ELSEVIER

Journal of Chromatography A, 781 (1997) 205–213

JOURNAL OF CHROMATOGRAPHY A

Analysis of organic acids in industrial samples Comparison of capillary electrophoresis and ion chromatography

Jian Chen*, Brett P. Preston, Melissa J. Zimmerman

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

Abstract

The determination of small organic acids in a variety of industrial samples by capillary electrophoresis was accomplished using a phthalate buffer and indirect UV detection. Various parameters affecting the analysis, including the composition and pH of the electrolyte, were optimized so that fast, sensitive and robust separation were possible. The sensitivity, limit of detection and reproducibility of the method were evaluated under optimized conditions. The method was found to be applicable to a wide variety of samples, ranging from simple aqueous solutions to complex plant organic streams. Comparison of this method to an ion chromatographic method used previously indicates that the CE technique offers a number of attractive features which significantly improve the efficiency and productivity of the organic acid analysis.

Keywords: Organic acids

1. Introduction

Organic acids are present in many industrial samples that originate from R&D, plant processes and finished products. In order to interpret reaction mechanisms, assess corrosion problems and determine the effects of acids on various applications, it is critical that a simple, fast and reliable analytical method is available to determine the organic acids in these samples.

Until a few years ago, organic acids have been commonly analyzed by chromatographic techniques, with ion chromatography (IC) and ion-exclusion chromatography (IEC) being the most commonly used. An IC method [1] was developed in this laboratory which allowed us to separate a total of 14 organic acids and 8 inorganic anions in a single, 40-min run. However, a solid-phase extraction (SPE) sample preparation step was required to remove the organic matrices prior to the IC analysis. This prolonged the overall analysis time and contributed additional error to the results. Extreme care had to be taken to prevent the NaOH eluent from being contaminated by CO_2. The IC column used was expensive and would only last for up to a few thousand injections. The combination of a long run time (40 min) and a fast flow rate (2 ml/min) required large volumes of eluents and limited the number of samples that could be analyzed during each run.

In recent years, capillary electrophoresis has emerged as an increasingly powerful separation tool that complements HPLC and IC. Many researches and applications concerning organic acid analysis have been reported in the literature [2–26]. A variety of UV active buffer systems, including those of

*Corresponding author.

0021-9673/97/$17.00
PII S0021-9673(97)00374-9

chromate [2–5], phthalate [6–12], benzoic acid derivatives [13–16] and other aromatic acids [17–19], have been employed. The detection of the organic acids was accomplished by indirect UV. Other UV transparent buffers [20–26], such as borate, phosphate and carbonate, have also been used in conjunction with direct UV detection. A wide range of samples, including inorganic materials [3,4], food and beverages [6–10,12], biological fluids [11,19,21,23,25,26] and environmental streams [15,20,22], have been analyzed. However, we were unable to find any paper that dealt with industry samples consisting of mostly organic materials.

The purpose of this work was to develop a "universal" CE method for the analysis of organic acids in a wide range of industrial samples, with minimal sample preparation and analysis time. In this paper, a CE method based on a phthalate buffer and indirect UV detection is described. Various aspects of the method, including speed, selectivity, sensitivity, reproducibility and ruggedness, have been investigated and compared with those of the IC method [1].

2. Experimental

2.1. Instrumentation

The experiments were performed on a Hewlett–Packard ^{3D}HPCE System (Hewlett–Packard, Wilmington, DE, USA), consisting of a photo-diode array detector and a 50-position autosampler. The system was controlled by a Hewlett–Packard Vectra XM Series 4 5/150 personal computer equipped with HP Chem Station software (Version 3.02). All data were collected on a VG Data Systems' (Cheshire, UK) Multichrom (Version 2.0) data system. All silica capillaries, autosampler vials and the buffer filtering system were purchased from Hewlett–Packard.

2.2. Chemicals

All chemicals were obtained from either Aldrich (Milwaukee, WI, USA) or Fisher Scientific (Ottawa, Canada) at the highest purity available and were used without further purification. All solutions, electrolytes and standards were prepared using deionized water (18.3 MΩ cm resistance), obtained by treating distilled water using a Barnstead (Dubuque, IA, USA) Nanopure water purification system.

2.3. Electrolytes and procedures

A 50 m*M* phthalate electrolyte concentrate was prepared by dissolving 4.128 g of phthalic acid in 25 ml methanol and 40 ml 1.0 *M* NaOH. The above solution was then diluted with about 300 ml DI water before 0.4755 g cetyltrimethylammonium bromide (CTAB) was added and dissolved. The pH of the solution was adjusted to 7.0 using 1.0 *M* NaOH before the total volume was brought to 500 ml. The 5 m*M* phthalate electrolyte used in most experiments was prepared by diluting the 50 m*M* concentrate using DI water.

Before each run, the buffer was degassed and filtered using the HP buffer degassing/filtering system. At the beginning of each run, the capillary was flushed with 1 *M* NaOH for 10 min, followed by DI water for 10 min and the 5 m*M* phthalate electrolyte for 10 min. Before each injection, the capillary was flushed with the BGE for 1.5 min. Both the inlet and outlet electrolytes were replenished after each injection. Vacancy (indirect) UV detection was made at 210 nm. To eliminate the need to switch the polarity of the data collection system in order to generate electropherograms with positive peaks, the "reference" wavelength was set at 210 nm (band width = 20 nm) and the "detection" wavelength was set at 340 nm (band width = 10 nm).

2.4. Experimental conditions

Unless specified otherwise, the conditions listed in Table 1 were used for all the experiments.

3. Results and discussion

3.1. Separation optimization

Initially, several electrolyte systems, including phthalic acid [6–12], 3,5-dinitrobenzoic acid [13] and 2,6-naphthalenedicarboxylic acid [18], were evaluated using a test mixture consisting of the

Table 1
Experimental conditions for the CE method

Instrument:	Hewlett–Packard ^{3D}HPCE
Voltage:	−20 kV
Capillary:	50 μm×45 cm bare silica
Electrolyte:	5 m*M* Phthalate+0.25 m*M* CTAB, pH 7.0
Injection size:	50 mbar, 10 s
Replenishing:	Every injection
Conditioning:	Electrolyte for 1.5 min, every injection
Detection:	Indirect UV.
	Detection wavelength=340 nm, BW=20 nm
	Reference wavelength=210 nm, BW=10 nm
Stop time:	4 min

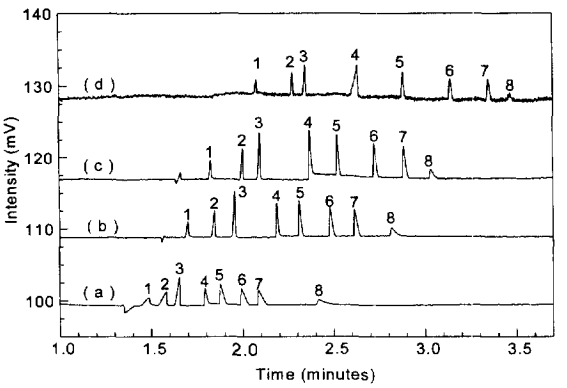

Fig. 1. Influence of phthalate concentration in electrolyte on separation. a=1 m*M* phthalate, b=5 m*M* phthalate, c=10 m*M* phthalate, d=25 m*M* phthalate. Peak identification: 1=oxalate, 2=malonate, 3=formate, 4=carbonate, 5=acetate, 6=propionate, 7=butyrate, 8=benzoate. Other conditions are given Section 2.

following acids: formic, acetic, propionic, butyric, oxalic, malonic and benzoic. The naphthalenedicarboxylic acid electrolyte did not provide desirable separation between butyric and benzoic acid. The 3,5-dinitrobenzoic acid system could not separate formic and malonic acid. Due to limited solubility in an aqueous media, these two acids were also more difficult to work with. Among the three, phthalic acid was the easiest to work with and gave the best overall separation of the above test mixture. Therefore, the phthalic acid system was chosen for our further investigations.

Most of the phthalate work reported previously [6–11] employed the conditions similar to [7]. These included 5 m*M* phthalate at pH 5.6, 0.5 m*M* OFM (osmotic flow modifier) and a detection wavelength of 254 nm. To ensure the optimized conditions are used for our applications, several important variables, including phthalate and CTAB concentration, electrolyte pH, organic modifiers and capillary dimensions, were systematically studied.

3.1.1. Concentration of phthalate

The concentration of the electrolyte can have a big impact on the baseline noise, sensitivity and linear dynamic range [2]. While most papers [6–10] reported using 5 m*M* phthalate, Weers et al. [12] reported using 25 m*M*. To find the optimal phthalate concentration, electrolytes containing 1, 5, 10 and 25 m*M* phthalate were tested using a set of standard mixtures containing 0.1, 0.5, 1, 5, 10, 20, 50 μg/ml each of the above seven organic acids. As shown in Fig. 1, the 1 m*M* phthalate buffer yielded relatively broad peaks, poor resolution and lower sensitivity. The linear dynamic range covered only from 0.1 to 20 μg/ml. At concentrations between 5 to 10 m*M*, both the signal-to-noise (*S/N*) ratio and peak efficiency reached a plateau. The *S/N* ratio was slightly lower at 10 m*M*, while the overall separation remained essentially the same. The linear dynamic range extended from 0.1 to 50 μg/ml. At 25 m*M*, the current rose from 5.6 μA at 5 m*M* to 28 μA and the baseline became excessively noisy. As a result, the *S/N* ratio dropped significantly. The gradual increase in migration time from 1 to 25 m*M* was probably due to the slowing down of the electroosmotic flow (EOF) as a result of the increased total ionic strength of the buffer.

3.1.2. Concentration of EOF modifier

Both tetradecyltrimethylammonium bromide (TTAB) [3–6,8,10] and CTAB [5,9,11–13] have been frequently used as a modifier to reverse the direction of EOF. By applying a negative voltage, the organic anions co-migrate with the EOF toward the detector situated at the anode end, thus speeding up the analysis. The effect of the modifier should be proportional to its concentration until an optimal concentration is reached. Concentration above the optimal concentration should be avoided to minimize the overall ionic strength of the electrolyte and to avoid the formation of micelles. Oefner [5] studied the influence of the chain length of the EOF modifiers on the separation of some organic and inorganic

anions. While both TTAB and CTAB yielded essentially the same selectivity and electrophoretic mobility, the latter provided a slightly better resolution between the test analytes. To determine the optimal concentration for our application, electrolytes consisting of 0.1 to 5 m*M* CTAB were prepared and a standard mixture was run under each concentration. At 0.1 m*M*, no organic acid peaks were detected, indicating the inability to reverse the EOF at such a low concentration. As shown in Fig. 2, between 0.25 and 2.0 m*M*, the separation remained essentially the same with the exception of benzoate, whose migration time increased from 2.83 to 3.08 min. This is most likely due to the interaction with the CTA^+ cations which migrate in the opposite direction of the EOF. A possible application of this phenomenon would be to improve the resolution of late-migrating acids through the use of higher EOF modifier concentrations.

3.1.3. Electrolyte pH

The pH of the electrolyte was varied from 5.5 to 11.0. At pH below 7.0, the oxalate peak suffered from severe broadening. The peak resolution was also not as good at pH 7.0 or above (Fig. 3). At pH above 9.0, the carbonate peak shifted forward and started to interfere with formate and malonate. Therefore, the optimal pH range was between 7.0 and 9.0. Another important factor to consider was the hydrolysis of the esters during the analysis. By using pH 7.0, at which the esters are much less likely to hydrolyze than at pH 9.0, the need to remove the esters by SPE [1] prior to the analysis was eliminated.

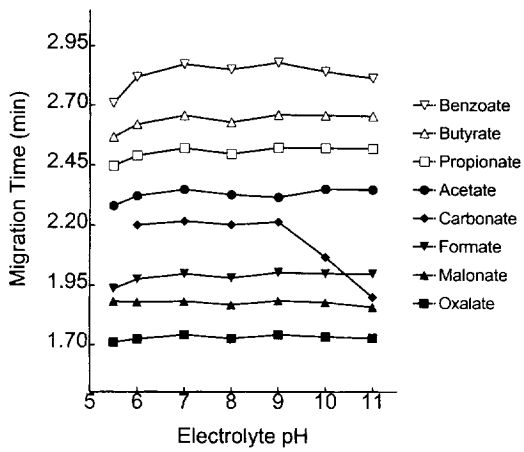

Fig. 3. Influence of electrolyte pH on separation. Separation conditions are given in Section 2.

3.1.4. Organic solvent

The effect of adding an organic solvent, such as methanol, to the electrolyte was investigated. Fig. 4 showed that when between 0 to 20% (v/v) methanol was added, the migration times increased almost

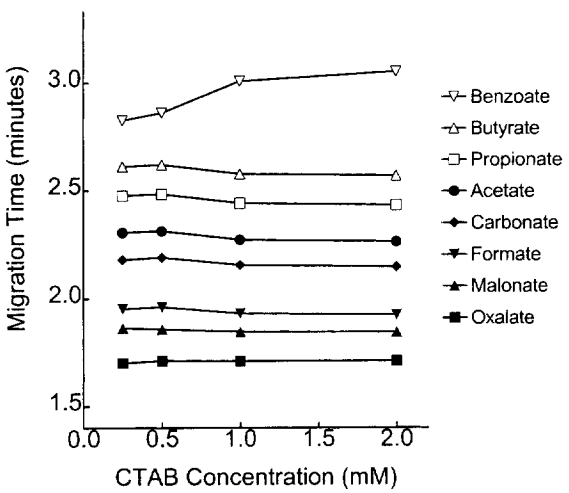

Fig. 2. Influence of CTAB concentration in electrolyte on separation. Separation conditions are given in Section 2.

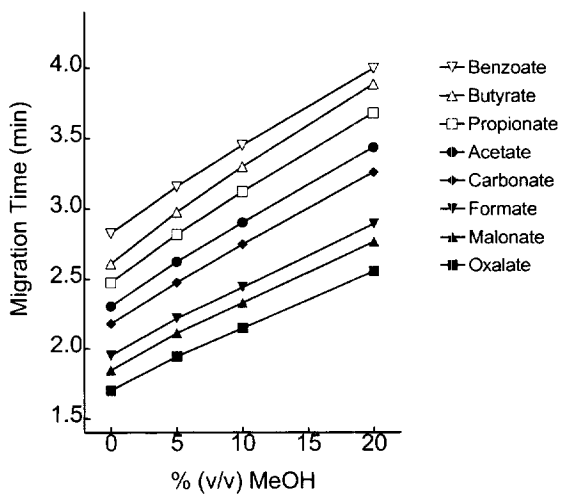

Fig. 4. Influence of methanol concentration in electrolyte on separation. Separation conditions are given in Section 2.

linearly. The degree of peak broadening for all peaks and peak tailing of the oxalate peak also increased. While resolution between most acids improved slightly with increased percentage of methanol, the resolution between butyric and benzoic acid deteriorated significantly. An electrolyte with 50% methanol was also tried, but the migration time became excessively long (>15 min) and the baseline became extremely wavy. Since all of the acids of interest have adequate solubility in the aqueous electrolyte, the addition of methanol was deemed unnecessary.

Based on the above experiments, an optimal electrolyte consisting of 5 m*M* phthalate at pH 7.0 and 0.25 m*M* CTAB was selected.

3.1.5. Capillary, sensitivity and limit of detection

In previous studies, capillaries of up to 100 cm in length [6–10] were used. To maximize the speed of analysis, we used only relatively short capillaries (48.5 cm total length, 40 cm effective length) with different inside diameters and detection path lengths. Fig. 5 shows three separations under the same conditions, using two 50 μm I.D. capillaries with and without extended light path (bubble cell), and a 75 μm I.D. capillary. The overall separation was about the same among the three capillaries. Instead of a two-fold increase in sensitivity as predicted by the extended light path [27], the bubble cell provided about a 1.2-fold increase in sensitivity. Except for the oxalate, only a slight increase in peak broadening was observed for other acids. The 75 μm I.D. capillary also provided about a 1.5-fold increase in sensitivity, presumably as a result of both increased sample size and detection path length. As evidenced by the shifting of the benzoate peak, the selectivity of the 75 μm I.D. capillary was slightly different from the 50 μm I.D. capillaries. The overall peak width at half height, however, was about 30–40% broader than the 50 μm I.D. capillaries, as predicted by the following dispersion equation [28]:

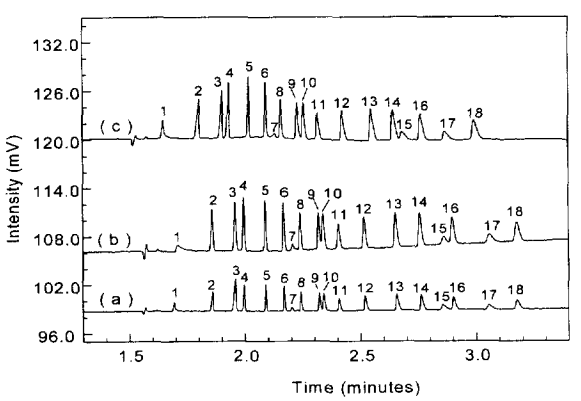

Fig. 5. Separation of 17 organic acids using capillaries of different dimensions. All capillaries are of 48.5 cm total length (40 cm effective length). a=50 μm I.D. capillary, b=50 μm I.D. capillary with extended light path (150 μm), c=75 μm I.D. capillary. Peak identification (concentrations are 5 ppm each unless given otherwise): 1=oxalate, 2=malonate, 3=formate, 4=succinate, 5=glutarate, 6=adipate, 7=carbonate, 8=pemilate, 9=suberate, 10=acetate, 11=acrylate (10 ppm), 12=propionate, 13=butyrate, 14=valerate, 15=benzoate (10 ppm), 16=hexanoate, 17=hydrocinnamate (10 ppm), 18=2-ethyl hexanoate (10 ppm). Other conditions are given in Section 2.

$$\sigma_T^2 = \sigma_{DIF}^2 + \sigma_{INJ}^2 + \sigma_{TEMP}^2 + \sigma_{ADS}^2 + \sigma_{DET}^2 + \sigma_{EDSP}^2$$

where the σ represents the variance and the subscripts refer to total, diffusion, injection, temperature gradient, adsorption, detection and electrodispersion, respectively. This suggests a decrease in overall efficiency when switching from a 50 μm I.D. to a 75 μm I.D. capillary. Since sensitivity was not an issue for most of our applications, a 48.5 cm×50 μm capillary was used throughout this work.

Using conditions outlined in Table 1, the absolute limit of detection for most acids tested was about 0.1–0.2 μg/ml (or about 1–2 pg based on the estimates provided in [28]). This is comparable to what we were able to achieve using IC [1]. If additional sensitivity is desirable, one can employ either a bigger injection size of up to 50 mbar×50 s, or a capillary of a larger inside diameter equipped with a bubble cell. Another method to improve sensitivity is to use electrokinetic injection. However, this injection technique is less reproducible because of its dependency on sample matrix. To maintain good reproducibilities for our applications, only hydrodynamic injections were used.

3.1.6. Detection wavelength

Most of the previous phthalate work [6–10] utilized 254 nm as the detection wavelength. The diode-array detector on our instrument allowed us to use 210 nm as the detection wavelength at which the absorptivity is about three times that at 254 nm.

Hence, a two-fold improvement in sensitivity was realized by using 210 nm as the detection wavelength.

3.2. Sample analysis

3.2.1. Sample preparation

One of the biggest advantages of the CE method, compared to the IC method [1] used previously, is the simplified sample preparation. Water-soluble organic compounds can result in interfering peaks on a conductivity detector used for IC. Esters will hydrolyze in the NaOH eluent to form additional acid anions and yield elevated acid numbers. As a result, organic matrices must be removed by SPE prior to the IC analysis [1]. Although the SPE procedure worked effectively, the sample preparation was tedious and time consuming. It also added additional variances to the overall analysis.

Conversely, only a simple sample dilution in deionized (DI) water was required by the CE method. With a 1:100 dilution used typically, all of the acids of interest were found to have sufficient solubility and distribution coefficients that allow them to be quantitatively extracted into the water phase. Table 2 shows quantitative recoveries were obtained for butyric, benzoic and sebacic acid which, were spiked into iso-propyl alcohol at a concentration range between 0.03–1.5% (w/w). The small amount [≤1% (w/w)] of water-soluble organic compounds from the sample had a negligible effect on the separation and detection. As neutral molecules, they co-migrate with the sample plug at the speed of the EOF and pass through the detector long after the organic anions. Since the electrolyte is at pH 7.0, water-soluble esters will not hydrolyze during the analysis. Consequently, no SPE treatment was necessary to remove the organic matrices including the esters. Any small amount [≤1% (w/w)] of water-insoluble organic materials will float on top of the water phase. By taking the sample from the middle of the water layer, the presence of a small amount of insoluble organic materials can be ignored.

3.2.2. Efficiency, speed and cost

Two other significant advantages of the CE method are its efficiency and speed. As shown in Fig. 6, a separation of 17 organic acids is completed within 3.2 min using CE. In contrast, the separation of similar acids required about 30 min using the IC method [1]. In fact, the entire CE separation is completed even before the first peak elutes off the IC column. This, combined with the simplified sample preparation, significantly shortened the overall analysis time and improved the productivity. As a result of the superior efficiency of CE, the resolution was also improved for most acids (Fig. 6).

The cost of the analysis was also dramatically lowered by switching from the expensive IC column and suppressor to the simple bare silica capillary. According to our experience [1], the average life of an IC column and suppressor was about six months, or 1500 samples. So far, the same CE capillary has

Table 2
Recovery of various acids spiked in iso-propanol

	Butyric acid (miscible with water at 20°C)					
Spiked (%, w/w)	1.45	0.773	0.303	0.143	0.089	0.047
Found (%, w/w)	1.36	0.770	0.291	0.145	0.089	0.050
Recovery (%)	93.8	99.6	96.0	101	100	106
	Benzoic acid (water solubility at 20°C = 0.34%, w/w)					
Spiked (%, w/w)	1.51	0.682	0.300	0.155	0.072	0.032
Found (%, w/w)	1.55	0.705	0.299	0.156	0.077	0.036
Recovery (%)	103	97.0	99.7	101	107	113
	Sebacic acid (water solubility at 20°C = 0.13%, w/w)					
Spiked (%, w/w)	1.42	0.699	0.311	0.147	0.079	0.033
Found (%, w/w)	1.39	0.728	0.309	0.135	0.079	0.032
Recovery (%)	98.4	104	99.4	91.8	100	97.0

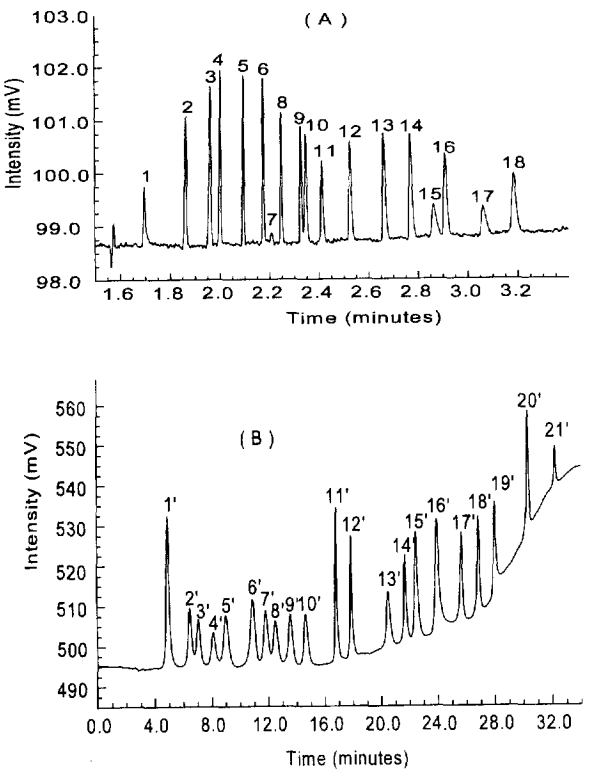

Fig. 6. Comparison of CE and IC separations of organic acids. A = CE separation. Peak identifications are the same as in Fig. 5; B = IC separation. Peak identification (concentrations are 10 ppm each unless given otherwise): 1′ = fluoride (5 ppm), 2′ = acetate, 3′ = propionate, 4′ = butyrate, 5′ = iso-valerate (20 ppm), 6′ = formate, 7′ = valerate (20 ppm), 8′ = iso-caproate (20 ppm), 9′ = pyruvate (20 ppm), 10′ = sec.- caproate (20 ppm), 11′ = chloride (5 ppm), 12′ = nitrite, 13′ = benzoate (20 ppm), 14′ = bromide, 15′ = nitrate, 16′ = carbonate, 17′ = malonate, 18′ = sulfate (5 ppm), 19′ = oxalate, 20′ = phthalate (20 ppm), 21′ = phosphate.

been in use for more than 12 months, with over 3000 samples analyzed. No noticeable change in the capillary has been observed. The less expensive capillary combined with the longer life time reduced the cost of CE consumables to a fraction of that of IC.

3.2.3. Accuracy and reproducibility

The accuracy of the method was evaluated by comparing the total acidity calculated from the CE method with that obtained using acid–base titration (Table 3). Four different sample types of varying acid concentrations and ester contents were analyzed and compared. In all cases, the total acidity numbers of both methods agreed well. This confirms that the CE method has good recovery of organic acids using the simple sample dilution scheme. It also verifies that esters are not hydrolyzed during the analysis.

Reproducibility used to be of great concern for any CE method. However, thanks to the improved instrument design in recent years and the chemistry employed in this case, the reproducibility of our method has been excellent. The relative standard deviation (R.S.D.) of the migration times within a run was better than ±0.3% for most acids. The day-to-day R.S.D. of migration times obtained during a 12-month period on two separate instruments using two different capillaries was better than ±0.8% for most acids. This is comparable to what we obtained using the IC method [1].

The reproducibility of actual sample analysis ranged from ±6.0% at about 50 ppm (before dilution) acid level to ±1.5% at 1000 ppm acid level. This was better than the ±10% allowed by the IC method [1]. A large part of the difference can be attributed to the SPE sample preparation step required by the IC method.

3.2.4. Scope

Over 20 different types of samples have been successfully analyzed using this CE method. These include organic reaction mixtures, plant streams, polymers, incineration residuals, catalyst extracts, foam extracts, coolants and final products, etc.. In general, the sample matrices can be categorized into the three groups: organic, inorganic, and polymeric materials. For the first two types, simple sample dilution aided by brief shaking or sonication is usually sufficient. For polymers, an organic solvent (such as methanol or tetrahydrofuran) may be used to dissolve the sample prior to further dilution in DI water. This would make it easier to quantitatively recover all of the organic acids contained in a polymeric material. The insoluble polymer would precipitate in water and be filtered out prior to the analysis. The separation of a variety of organic acids in three different types of samples, a polymeric resin, a used coolant and a complex plant stream, are shown in Fig. 7. An example of how the method can be utilized in process monitoring is given in Fig. 8. In this case, the levels of organic acids in most

Table 3
Comparison of total acidity results obtained by CE and acid–base titration

Sample no.	Type	Individual acids found by CE (ppm)					Total acidity (μequiv./g) by titration	
		Formic	Acetic	Propionic	Butyric	Benzoic by CE		
1	I	31	54				0.0016	0.0016
2	I	26	42				0.0012	0.0012
3	I	314	849	30			0.021	0.022
4	I	418	1096	56			0.028	0.029
5	II	28	11	34			0.0013	0.0013
6	II	26	18	21			0.0013	0.0013
7	II	14	17	30			0.0010	0.0012
8	II	21	59	36			0.0022	0.0028
9	III	45	29	121		605	0.0081	0.0084
10	III	67	34	56		150	0.0040	0.0043
11	III	65	34	61		158	0.0041	0.0042
12	III	68	34	63		175	0.0042	0.0044
13	IV	1393	1398	74	1748		0.074	0.073
14	IV	1899	2692	150	1862		0.109	0.11
15	IV	4393	5184	315	6840		0.263	0.26
16	IV	6675	10 200	534	7324		0.406	0.41

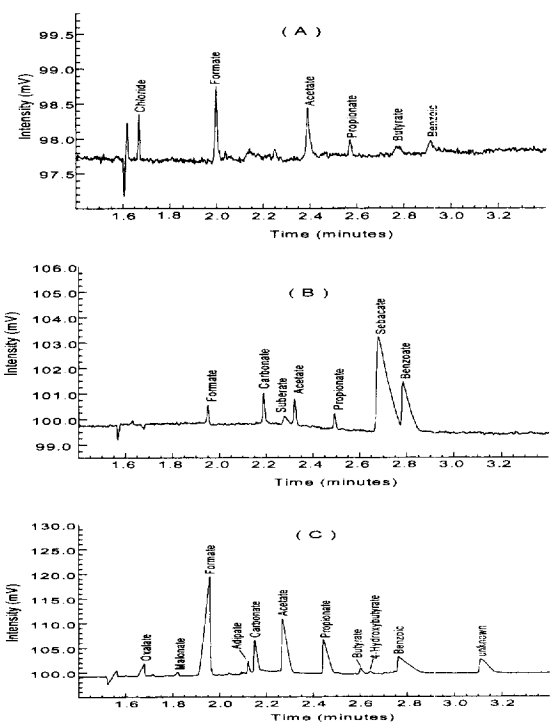

Fig. 7. Separation of organic acids in three different types of samples. A = polymeric resin based on polystyrene/maleic anhydride, B = used coolant, C = plant stream.

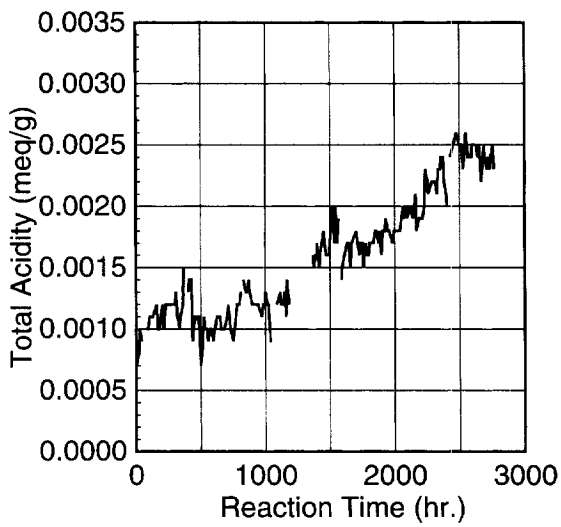

Fig. 8. Determination of low ppm levels of organic acids in process monitoring.

samples were too low to be determined using acid–base titration. However, the CE method allowed us to determine the organic acids at low ppm levels and provide the total acidity necessary to monitor changes in the process.

4. Conclusion

A method based on a phthalate buffer and indirect UV detection was developed which allowed fast, sensitive and accurate analysis of a large number of organic acids in a wide range of industrial samples. As a result of the chemistry used, the need for removal of organic matrices by SPE, as required by an IC method used previously, was eliminated. The speed of separation, simplified sample preparation, combined with lower operational cost, rendered CE a superior technique for organic acid analysis.

References

[1] J. Chen, J. Chromatogr. 739 (1996) 273.
[2] P. Jandik, W.R. Jones, J. Chromatogr. 546 (1991) 431.
[3] P.R. Haddad, A.H. Harakuwe, W. Buchberger, J. Chromatogr. A 706 (1995) 571.
[4] J. Boden, M. Darius, K. Bächmann, J. Chromatogr. A 716 (1995) 311.
[5] P.J. Oefner, Electrophoresis 16 (1995) 46.
[6] B.F. Kenney, J. Chromatogr. 546 (1991) 423.
[7] S.P.D. Lalljie, J. Vindevogel, P. Sandra, J. Chromatogr. A 652 (1993) 563.
[8] K.J. DeVries, J. Am. Soc. Brew. Chem. 51 (1993) 155.
[9] V. Levi, T. Wehr, K. Talmadge, M. Zhu, Am. Lab. 25 (1993) 29.
[10] D. Lagoutte, G. Lombard, S. Nisseron, M.P. Papet, Y. Saint-Jalm, J. Chromatogr. A 684 (1994) 251.
[11] H. Chen, Y. Xu, F. Van Lente, M.P.C. Ip, J. Chromatogr. B 679 (1996) 49.
[12] M. Weers, H. Balzer, A. Bradbury, O.G. Vitzthum, Seizieme Colloque Scientifique International sur le Cafe 1 (1995) 218.
[13] G. Gutnikov, W. Beck, H. Engelhardt, J. Microcol. Sep. 6 (1994) 565.
[14] O. Devêvre, D.P. Putra, B. Botton, J. Garbage, J. Chromatogr. A 679 (1994) 349.
[15] A. Röder, K. Bächmann, J. Chromatogr. A 689 (1995) 305.
[16] R. Roldan-Assad, P. Gareil, J. Chromatogr. A 708 (1995) 339.
[17] S.A. Shamsi, N.D. Danielson, Anal. Chem. 66 (1994) 3757.
[18] E. Dabek-Zlotorzynska, J.F. Dlouhy, J. Chromatogr. A 685 (1994) 145.
[19] J.M. Schrickx, M.J.H. Raedts, A.H. Stouthamer. H.W. van Verseveld, Anal. Biochem. 231 (1995) 175.
[20] W.C. Brumley, C.M. Brownrigg, J. Chromatogr. A 646 (1993) 377.
[21] M. Shirao, R. Furuta, S. Suzuki, H. Nakazawa, S. Fujita, T. Maruyama, J. Chromatogr. A 680 (1994) 247.
[22] S. Turcat, P. Masclet, T. Lissolo, Sci. Total Environ. 158 (1994) 21.
[23] V. Dolník, J. Dolníková, J. Chromatogr. A 716 (1995) 269.
[24] G. Cartoni, F. Coccioli, R. Jasionowska, J. Chromatogr. A 709 (1995) 209.
[25] C.J. Petucci, H.L. Kantes, T.G. Strein, H. Veening, J. Chromatogr. B 668 (1995) 241.
[26] C.M. Fariego, A. Hernanz, Clin. Chem. 42 (1996) 477.
[27] Hewlett–Packard Product Catalog, Capillaries, Reagents and Supplies for Capillary Electrophoresis, 1996.
[28] D.N. Heiger, Hige Performance Electrophoresis — An Introduction, Hewlett–Packard, 1992.