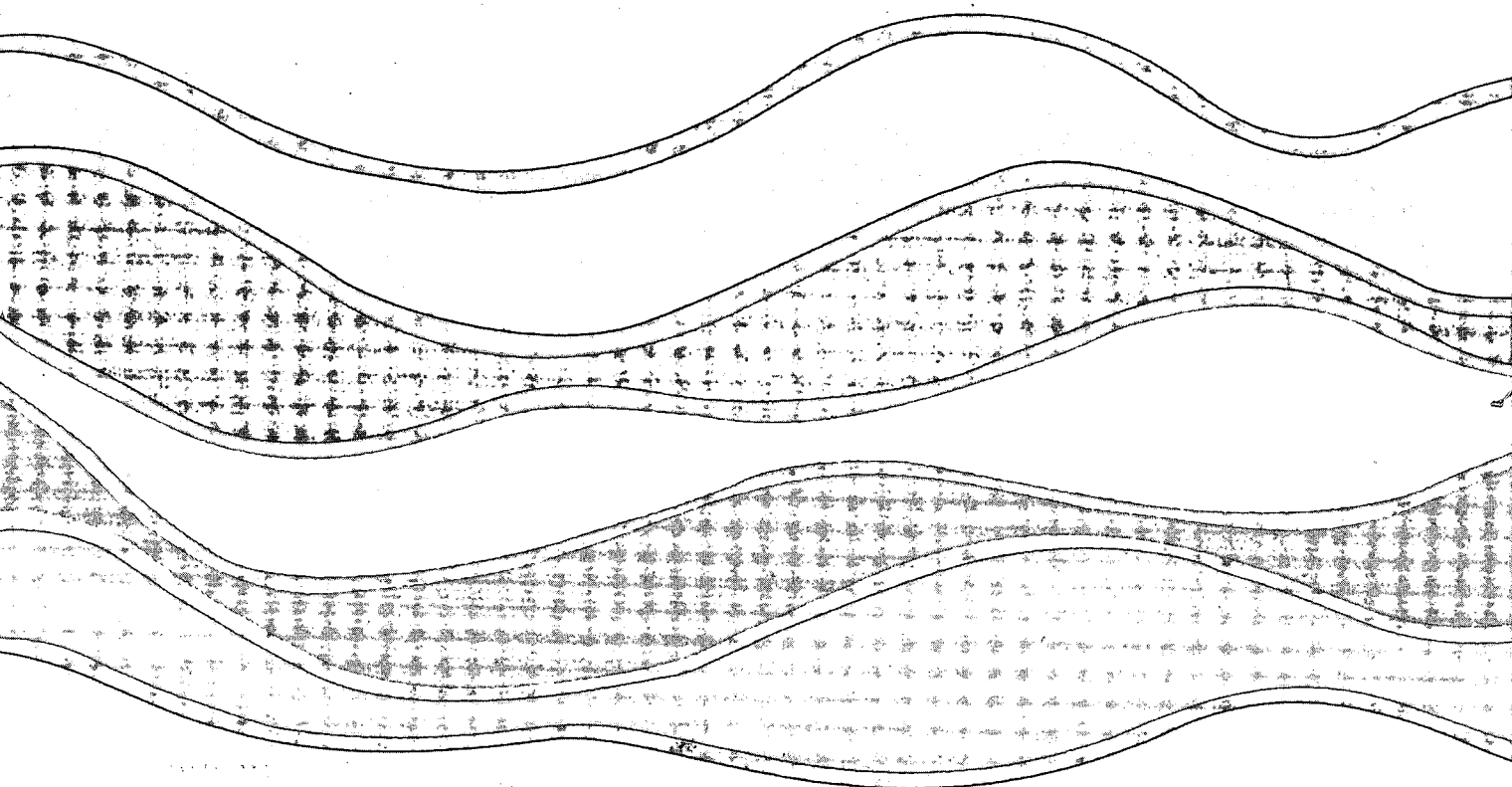


Fig. 4 Chromatogram of a spiked QC sample (EU-AN-I):1= Inorganics (HCl , H_2SO_4 , HNO_3 , H_3PO_4), $\text{CH}_3\text{SO}_3\text{H}$, $\text{HOCH}_2\text{SO}_3\text{H}$, and Oxalic;
 2 = Citric 1.1 ppm; 3 = HF 0.2 ppm; 4 = Lactic 0.6 ppm;
 5 = Glycolic 0.5 ppm; 6 = Formic 0.4 ppm;
 7 = Acetic 1.1 ppm; 8 = Propionic 1.1 ppm;
 9 = Butyric 1.0 ppm.

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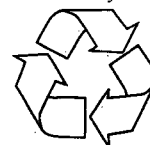
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