ELSEVIER

Journal of Chromatography A, 739 (1996) 273–280

JOURNAL OF CHROMATOGRAPHY A

Determination of organic acids in industrial streams by ion chromatography after solid-phase extraction

Jian Chen

ARCO Chemical Company, 3801 West Chester Pike, Newtown Square, PA 19073, USA

Abstract

Organic acids are frequently found in various industrial streams. Historically, ion-exclusion chromatography has been the method of choice for organic acid analyses. However, because of the gel-type packings used and the large column diameter required, ion-exclusion chromatographic methods are usually associated with relatively low column efficiency and moderate detection sensitivity. Furthermore, due to the separation mechanism, gradient elution is not practical in ion-exclusion chromatography. Hence, simultaneous separation of a wide range of organic acids by ion-exclusion chromatography becomes difficult. Ion-exchange chromatography based on high-performance column packings, on the other hand, offers excellent column efficiency, high detection sensitivity and wide separation capacity. In this work, we report a gradient method using an anion-exchange column. Using this method, mono-, di- and tricarboxylic acids, aromatic acids and inorganic anions can be routinely separated in a single run. To avoid interferences from a variety of organic matrices, a sample preparation procedure based on solid-phase extraction has been devised in conjunction with this method.

Keywords: Process monitoring; Organic acids; Inorganic anions

1. Introduction

Organic acids are the oxidation or degradation products of various organic molecules. As a result, they can be found in many organic reaction mixtures and even in final products. The benefits of being able to determine organic acids in industrial streams are manyfold. Interpreting reaction mechanisms, optimizing reaction conditions, assessing potential corrosion problems and determining effects of acids on application processes are just a few examples.

To determine the total amount of organic acids, acid–base titration has been the method of choice. Alternatively, chromatographic methods can provide not only the measurement of total acidity, but also the identification of the organic acids present. Traditionally, most organic acid methods found in the literature [1–7] have been based on ion-exclusion chromatography. However, there are several drawbacks associated with this technique, including low sensitivity, inadequate limit of detection and inability to perform gradient elution. Additionally, inorganic anions are frequently present in industrial samples. Because they elute at the void volume on an ion-exclusion chromatographic column, a second method must be utilized if they are to be analyzed.

Ion-exchange chromatography (IEC), on the other hand, is much more efficient and versatile. In recent years, new ion-exchange columns, such as Dionex IonPac AS11 and OmniPac PAX-500, which offer improved efficiency and selectivity, have become available. As a result, a number of environmental and food applications based on ion-exchange separation of organic acids have been published [8–19].

0021-9673/96/$15.00
PII S0021-9673(96)00036-2

However, the analysis of organic acids in matrices consisting of mostly organic materials has not been found.

One of the problems often encountered in organic acid determination, regardless of the technique used, is the interferences from the sample matrices. This is especially the case for industrial samples, which are usually very complex in composition. Sample matrices can be adsorbed onto the column, effecting column performance and shortening column life. Water soluble organic compounds can sometimes co-elute with organic acids and yield system peaks that interfere with organic acid detection. Esters can hydrolyze in both acidic and basic eluents and release additional acid anions. Therefore, it is desirable to remove the organic matrices before analysis by either ion-exclusion chromatography or IEC.

In this work, a simultaneous separation of organic and inorganic anions on an anion-exchange column is described. A solid-phase extraction (SPE) procedure for the removal of organic sample matrices, using a polymeric reversed-phase cartridge, is proposed. The method has proven to be both sensitive and rugged. A variety of complex industrial samples have been successfully analyzed using this method.

2. Experimental

2.1. Reagents and standards

Whenever possible, organic acid salts, purchased from Aldrich (Milwaukee, WI, USA), were used to prepare standard solutions without further purification. When a salt was not available, the corresponding organic acid was neutralized using 1 *M* NaOH before the standard solution was made. A 50% (w/v) NaOH solution, used to prepare the eluents, was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Type I reagent-grade (DI) water (with a specific resistance of 17.8 MΩ·cm or greater) was obtained with a Nanopure water purification system from Barnstead (Dubuque, IA, USA).

2.2. Instrumentation

All experiments were conducted on a Dionex DX-300 ion chromatography system (Dionex, Sunnyvale, CA, USA), consisting of a quaternary AGP advanced gradient pump, an AS-3500 autosampler and a PED-2 pulsed electrochemical detector in conductivity mode. The system was controlled by a Dell 425 s/L personal computer, equipped with Dionex AI-450 chromatography software. Chromatographic data were collected on a VG Data Systems' (Chesire, UK) Multichrom (Version 2.0) data system. A Dionex ATC-1 anion trap column (24×9 mm) was placed immediately after the pump gradient mixer to smooth the baseline. A Dionex IonPac AG11 guard column (50×4 mm) and a Dionex OmniPac PAX-500 analytical column (250×4 mm) were used in series for the separation. A Dionex anion self-regenerating suppressor (ASRS, 4 mm) was used in recycle mode to reduce eluent background conductivity. A Baker-10 SPE System (J.T. Baker, Phillipsburg, NJ, USA) was employed for the SPE process.

A comparison with ion-exclusion chromatography was made by using a Dionex ICE-AS1 column (250×9 mm), a 1 m*M* HCl eluent, a 1 ml/min flow-rate and a 25-μl injection volume. A suppressor column (15×9 mm), consisting of a cation-exchange resin in Ag^+ form, was placed before the conductivity detector to reduce the background signal of the eluent.

2.3. Sample preparation

Organic samples (typically 0.05 to 0.1 g, depending on the acid concentration) were added to 10.00 ml of DI water together with 0.25 ml of 200 m*M* $NaHCO_3$ buffer and shaken briefly to mix, shortly before SPE. The solution was then passed through a Dionex OnGuard-RP cartridge pretreated with 10 ml of methanol and washed with 10 ml of DI water [20]. The first 3 ml of sample were discarded before a 1-ml sample was collected for analysis. Various C_{18} SPE cartridges (see Table 2) have also been tested using the above procedure.

2.4. Column cleaning and system equilibration

The following procedure, not recommended by the column manufacturer, was used without any noticeable problem. When a new PAX 500 column was received, it was washed with an aqueous solution containing 20% (v/v) acetonitrile (ACN) for 1 h at a flow-rate of 1 ml/min. The ACN was then washed off the column with DI water for 30 min at the same

Table 1
NaOH step gradient for the simultaneous separation of organic and inorganic anions on a Dionex PAX-500 column

Time (min)	%Eluent 1 (DI water)	%Eluent 2 (1 m*M* NaOH)	%Eluent 3 (5 m*M* NaOH)	%Eluent 4 (200 m*M* NaOH)	Eluent concentration NaOH (m*M*)
0	65	35	0	0	0.35
9.5	65	35	0	0	0.35
12.0	90	0	10	0	0.5
15.0	0	0	100	0	5.0
25.0	0	0	94	6	16.7
30.0	78	0	0	22	44
33.0[a]	78	0	0	22	44

[a] Late-eluted acids, such as citric and sebacic acid, require the last gradient step to be held for an additional 5 min.

flow-rate. Before each run, the impurity anions accumulated from the previous run were removed by first disconnecting the ATC column from the autosampler and washing it with 100 m*M* NaOH for 30 min at a flow-rate of 2 ml/min. Then, the ATC column was re-connected and the columns were washed with 100 m*M* NaOH for about 1 h at a flow-rate of 1 ml/min. Finally, with the suppressor and the detector turned on, the entire system was equilibrated with the initial eluent for at least 1 h. The gradient program employed in the method is listed in Table 1.

2.5. Eluent preparation

DI water was degassed using a combination of vacuum and magnetic stirring for at least 30 min. The water was then sparged with helium for 10 min to further remove CO_2. A 200 m*M* NaOH solution was prepared by pipeting 10.2 ml of a 50% NaOH solution into a solvent reservoir containing 1 l of DI water. The solution was thoroughly mixed by continuing to sparge He through it for at least 10 min. The 5 m*M* and 1 m*M* NaOH eluents were prepared by diluting the 200 m*M* NaOH, following the same mixing procedure.

3. Results and discussion

3.1. Column

Initially, a Dionex IonPac AS11 column had been considered. Using a NaOH gradient, this column provides excellent resolution of most organic acids and inorganic anions. It is also totally compatible with common organic solvents. However, formate and butyrate co-elute on this column. Because it was very likely for a sample to have both acids, this column was deemed unacceptable for our purposes.

A Dionex OmniPac PAX-500 column (250×4 mm) coupled with a Dionex IonPac AG11 guard column (50×4 mm) was found to allow almost baseline separation of acetate, propionate, butyrate, formate, and nine other organic acids commonly found in our samples (Fig. 1). Eight inorganic anions were also separated within the same run. This kind of separation was not possible for ion-exclusion chromatography. The use of an AG11 guard column delays the elution of propionate and butyrate and, therefore, improves the separation between acetate,

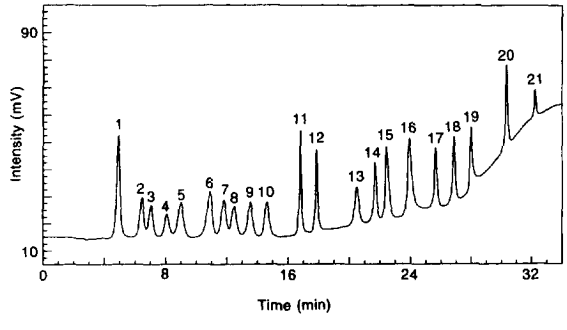

Fig. 1. Separation of thirteen organic acids and eight inorganic anions on a Dionex OmniPac PAX-500 column. Injection volume was 10 μl. Other chromatographic conditions are given in Section 2. Peaks: 1=fluoride (5 ppm), 2=acetate (10 ppm), 3=propionate (10 ppm), 4=butyrate (10 ppm), 5=iso-valerate (20 ppm), 6=formate (10 ppm), 7=valerate (20 ppm), 8=iso-caproate (20 ppm), 9=pyruvate (20 ppm), 10=*sec.*-caproate (20 ppm), 11=chloride (5 ppm), 12=nitrite (10 ppm), 13=benzoate (20 ppm), 14=bromide (10 ppm), 15=nitrate (10 ppm), 16=carbonate, 17=malonate (10 ppm), 18=sulfate (5 ppm), 19=oxalate (10 ppm), 20=phthalate (20 ppm) and 21=phosphate (10 ppm).

propionate and butyrate. The PAX-500 column is also solvent compatible and offers excellent column-to-column reproducibility. With the exception of the example shown in Fig. 2, all of the data presented in this work have been obtained with a PAX-500 column coupled with an AG11 column.

According to the column manufacturer, at least 1% organic solvent should be used in the eluents for a PAX-500 column [21]. We have found that the use of 1% organic solvent (ACN) caused noticeable peak-broadening and thus lowered the column efficiency. The use of organic solvent also made it unacceptable to recycle the eluent as the regenerant for the ASRS. Instead, an external DI water supply must be set up and used [22], making it more cumbersome to operate the system. The use of 100% aqueous eluents, on the other hand, has allowed us to obtain sharp peaks and operate the ASRS in recycle mode. No noticeable problems have been encountered without using the 1% organic solvent. On average, a column can last for at least six months, or about 1500 sample injections. The 100% aqueous eluent is also more environmentally friendly and costs less to be disposed of.

3.2. Solid-phase extraction

As was discussed in Section 1, organic sample matrices must be removed prior to the chromatographic separation. Fig. 2a shows a sample chromatogram containing matrix peaks interfering with the detection of *p*-toluenesulfonic acid (PTSA). Fig. 2b shows the chromatogram of the same sample after matrices were removed by SPE. Another major concern has been the esters which are frequently found in many organic reaction mixtures containing organic acids. Since esters hydrolyze easily in NaOH eluents used for the gradient elution, higher acid numbers have been observed if esters were not removed before injection. Fig. 3a shows a prominent acetate peak as a result of the hydrolysis of 2-propanol acetate on-column. No acetate was detected after 2-propanol acetate was removed by SPE (Fig. 3b).

A polymeric RP and four C_{18} cartridges from different sources were evaluated for the removal of organic matrix, using six model compounds (Table 2). In this approach, an aqueous buffer solution containing the organic acid anions and the sample matrices is passed through an SPE cartridge. The acid anions have little affinity for the reversed-phase packing and are carried through by the aqueous buffer, while neutral organic matrices are adsorbed onto the cartridge. The Dionex OnGuard-RP cartridge was selected for our method because it removed quantitatively almost all of the test compounds. The superior performance offered by this cartridge is likely to be a result of its more hydrophobic polymeric packing, based on styrene–divinylbenzene [20].

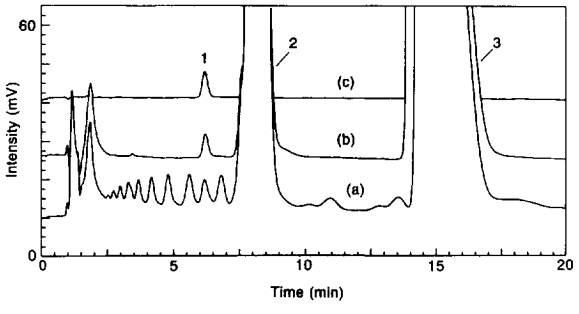

Fig. 2. Removal of sample matrices by solid-phase extraction (SPE) using a Dionex OnGuard-RP cartridge and a 5 m*M* $NaHCO_3$ buffer at pH 8.5. Column, Dionex IonPac AS4A, 250×4 mm; Eluent, 1.7 m*M* $NaHCO_3$–1.8 m*M* Na_2CO_3. Flow-rate, 1.0 ml/min; Detection, suppressed conductivity using ASRS in recycle mode. a=Sample before SPE; b=sample after SPE; c=*p*-toluenesulfonic acid standard. Peaks: 1=*p*-toluenesulfonic acid, 2=maleic acid and 3=fumaric acid.

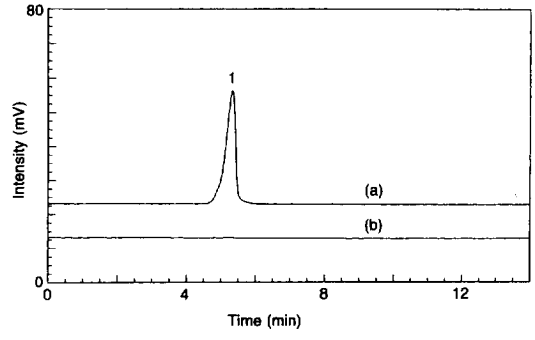

Fig. 3. Removal of esters by SPE using a Dionex OnGuard-RP cartridge and a 5 m*M* $NaHCO_3$ buffer at pH 8.5. a=Before SPE, acetate was detected as a result of hydrolysis of 2-propanol acetate on-column. b=after SPE, no acetate was detected, indicating total removal of 2-propanol acetate. Chromatographic conditions are the same as those given in Fig. 1. Peak: 1=acetate.

Table 2
Removal of organic compounds by various SPE cartridges

Type of SPE cartridge	% Removal[a] (n=3)					
	Ethyl acetate[b]	MBA[c,d]	MBA formate[d]	Acetophenone[d]	Ethyl benzene[d]	TBHP[b,e]
Dionex OnGuard-RP	100	100	100	100	100	85
Waters Sep-Pak Plus	19	80	75	100	100	10
Rainin Spice C_{18}	65	85	100	100	100	35
Alltech Maxi-Clean C_{18}	88	90	100	100	100	40
Alltech Maxi-Clean IC-RP	7	11	17	20	90	5

[a] Organic compounds (0.1 g) were added individually to 10 ml of deionized water, shaken to mix, and allowed to equilibrate. The water layers were then passed through different SPE cartridges and analyzed by GC or HPLC for remaining organic compounds. The percentage removal was then calculated based on the organic content in the water layer before and after SPE.
[b] Determined by GC.
[c] α-Methylbenzyl alcohol.
[d] Determined by HPLC–UV.
[e] *tert.*-Butyl hydroperoxide.

Table 3 shows the recoveries of organic acids after SPE using a Dionex OnGuard-RP cartridge. Both the 5 m*M* $NaHCO_3$ buffer (pH 8.5) and the 5 m*M* NaOH solution (pH 11.7) offered close to 100% recoveries for C_1–C_4 acids at a level of 10 ppm. For samples of high acid content, the concentration of the buffer has to be adjusted accordingly to maintain the pH (8.5) necessary for the quantitative recovery of organic acids. For bigger acids, the recoveries using a 5 m*M* $NaHCO_3$ buffer become significantly lower than those obtained using 5 m*M* NaOH (Table 3). This requires pre-determination of the recovery for an individual acid and making adjustment during the final calculation. For most of our samples, acids bigger than C_4 were not present. Therefore, extensive studies on the recoveries of long-chain organic acids were not carried out.

Table 3
Recoveries of organic acids after SPE using Dionex OnGuard-RP cartridges

Organic acid	Recovery (%, n=5)[a]	
	5 m*M* $NaHCO_3$	5 m*M* NaOH
Formic acid	99	99
Acetic acid	101	102
Propionic acid	100	100
Butyric acid	96	100
Valeric acid	92	99
Isocaproic acid	85	96
Oxalic acid	102	102
Malonic acid	95	101
Benzoic acid	94	97
Phthalic acid	98	100

[a] Solution containing 10 ppm of each organic acid was used. The SPE procedure is given in Section 2.

For samples containing esters, the 5 m*M* $NaHCO_3$ buffer does offer an advantage over the 5 m*M* NaOH solution. Because esters hydrolyze very slowly in the 5 m*M* $NaHCO_3$ buffer, they can be quantitatively removed by SPE prior to analysis. The hydrolysis speed of esters in 5 m*M* NaOH, on the other hand, was too fast to ensure the total removal of the esters. This means that the 5 m*M* NaOH can only be used if the sample does not contain esters. Another possible application of the NaOH system would be the analysis of esters. Fig. 4a represents free organic acids in a sample after esters were removed by SPE using the 5 m*M* $NaHCO_3$ buffer. Fig. 4b shows the increase in organic acid peak height after the sample was treated with 10 m*M* NaOH for 1 h. This increase was due to the additional acid anions released from the hydrolyzed esters.

3.3. Sensitivity, limit of detection, linearity and reproducibility

As listed in Table 4, the sensitivity and LOD of the ion-exchange method were about 10- and 100-times better, respectively, than those of ion-exclusion

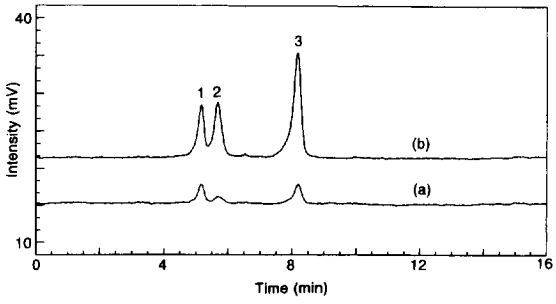

Fig. 4. Determination of esters by ion chromatography. a=Sample with esters removed by SPE using a Dionex On-guard RP C_{18} cartridge and a 5 m*M* $NaHCO_3$ buffer at pH 8.5. b=Sample with esters hydrolyzed using 10 m*M* NaOH. Chromatographic conditions are the same as those given in Fig. 1. Peaks: 1=acetate, 2=propionate and 3=formate.

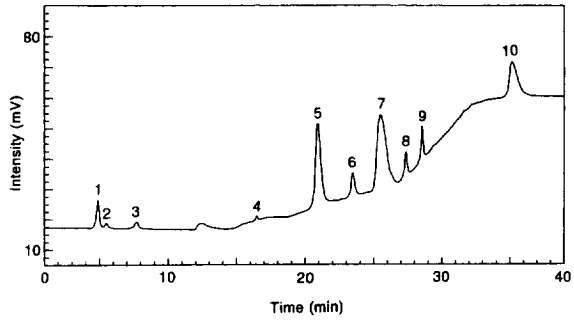

Fig. 5. Separation of a used coolant sample. Chromatographic conditions are the same as those given in Fig. 1. Peaks: 1=acetate, 2=iso-butyrate, 3=formate, 4=chloride, 5=benzoate, 6=nitrate, 7=carbonate, 8=succinate, 9=sulfate and 10=sebacate

chromatography. As mentioned in Section 1, these improvements can be attributed to a combination of more efficient column packing, smaller column diameter and a more efficient ASRS. As a result, the ion-exchange method permits much better peak shape and lower background conductivity. With a typical 10 μl injection, the LOD (expressed in concentration) is in the order of 0.1 ppm for organic acids. If a lower concentration range is desirable, a larger injection volume can be employed. The calibration curves for all tested compounds shown in Fig. 1 were found to be linear within 0–50 ppm. This permits a sample concentration of an individual acid up to 5000 ppm, using the typical 10 μl injection. At acid levels higher than 100 ppm (before dilution), the same-day reproducibility of the method was better than ±6%, while the day-to-day and operator-to-

Table 4
Sensitivity and limit of detection by ion-exchange and ion-exclusion methods

Analyte	Limit of detection[a] (ng)		Sensitivity (area count/ng)	
	Ion-exchange	Ion-exclusion[b]	Ion-exchange	Ion-exclusion[b]
Fluoride	0.1	- -[c]		
Chloride	0.2	- -		
Bromide	1	- -		
Nitrite	0.5	- -		
Nitrate	1	- -		
Sulfate	0.5	- -		
Phosphate	1	- -		
Formate	0.5	50	$12 \cdot 10^3$	$1.8 \cdot 10^3$
Acetate	1	100	$7.4 \cdot 10^3$	$0.63 \cdot 10^3$
Propionate	1	100	$6.7 \cdot 10^3$	0.56·10
Butyrate	2	100	$5.2 \cdot 10^3$	$0.44 \cdot 10^3$
Valerate	2	- -		
Isocaproate	2	- -		
Pyruvate	2	- -		
Oxalate	1	- -		
Malonate	1	- -		
Benzoate	2	- -		
Phthalate	2	- -		

[a] Based on S/N=3.
[b] See Section 2.
[c] Could not be determined by the method used.

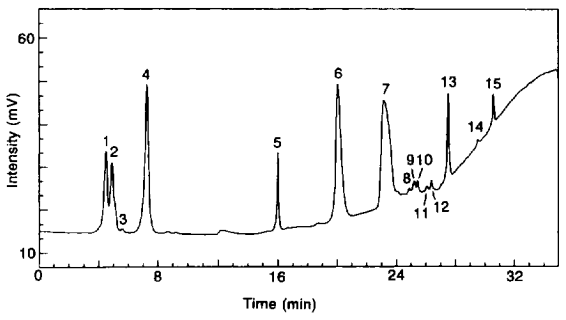

Fig. 6. Separation of a plant bottom stream. Chromatographic conditions are the same as those given in Fig. 1. Peaks: 1=acetate, 2=propionate, 3=butyrate, 4=formate, 5=chloride, 6=benzoate, 7=carbonate, 8=succinate, 9=glutarate, 10=malonate, 11=maleate, 12=sulfate, 13=oxalate, 14=phthalate and 15=molybdate.

operator reproducibilities were about ±10%. Column-to-column reproducibilty and performance have been excellent during the past two years.

3.4. Sample analysis

More than fifteen different sample types have been analyzed using this method. These include organic reaction mixtures, process development streams, plant streams, final products, polymers, waste streams, liquid–liquid extraction fluids, incineration residuals, catalyst extracts, foam extracts, etc. In general, the sample matrices can be categorized into the following groups; water soluble organics, water insoluble organics, inorganic materials and polymers. For the first three types of samples, organic acids present can usually be extracted into the aqueous buffer without special sample treatment. For polymers, an organic solvent (such as methanol or tetrahydrofuran) should be used to dissolve the sample, to help in the extraction of the acids before SPE. Fig. 5 and Fig. 6 show the separation of a variety of organic acids and inorganic anions in a used coolant and in a plant bottom stream, respectively.

The accuracy of the method was evaluated by comparing the total acidity calculated from our method with that obtained using acid–base titration (Table 5). Four different sample types, including a synthetic control, of varying acid concentrations and ester contents, were analyzed and compared. In all cases, the total acidity numbers of both methods agreed well. This indicates that this method has good recovery of organic acids after SPE. It also confirms

Table 5
Comparison of total acidity by the ion-exchange method and by acid–base titration

Sample number & source	Organic acid found by IEC (ppm)								Total acidity (mequiv./g)	
	Formic	Acetic	Propionic	Butyric	Isobutyric	Oxalic	Malonic	Benzoic	Calculated by IEC	Titration
1, I	74	689							0.013	0.013
2, I	48	568							0.011	0.010
3, I	406	659							0.020	0.021
4, I	2680	6990							0.178	0.17
5, I	1680	4530							0.114	0.11
6, II	175	270	92		12				0.0097	0.011
7, II	1269	4040	188		2780				0.131	0.14
8, II	1150	4300	207		3410				0.140	0.14
9, II	18								0.00040	0.0005
10, II	20								0.00044	0.0005
11, III	7560	4950	4060	171	2150	6270	1030	1840	0.512	0.51
12, III	1190	2110	7650	927		521		171 000	1.59	1.65
13, III	54	21	1110					199	0.018	0.019
14, III	56	38	1060					243	0.018	0.019
15, III	6110	3100	2830		1991	5680	343		0.386	0.40
16, IV[a]	1410	2020		2360		1160		1820	0.134	0.13

[a] A synthetic control sample containing the following: formic acid, 1400 ppm; acetic acid, 2000 ppm; butyric acid, 2450 ppm; oxalic acid, 1150 ppm; benzoic acid, 1900 ppm; ethyl acetate, 1.0 wt.%; 2-propanol formate, 1.0 wt.%; 2-propanol, 40 wt.%, α-methylbenzyl alcohol, 30 wt.%, ethyl benzene, 20 wt.% and acetophenone, 7.0 wt.%.

that esters can be effectively removed by SPE without being hydrolyzed in the $NaHCO_3$ buffer.

Acknowledgments

The author wishes to thank Jacqueline P. Williams, Katherine A. Velo and Melissa J. Zimmerman for their assistance in conducting some experiments.

References

[1] P.R. Haddad and P.E. Jackson, Ion Chromatography — Principles and Applications, Elsevier, Amsterdam, 1990, Ch. 7, p. 195 and Ch. 18, p. 593.
[2] D.T. Gjerde and J.S. Fritz, Ion Chromatography, Huthig, Heidelberg, 2nd ed., 1987, Ch. 10, p. 235.
[3] J.S. Fritz, J. Chromatogr., 546 (1991) 111.
[4] B.K. Glod and W.J. Kemula, J. Chromatogr., 366 (1986) 39.
[5] D.T. Gjerde and H. Mehra, Advances in Ion Chromatography, Vol. 1, Century International, Medfield, MA, 1989, p. 139.
[6] D.P. Lee and A.D. Lord, LC·GC, 4 (1987) 261.
[7] J.B. Morris and J.S. Firtz, LC·GC, 11 (1993) 513.
[8] A.A. Ammann and T.B. Ruttimann, J. Chromatogr. A, 706 (1995) 259.
[9] C. Scheuer, B. Wimmer, H. Bischof, L. Nguyen, J. Maguhn, P. Spitzauer, A. Kettrup and D. Waoner, J. Chromatogr. A, 706 (1995) 253.
[10] M.Y. Ding, H.K. Koizumi and Y. Suzuki, Anal. Sci., 11 (1995) 239.
[11] M.P. Cano, E. Torija, M.A. Marín and M. Cámara, Z. Lebensm Unters Forsch, 199 (1994) 214.
[12] S. Rabin, J. Stillian, V. Barreto, K. Friedman and M. Toofan, J. Chromatogr., 640 (1993) 97.
[13] M. Legrand, M.D. Angelis and F. Maupetit, J. Chromatogr., 640 (1993) 251.
[14] E.D. Zlotorzynska and J.F. Dlouhy, J. Chromatogr., 640 (1993) 217.
[15] R.D. Rocklin, C.A. Pohl and J.A. Schbler, J. Chromatogr., 411 (1987) 107.
[16] D.M. Davies and J.P. Ivey, Anal. Chim. Acta, 194 (1987) 275.
[17] J.P. Ivey and D.M. Davies, Anal. Chim. Acta, 194 (1987) 281.
[18] D. Brocco and R. Tappa, J. Chromatogr., 367 (1986) 240.
[19] C. Saigne, S. Kirchner and M. Legrand, Anal. Chim. Acta, 203 (1987) 11.
[20] Dionex, Installation Instructions and Troubleshooting Guide for the OnGuard Cartridges, 1995.
[21] Dionex, Installation Instructions and Troubleshooting Guide for the OMNIPAC PAX-500 ANALYTICAL COLUMN, 1993.
[22] Dionex, Installation Instructions and Troubleshooting Guide for the ASRS (4 mm), 1993.