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ISOCRATIC ANION CHROMATOGRAPHIC METHOD AND COMPARISON OF METHODS FOR THE DETERMINATION OF ORGANIC AND INORGANIC ACIDS IN PRECIPITATION SAMPLES

V. Cheam

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ISOCRATIC ANION CHROMATOGRAPHIC METHOD AND COMPARISON OF METHODS FOR THE DETERMINATION OF ORGANIC AND INORGANIC ACIDS IN PRECIPITATION SAMPLES

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MANAGEMENT PERSPECTIVE

Organic acids originating from biogenic and anthropogenic sources are now known to play an important role in environmental chemistry. Both organic and inorganic acids need to be determined accurately in order to properly explain atmospheric chemistry processes and precipitation ionic balances. This report describes an isocratic anion chromatographic method for the analysis of samples containing these acids and assesses its performance against that of a gradient method and an ion-exclusion method. The assessment results show that in order to adequately determine all acids of concern, the gradient and ion-exclusion methods should be jointly used to analyse precipitation samples.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Il est maintenant connu que des acides organiques d'origine biosynthétique et anthropique jouent un rôle important dans le domaine des propriétés chimiques de l'environnement. Il faut doser avec précision les acides organiques et inorganiques afin de bien expliquer les processus de chimie de l'atmosphère et l'équilibre ionique des précipitations. Le présent rapport décrit une méthode de chromatographie isocratique par échange d'anions pour l'analyse d'échantillons contenant ces acides et évalue son rendement par rapport à celui de la méthode du gradient et de la méthode d'exclusion d'ions. Les résultats de l'évaluation montrent que pour doser convenablement tous les acides qui nous intéressent, les méthodes du gradient et d'exclusion d'ions devraient être appliquées conjointement aux fins d'analyse des échantillons de précipitations.

ABSTRACT

An isocratic anion chromatographic method is described for the analysis of preserved (0.2% $CHCl_3$) samples containing organic and inorganic acids. The analyzable analytes are methanesulfonic, hydrochloric, nitrous, nitric, phosphoric, hydroxymethylsulfonic, sulfuric, and oxalic acids. The method is assessed against the gradient and ion-exclusion (IE) chromatographic methods, in terms of analytical capability and suitability for the determination of organic and inorganic acids commonly found in precipitation samples. The gradient method has been shown to provide reliable results for formic and hydrofluoric acids (more precise results than the IE method). The IE method has proven to be reliable for the determination of acetic and lactic acids and its application for the determination of other organic acids can be useful for double-checking purposes. The inorganic acids are adequately determined by the gradient method. The combination of isocratic-IE methods will not satisfactorily give the complete spectrum of analytes because of the imprecision associated with the analysis of formic, hydrofluoric and methanesulfonic acids.

If only one method should be used, the gradient method is most suitable as it can determine the majority of the acids of interest. To adequately cover all acids of interest, the combination of the gradient and the ion-exclusion methods must be used.

RÉSUMÉ

L'auteur du présent rapport décrit une méthode de chromatographie isocratique par échange d'anions pour l'analyse d'échantillons conservés (O,2 % $CHCl_3$) contenant des acides organiques et inorganiques. Les acides méthane-sulfonique, hydrochlorique, nitreux, nitrique, phosphorique, hydroxyméthylsulfonique, sulfurique et oxalique sont les composés analysables. La méthode est évaluée par rapport aux méthodes chromatographiques du gradient et d'exclusion d'ions, en fonction de son potentiel d'application pour le dosage des acides organiques et inorganiques habituellement présents dans des échantillons de précipitations. La méthode du gradient permet d'obtenir des résultats fiables dans le cas des acides formique et hydrofluorique (résultats plus précis que ceux de la méthode d'exclusion d'ions). La méthode d'exclusion d'ions est fiable pour le dosage des acides acétique et lactique et son utilisation pour le dosage d'autres acides organiques peut être utile à des fins de contre-vérification. Les acides inorganiques sont bien dosés par la méthode du gradient. La combinaison des méthodes de chromatographie isocratique et d'exclusion d'ions ne permettra pas d'obtenir d'une manière satisfaisante le spectre complet des composés à analyser en raison de l'imprécision associée à l'analyse des acides formique, hydrofluorique et méthane-sulfonique.

Si une seule méthode doit être utilisée, la méthode du gradient est celle qui convient le mieux puisqu'elle permet de doser la majorité des acides qui nous intéressent. Si l'on veut couvrir tous les acides, il faut avoir recours à la combinaison des méthodes du gradient et d'exclusion d'ions.

INTRODUCTION

The importance of organic acids in precipitation samples has been well documented[1-10]. Recently, Cheam described a powerful gradient ion chromatographic method for simultanous determination of inorganic and organic acids in preserved precipitation samples[11]. Although the method is capable of determining most acids commonly reported for these samples (Table 1), it could not resolve lactic and acetic acids, the latter being a major organic acid. In another report, the same author described an ion-exclusion chromatographic method[12], which mainly resolves organic acids including lactic and acetic, leaving however, most of the major inorganic acids unresolved. A method which resolves these latter acids for the same type of samples would be desirable as it could supplement the ion-exclusion method to determine the complete spectrum of acids of interest. The combined performance of these two methods can then be compared to the performance of the gradient method in term of key characteristics such as analyzable analytes, analysis time, detection limit, interference, and overall usefulness.

This report has two objectives. First, it describes an isocratic anion chromatographic method for the analysis of acids (mainly inorganic acids) commonly found in preserved (0.2% $CHCl_3$) precipitation samples; and secondly it assesses the three methods to find the most suitable method or combination of methods for the determination of the complete spectrum of specific acids.

EXPERIMENTAL

Chemicals

High-purity chemicals were used: Milli-Q water (18 MΩ), sulfuric acid, sodium and potassium salts: carbonate, bicarbonate, chloride, nitrite, nitrate, methanesulfonate, hydroxymethylsulfonate, sulfate, oxalate, phosphate, citrate, fluoride, glycolate, lactate, formate,

acetate, propionate, and butyrate. A stock solution of 1000 ppm (mg/L) was prepared for each acid and the organic acids were preserved with 0.2% HPLC grade $CHCl_3$. All standards and spiked samples were also preserved likewise.

Equipment and operation conditions

The equipment comprises Dionex's system 2020i as detailed previously[12]. The carbonate/bicarbonate eluent was pumped at a rate of 2 mL/min through a load/inject valve, an analytical column, a micromembrane suppressor and a conductivity detector CDM-1. The pump, the valve and the detector are controlled by a Dionex software autoion 400. The operating conditions are given in Table 2.

RESULTS AND DISCUSSION

Commonly reported acids

The acids commonly reported and found in precipitation-related samples are sulfuric, nitric, hydrochloric, hydrofluoric, formic and acetic, as well as propionic, lactic, glycolic, butyric, methanesulfonic, oxalic, hydroxymethylsulfonic, nitrous, phosphoric, and citric as shown in Table 1[4,6-9,11-17].

Eluents

The working standard eluent used was prepared with 1g Na_2CO_3 and 1g $NaHCO_3$ in 4 litres of water. Three other eluents were likewise prepared using 1.1g, 0.75g and 0.65g of each salt. Figure 1 shows four chromatograms obtained from the analysis of a standard using the 4 different eluents. As can be seen each eluent is suitable for use and has its own merit. For example, the eluent prepared from 1.1g of each salt produces the shortest analysis time and well

defined, sharp peaks, but with samples having markedly different concentrations of analytes, the closely eluted peaks are prone to have peak overlap or shoulder. When using the eluent prepared from 0.65g of each salt, very well separated peaks are obtained, but the last peak is very broad and elutes very late. Figure 1 also shows the interesting elution patterns of phosphate and nitrate depending on eluent strength: the phosphate peak elutes before the nitrate peak at 1.1g and 1g strengths but elutes after at 0.75g and 0.65g strengths.

Interference

Hydrofluoric, glycolic, formic, acetic, lactic, propionic, and butyric acids coelute. Phosphoric and nitric acids could coelute (Fig. 1) but an appropriate eluent will alleviate this. Although citric acid coelutes with sulfuric acid, it is considered not to be an interfering-species because its response factor is about 100 times less than that of sulfuric acid, and its concentration is usually much lower than sulfuric acid concentration in these samples.

Sensitivity

Method sensitivity has several definitions in the literature as recently discussed[11]. It is depicted in this report, as it has been earlier[11,12], as the response in function of concentrations at the low end of analytical curves (Fig. 2). Each point represents an average value of 3 analyses. For each acid at four concentration levels, a line was manually drawn and the regression parameters were calculated and are shown in the legend of Figure 2. Since sensitivity can be expressed as the response per unit concentration, it is equated here to the slope of each line. Table 3 compares the method sensitivity for the various acids, showing the method to be most sensitive to hydrochloric acid but least sensitive to HOMS. Figure 2 also illustrates this comparison.

Performance indicators

Natural waters were used for recovery studies: a rain sample collected from Sibley, Ontario by the surveillance and monitoring group, and a quality control sample (EU-ANI-1, a composite rain sample) prepared by the quality assurance group. Both samples were originally unpreserved (as dictated by the protocol of these two groups), but were preserved with 0.2% $CHCl_3$ when used in our studies. For each rain water sample and for each acid analyzed, five replicate analyses were made. The recovery and precision data obtained from these experiments are presented in Tables 4 and 5 and are considered to be acceptable.

The detection limits, listed in Table 6, were derived as follows using a 50 μL sample loop. Each limit was equated to 3 times the standard deviation of 8 replicate analyses of a standard containing 5 times the estimated detection limit. The latter limit was the concentration giving a signal equal to 2-3 times that of the noise.

METHODS COMPARISON

Analytes and analysis time

Table 7 summarizes the analyzable analytes as well as the coelutants and the total analysis time required by each of the three methods. Figure 3 shows the actual resolution of analytes and the analysis time for a standard containing acids commonly found in precipitation samples. The resolution quality, however good it may be for each method, is plagued by some drawbacks. For example, the resolution of acetic, propionic, glycolic and butyric acids may be poor in the gradient method as reported earlier[11]. In the isocratic method, methanesulfonic acid is at the edge of the void volume, and phosphoric-nitric acids resolution can be poor although it can be remedied by adjusting the eluent strength. In the ion-exclusion method (IE), the citric

acid peak is very close to the void volume, whereas hydrofluoric, lactic, glycolic and formic acids at times are not well resolved.

The resolution efficiency and the total analysis time for the gradient method (16 analytes in 16 minutes) is overall better than the isocratic (8 analytes in 10 minutes) and the ion-exclusion methods (8 analytes in 19 minutes). But the gradient method has some limitations: acetic and lactic acids coelute and, as mentioned above, the resolution of some organic monoprotic acids can be poor especially after each eluent change. The ion-exclusion method on the other hand effectively resolves the two acids, and the acetic peak consistently is a reliable peak in chromatograms. The resolution for formic acid, however, is more reliable with the gradient than with the ion-exclusiom method[11,12]. Thus, the combination of the resolution power of the gradient method (HF, formic, inorganics,...) and the ability of the IE method to resolve key analytes (lactic, acetic, propionic) would give adequate capability to cover all the acids of interest. This combination of the two methods has also the advantage of providing duplicate data for a number of organic acids, a useful feature for double-checking purposes.

The combination of the isocratic and ion-exclusion methods does not offer a valuable alternative on account of the following limitations that make it impossible to obtain the complete spectrum of analytes. Formic acids cannot be determined by the isocratic method and, even though IE provides it, its poor precision[12] would give unreliable results. Two other limitations as mentioned earlier in this section (the determination of HF by the IE method, and methanesulfonic acid by the isocratic method) constitute also arguments against the combination of these two methods to provide adequate capability for the determination of acids in precipitation samples.

Detection limit and sensitivity

Table 8 and Figure 4 provide a comparison of the detection limits obtained for the 3 methods, based on measurements using a 50 μL sample loop. The detection limits for the IE

method are higher than those for gradient and isocratic methods, the latter two being comparable in that respect (Figure 4).

Although the detection limit is the most commonly referenced performance indicator, sensitivity may give rise to some unexpected information. For example Table 9 shows the gradient sensitivity being much greater than IE sensitivity, and as expected the gradient detection limit is smaller than IE detection limit. However, even though the gradient sensitivity is greater than the isocratic sensitivity, the detection limits are comparable (Table 9, Fig. 4). This may be explained by the following: 1) the gradient detection limits were estimated from data generated on 5 different days in a 3-week period involving change of eluents, which caused less precise results (larger standard deviation) thus larger detection limits[11]; 2) it could be that better sensitivity does not necessarily imply better detection limit because the greater the sensitivity (slope of the response-concentration plot) the lower the intercept, which could be negative, which in turn means positive concentration intercept suggesting large detection limit. On the other hand, the lower the sensitivity the higher the intercept, which could be zero suggesting small detection limit. More data are needed to test this concept, but it would be beyond the scope of this report.

Precision and accuracy

Table 10 compares the relative standard deviations (RSD) obtained for two natural waters (Sibley and EU-ANI-1), using the three methods. It can be seen that the IE method is overall less precise than the gradient and the isocratic methods, and specifically, it produced inferior reproducibility for the determination of HF, lactic, glycolic and formic acids. The gradient method also has poor reproducibility for acetic, propionic, glycolic, and butyric acids. The isocratic method produced precise results for methanesulfonic even though this acid elutes right after the void volume region. Perhaps this "ruggedness" of the isocratic method helps contribute to the very precise results and therefore small detection limits as discussed above (since detection limit is a precision statement).

The % recoveries were likewise obtained and are compared in Table 11. The recoveries are in general well within 100±10% except for formic and lactic acids by IE.

Interference and coelution

In the gradient method there are two coelutants, acetic and lactic acids. In the isocratic method, sulfuric, citric and succinic acids coelute but the method sensitvity for sulfuric acid is about 100 times that for citric acid, and about 20 times that for succinic acid; the coelutants in the water dip region are: hydrofluoric, glycolic, formic, acetic, lactic, propionic, and butyric acids. In the IE method, carbonic acid coelutes with propionic acid; the coelutants at void volume are: sulfuric, phosphoric, hydrochloric, oxalic, nitric, nitrous, methanesulfonic, and hydroxymethylsulfonic acids.

CONCLUSION

If only one method should be used, the gradient is the method of choice as it can determine the majority of the acids of interest. To fully cover all common acids of interest, the best combination is gradient and ion-exclusion methods as the gradient provides data for formic and hydrofluoric acids reliably (more precise than IE), whereas the IE provides results for acetic and lactic acids plus some duplicate data for double-checking purpose. The inorganic acids are adequately determined by the gradient method.

The ion-exclusion method provides data for most organic acids, resolves acetic and lactic acids, but is the least precise of the three methods. The gradient method provides results for most analytes, but acetic and lactic acids coelute. The isocratic method is a precise method but provides mainly data for inorganic acids.

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Table 1. Acids commonly reported in precipitation-related samples

ACIDS	FORMULA
Formic	$HCOOH$
Acetic	CH_3COOH
Oxalic	$HOOCCOOH$
Glycolic	$HOCH_2COOH$
Propionic	CH_3CH_2COOH
Lactic	$CH_3CHOHCOOH$
Butyric	$CH_3CH_2CH_2COOH$
Citric	$HOC(CH_2COOH)_2COOH$
Methanesulfonic (MS)	CH_3SO_3H
Hydroxymethylsulfonic (HOMS)	$HOCH_2SO_3H$
Sulfuric	H_2SO_4
Nitric	HNO_3
Hydrochloric	HCl
Hydrofluoric	HF
Phosphoric	H_3PO_4
Nitrous	HNO_2

Table 2. Operating Conditions

Eluent = $Na_2CO_3/NaHCO_3$ (either one of the 3 mixtures in mM): 2.60/3.27; 2.36/2.98; 1.77/2.23

Flow rate = 2.0 ml/min

Sample loop = 50 μL

Guard column = HPIC-AG4A (50 x 4 mm)

Separator = HPIC-AS4A (250 x 4 mm)

Suppressor = Anion MicroMembrane Suppressor (AMMS)

Regenerent / flow rate = 0.025 N H_2SO_4 / 2 ml min^{-1}

Detector = conductivity, CDM-1

Analytes = methanesulfonic, hydrochloric, nitrous, phosphoric, nitric, hydroxymethylsulfonic, sulfuric, and oxalic

Table 3. Method sensitivity for the acids (response counts/ppm)

ACID	SENSITIVITY
Hydrochloric	4214
Nitrous	3896
Nitric	3814
Methanesulfonic (MS)	2010
Phosphoric	1279
Sulfuric	1201
Oxalic	426
Hydroxymethylsulfonic (HOMS)	271

Table 4. Spike recoveries for Sibley rain water (in ppm and in %)

ACIDS	Sibley mg/L	RECOVERY± S.D. mg/L	RSD %	%REC
Methanesulfonic	---	0.53±0.04	8.4	105
Hydrochloric	0.058	0.16±0.01	4.9	98
Nitrous	---	0.10±0.01	4.2	96
Phosphoric	---	0.20±0.01	1.8	98
Nitric	0.138	0.33±0.01	2.7	97
HOMS[1]	---	2.44±0.03	1.3	98
Sulfuric	0.799	1.30±0.03	2.1	100
Oxalic	---	0.48±0.03	6.9	97

[1] Hydroxymethylsulfonic acid

Table 5. **Spike recoveries for a Eulerian quality control sample, EU-ANI-1 (in ppm and in %)**

ACIDS	EU-ANI-1 mg/L	RECOVERY± S.D. mg/L	RSD %	%REC
Methanesulfonic	---	0.51±0.01	1.6	102
Hydrochloric	0.018	0.11±0.01	5.4	97
Nitrous	---	0.10±0.00	2.3	100
Phosphoric	---	0.20±0.01	4.2	102
Nitric	---	0.21±0.01	5.9	103
HOMS[1]	---	2.39±0.03	1.3	95
Sulfuric	0.031	0.54±0.01	2.6	103
Oxalic	---	0.50±0.01	2.1	99

[1] Hydroxymethylsulfonic acid

Table 6. Detection limit of the acids, in ppm

ACIDS	DETECTION LIMIT
Methanesulfonic	0.05
Hydrochloric	0.015
Nitrous	0.01
Phosphoric	0.03
Nitric	0.01
Hydroxymethylsulfonic	0.25
Sulfuric	0.04
Oxalic	0.20

Table 7. **COMPARISON OF RESOLUTION AND TOTAL ANALYSIS TIME OF THE 16 ACIDS COMMONLY FOUND IN PRECIPITATION SAMPLES**

ACIDS	ANION EXCHANGE CHROM. GRADIENT MODE	ANION EXCHANGE CHROM. ISOCRATIC MODE	ION EXCLUSION CHROM. ION EXCLUSION MODE
FORMIC	YES	COELUTE: F,GLY,FORM,	YES
ACETIC	(COELUTE/ LACTIC)	AC,LACT,PROP,BUTYR	YES
GLYCOLIC	YES	NO	YES
PROPIONIC	YES	NO	YES
LACTIC	(COELUTE/ ACETIC)	NO	YES
BUTYRIC	YES	NO	YES
OXALIC	YES	YES	COEL. OXAL,SO4,NO3,*
CITRIC	YES	COELUTE/ SO4, << SO4	YES
MS	YES	YES (END OF WATER DIP)	NO
HOMS	YES	YES	NO
HYDROFLUORIC	YES	NO	YES
HYDROCHLORIC	YES	YES	NO
NITROUS	YES	YES	NO
NITRIC	YES	YES	NO
SULFURIC	YES	YES AS >> SENS THAN CIT	NO
PHOSPHORIC	YES	YES	NO
ANALYSIS TIME	**16 MINUTES**	**10 MINUTES**	**19 MINUTES**

* and H_3PO_4, HCl, HNO_2, MS, HOMS.

Table 8. Comparison of detection limits, in ppm, based on 50 μL sample loop

ACIDS	ANION EXCHANGE GRADIENT MODE	ANION EXCHANGE ISOCRATIC MODE	ION EXCLUSION ION EXCLUSION MODE
FORMIC	0.04	--	0.4
ACETIC	0.06	--	0.2
GLYCOLIC	0.04	--	0.2
PROPIONIC	0.06	--	0.3
LACTIC	--	--	0.3
BUTYRIC	0.07	--	0.4
OXALIC	0.07	0.20	--
CITRIC	0.07	--	0.4
MS	0.05	0.05	--
HOMS	0.08*	0.25	--
HF	0.01	--	0.1
HCL	0.02	0.015	--
HNO_2	0.01	0.01	--
HNO_3	0.01	0.01	--
H_2SO_4	0.04	0.04	--
H_3PO_4	0.03	0.03	--

* 0.08 is for succinic acid. The limit was not determined for HOMS as it coelutes with succinic.

Table 9. **Sensitivity ratio and detection limit ratio for gradient (G) vs. ion - exclusion (IE) and gradient (G) vs. isocratic (ISO) based on 50 μL sample loop**

ACIDS	GRADIENT VS. ION - EXCLUSION		GRADIENT VS. ISOCRATIC	
	SENSITIVITY RATIO (G/IE)	DETECTION LIMIT RATIO (IE/G)	SENSITIVITY RATIO (G/ISO)	DETECTION LIMIT RATIO (ISO/G)
NITROUS	---	---	5.3	1.0
NITRIC	---	---	5.0	1.0
HYDROCHLORIC	---	---	2.8	0.75
HYDROFLUORIC	15.4	10.0	---	---
SULFURIC	---	---	5.9	1.0
PHOSPHORIC	---	---	5.3	1.0
OXALIC	---	---	12.5	2.9
FORMIC	7.0	10.0	---	---
GLYCOLIC	11.8	5.0	---	---
HOMS	---	---	*9.1	*2.1
ACETIC	8.0	3.3	---	---
LACTIC	---	---	---	---
CITRIC	6.6	5.7	---	---
METHANESULFONIC	---	---	1.0	1.0
PROPIONIC	11.0	5.0	---	---
BUTYRIC	16.2	5.7	---	---

* Values from the gradient method are for succinic acid. The sensitivity and detection limit for HOMS were not determined as HOMS coelutes with succinic in the gradient method.

Table 10. Comparison of precision, RSD, for Sibley water and (EU-ANI-1) recovery studies

ACIDS	ANION EXCHANGE GRADIENT MODE	ANION EXCHANGE ISOCRATIC MODE	ION EXCLUSION ION EXCLUSION MODE
FORMIC	7.3 (8.3)	--	16.4 (13.1)
ACETIC	5.3 (10.8)	--	11.5 (6.6)
GLYCOLIC	2.5 (9.7)	--	20.0 (13.8)
PROPIONIC	1.7 (10.0)	--	14.6 (8.4)
LACTIC	--	--	12.9 (23.4)
BUTYRIC	2.1 (6.7)	--	31.0 (12.9)
OXALIC	0.9 (2.4)	6.9 (2.1)	--
CITRIC	3.2 (2.0)	--	5.9 (8.2)
MS	3.9 (3.6)	8.4 (1.6)	--
HOMS	4.3 (2.1)*	1.3 (1.3)	--
HF	4.0 (7.3)	--	17.3 (8.8)
HCL	6.1 (6.2)	4.9 (5.4)	--
HNO_2	12.9 (2.0)	4.2 (2.3)	--
HNO_3	1.9 (1.7)	2.7 (5.9)	--
H_2SO_4	2.2 (1.9)	2.1 (2.6)	--
H_3PO_4	3.8 (3.0)	1.8 (4.2)	--

* Values for succinic acid.

Table 11. Comparison of accuracy, % recovery, for Sibley water and (EU-ANI-1) recovery studies.

ACIDS	ANION EXCHANGE GRADIENT MODE	ANION EXCHANGE ISOCRATIC MODE	ION EXCLUSION ION EXCLUSION MODE
FORMIC	94 (94)	--	97 (86)
ACETIC	103 (96)	--	99 (108)
GLYCOLIC	98 (103)	--	103 (102)
PROPIONIC	106 (106)	--	103 (105)
LACTIC	--	--	101 (122)
BUTYRIC	103 (102)	--	105 (100)
OXALIC	108 (100)	97 (99)	--
CITRIC	106 (100)	--	106 (106)
MS	108 (101)	105 (102)	--
HOMS	104 (99)*	98 (95)	--
HF	106 (110)	--	100 (96)
HCL	105 (105)	98 (97)	--
HNO_2	106 (104)	96 (100)	--
HNO_3	100 (95)	97 (103)	--
H_2SO_4	99 (99)	100 (103)	--
H_3PO_4	104 (99)	98 (102)	--

* Values for succinic acid.

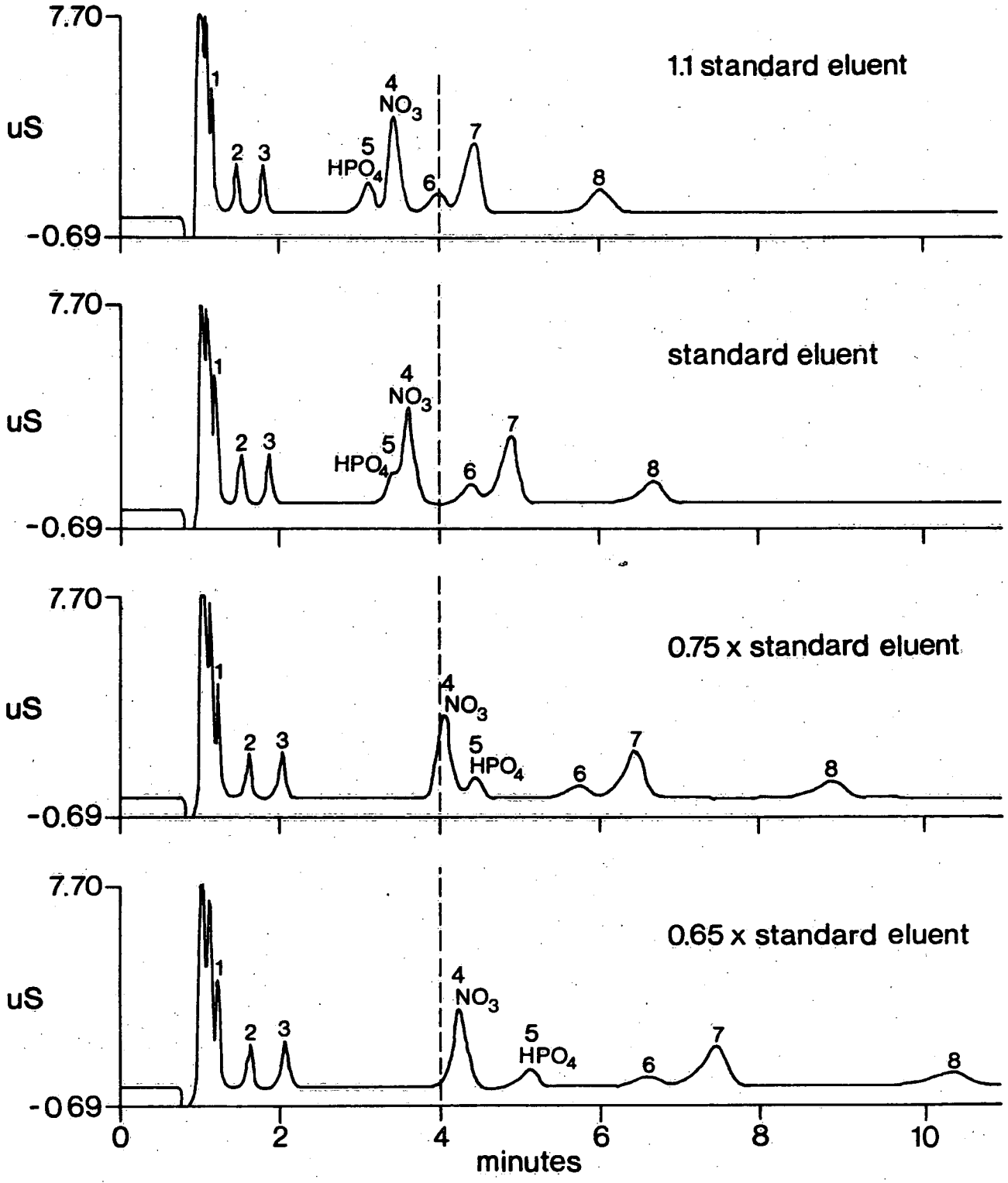

Figure 1 Elution patterns at four different eluent strengths:
1= methanesulfonate (2.5 ppm); 2= chloride (.5 ppm);
3= Nitrite (.5 ppm); 4=NO_3(1ppm); 5=HPO_4(1ppm);
6=HOMS (5 ppm); 7= SO_4 (2.5 ppm); 8= OXAL (2.5 ppm)

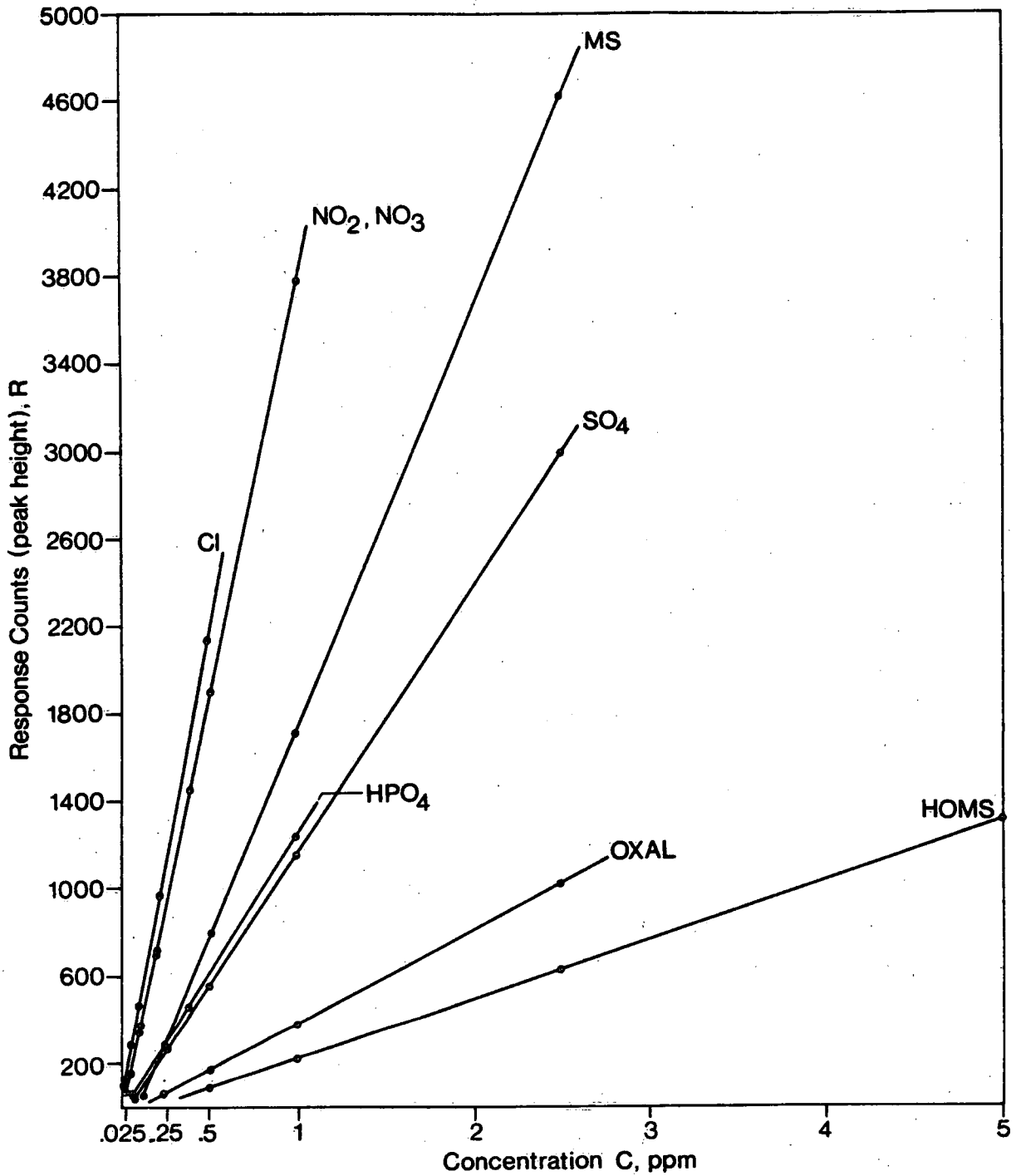

Figure 2 Sensitivity of the acids studied. Concentration regression equations (r= correlation coefficients) are:

Cl= -0.016 + 0.0002373R (r= .9990);
NO_2= 0.0087 + 0.0002567R (r= .9990);
NO_3= 0.0081 + 0.0002622R (r= .9999);
MS= 0.106 + 0.0004976R (r= .9998);
HPO_4= 0.02134 + 0.0007822R (r= .9998)
SO_4= 0.015 + 0.000833R (r= .9997);
OXAL= 0.08577 + 0.002346R (r= 1.0000);
HOMS= 0.1463 + 0.003684R (r= .9999)

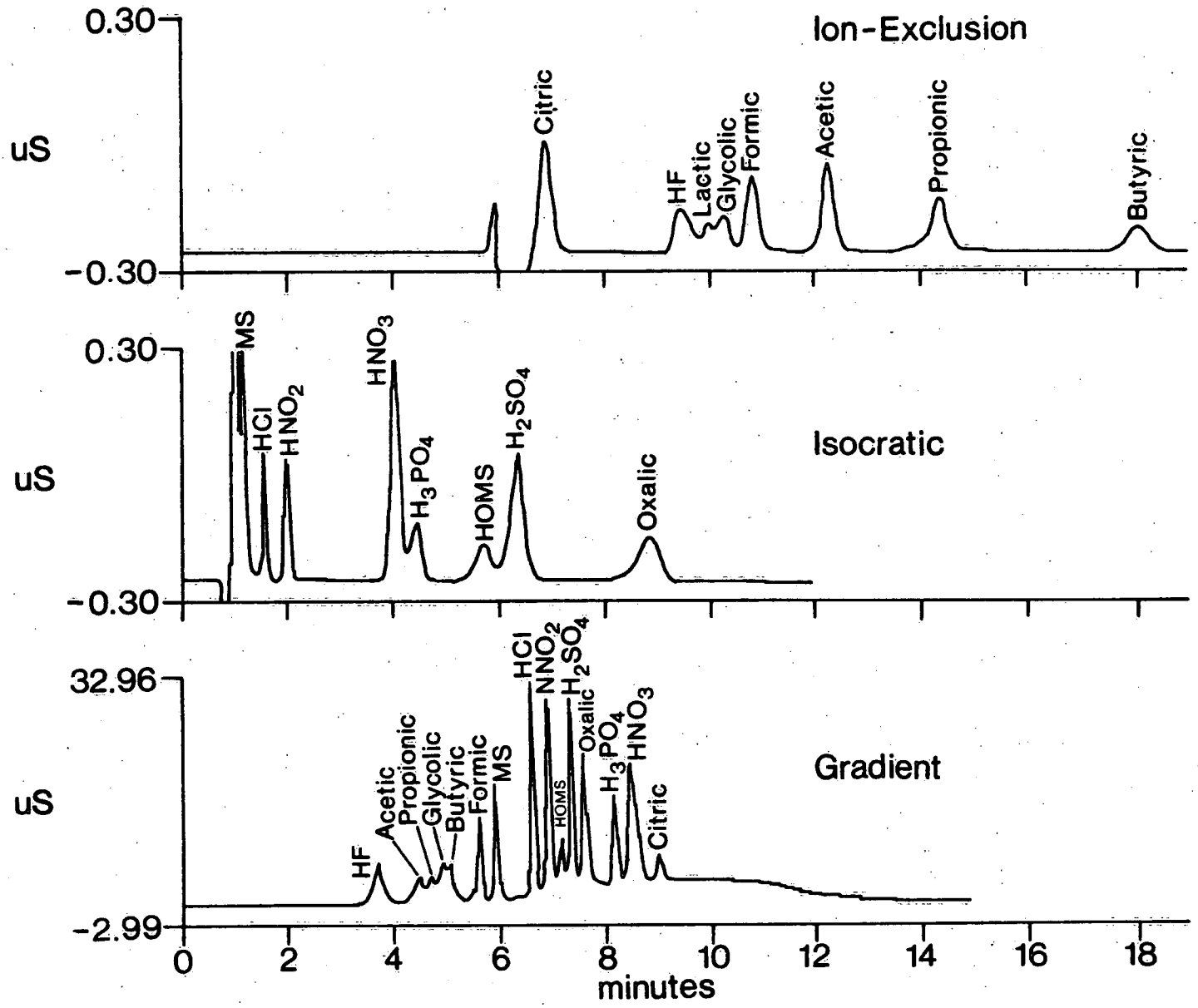

Figure 3 Analytes and analysis time for the 3 methods- Ion-exclusion, Isocratic anion and gradient anion chromatographies

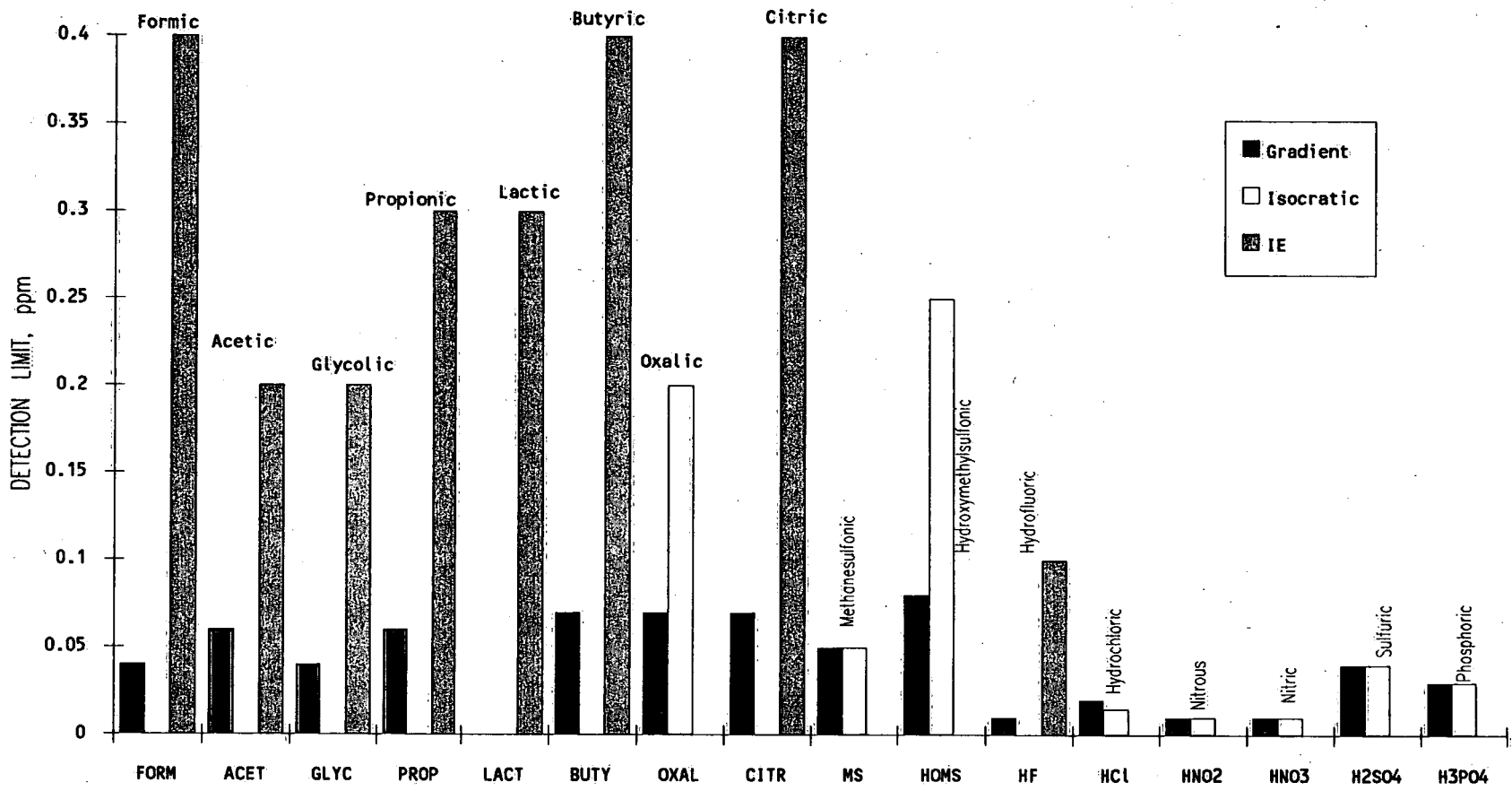

FIGURE 4. COMPARISON OF DETECTION LIMITS

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