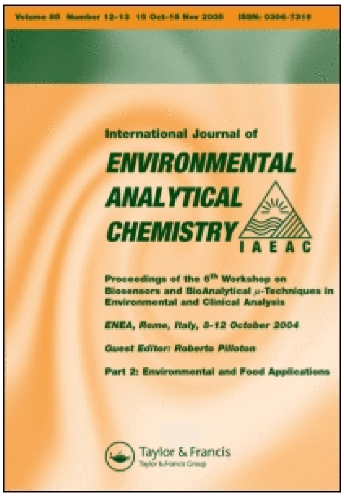

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of formic and acetic acid in rain water by capillary electrophoresis

Rosa Castedo; Rosa M. Peña; Carlos Herrero; Sagrario Garcí-Martín

To cite this Article Castedo, Rosa , Peña, Rosa M. , Herrero, Carlos and Garcí-Martín, Sagrario(2003) 'Analysis of formic and acetic acid in rain water by capillary electrophoresis', International Journal of Environmental Analytical Chemistry, 83: 3, 247 — 253

To link to this Article: DOI: 10.1080/0306731021000053748

URL: http://dx.doi.org/10.1080/0306731021000053748

Intern. J. Environ. Anal. Chem., Vol. 83, No. 3, pp. 247–253

Taylor & Francis
Taylor & Francis Group

ANALYSIS OF FORMIC AND ACETIC ACID IN RAIN WATER BY CAPILLARY ELECTROPHORESIS

ROSA CASTEDO, ROSA M. PEÑA,
CARLOS HERRERO and SAGRARIO GARCÍA-MARTÍN*

Dpto. Química Analítica, Nutrición y Bromatología. Facultad de Ciencias, Universidad Santiago de Compostela, Avda. Alfonso X El Sabio s/n, 27002 – Lugo, Spain

(Received 8 May 2002; In final form 3 September 2002)

A simple technique is described for the routine capillary electrophoretic determination of formic and acetic acid in rain water. These acids were determined simultaneously in approximately 6 min using a carrier electrolyte containing 10 mM phosphate and 0.5 mM myristyltrimethylammonium bromide (MTAB) as electroosmotic flow (EOF) modifier at pH 6.5 and direct UV detection at 185 nm. The method is quantitative, with recoveries in the 99–101% range and linear up to 5 mg L^{-1}. The precision is better than 2.1% and the procedure shows the appropriate sensitivity, with detection limits between 0.042 and 0.055 mg L^{-1}. The proposed method was successfully employed for the determination of formic and acetic acid in 57 rain water samples, collected from October 2000 to February 2001 in four different sampling stations located in Galicia (NW Spain), by direct sample injection after filtration.

Keywords: Capillary electrophoresis; Formic acid; Acetic acid; Rain water

INTRODUCTION

Carboxylic acids are considered a dominant class of organic compounds found in the atmosphere distributed in the gaseous, aqueous, and particulate phase. In the gaseous phase the volatile low molecular weight carboxylic acids like acetic and formic are predominant, which due to their water solubility also are found in the aqueous phase. On the other hand, the low volatileness and high molecular weight carboxylic acids are habitually found in the particulate phase [1].

Carboxylic acids can be directly emitted, primary pollutants, or they can be formed in the atmosphere through chemical reactions, secondary pollutants [2]. Although the inorganic acids have an important role in the atmospheric acidity, the carboxylic acids represent from 16 to 35% of the free acidity in the rainwater in urban atmospheres

---

*Corresponding author. Fax: +34-982 22 49 04. E-mail: sgarciam@lugo.usc.es

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731021000053748

and 65% in remote areas approximately [3]. The acid fraction of the atmosphere can be the cause of the metal and metallic ligands destruction exposed to the air, recent studies demonstrate the effect of acetic, and formic acids in the atmospheric metal corrosion. It is also known that high concentrations of carboxylic acids are detrimental for the human health, being able to cause from irritations in the eyes to respiratory problems [4].

In the last years, the organic acids have waked up a great interest between the investigators due to the diversity of these compounds in the atmosphere. The possible sources of emission, the formation *in situ* of carboxylic acids, as well as its influence in the climatic variations are object of investigation in several places [2].

The atmospheric pollution caused by photochemical smog includes the participation of numerous chemical reactions with different organic volatile compounds present in the atmosphere. The knowledge of the chemical composition of the atmospheric aerosol responsible for the formation of photochemical smog is fundamental to know the causes that lead to the formation of this type of pollution in the atmosphere.

The studies of chemical characterization of oxygenated compounds implied in the photochemical smog process began around 1970. Since then the carboxylic acids have been detected in atmospheric air samples, in the phases gaseous, aqueous, and particulate in different environments.

The main mechanisms of elimination of carboxylic acids are based on the dry and humid deposition. The dry deposition implies the particle sedimentation and the humid one is associated with the elimination of gases and particles by drops of water in clouds (rainout) and rains (washout). On general when the elimination is by deposition, the time of residence of carboxylic acids in the atmosphere is comparatively small being able to vary from some hours to some few days [2]. The elimination of these species is related directly to the degree of partition between the gaseous species and the water in the aerosol, clouds and rains [5].

Generally, organic acids have been determined by a range of chromatographic techniques such as gas chromatography (GC) [6–8], high performance liquid chromatography (HPLC) [9–13] and ion chromatography (IC) [14–16]. These methods are precise and accurate but there is still a demand for techniques that while offering the same degree of automatization provide better separation efficiency than those obtained in liquid chromatography and that can avoid time-consuming derivatization procedures often necessary in GC. Taking into account the above considerations, the need for alternative methods of determination for organic acids is clear. In the last few years, capillary electrophoresis (CE) has become a versatile analytical technique employed in the determination of different types of analytes in a great variety of matrices [17–21] due to its adequate analytical characteristics such as low consumption of chemicals, high resolution, high speed, and simplicity.

Since the first works on modern capillary electrophoresis, in fused silica capillaries [22,23], this technique began to settle down like a routine technique in numerous fields of the analysis such as the environmental field [17,24–28].

In this work, an electrophoretic method employing phosphate as carrier electrolyte was evaluated for the determination of formic and acetic acid in rain water. The optimization of the proposed analytical procedure was carried out and the applicability of the method was demonstrated by the simultaneous and rapid determination of formic and acetic acid in real samples of rain water.

EXPERIMENTAL

Instrumentation

All experiments were performed using a Waters Quanta 4000 capillary electrophoresis system (Waters Chromatography, Milford, MA) equipped with a UV on-column detector and a negative power supply. Separation was carried out on fused silica capillaries with 60 cm total length × 75 µm of inner diameter (Composite Metal Services Ltd., UK). Data acquisition and processing were performed by means of the Package Millennium v. 2.15 (Waters Chromatography, Milford, MA) in a Digital Venturis 446 computer. Filtration was performed by an All-Glass filter support through 0.45 µm HA membrane filters (Millipore Co. Bedford, MA). The pH measurements were made using a Digilab 517 pH meter (Crison Instrumental S.A., Barcelona, Spain).

Reagents and Samples

All chemicals, obtained from different suppliers, were of analytical grade and all of them were used without any purification. Carrier electrolyte and standard solutions were prepared in ultra-pure water provided by a Milli-Q system (Millipore Co. Bedford, MA).

Organic Acids

Formic acid (sodium salt) and butyric acid were obtained from Aldrich (Madrid, Spain). Acetic acid (potassium salt) was purchased from Avocado (Barcelona, Spain). Standards of the organic acids were daily prepared from a 1 g L^{-1} stock solution and diluted to the required concentration before use.

Background Electrolyte (BGE) and Carrier Electrolyte Preparation

NaH_2PO_4 was supplied by Panreac (Barcelona, Spain); Na_2HPO_4 by Acros Organics (Geel, Belgium) and myristyltrimethylammonium bromide (MTAB) by Aldrich (Madrid, Spain). The carrier electrolyte was daily prepared, filtered through a Millipore 0.45 µm HA membrane filter and degassed in an ultrasonic bath before use. The carrier was optimized, and its composition was as follows: 10 mM phosphate with 0.5 mM MTAB as EOF modifier at pH 6.5.

Samples

From October 2000 to February 2001, precipitation samples were collected in Galicia at four different sampling stations belonging to the SIAM (Environmental Information System of Galicia). A total of 57 precipitation samples were collected.

In each of the sampling stations, according to the Spanish Legislation, an automatic sequential sampler equipped with polyethylene bottle reservoirs (protected from sunlight), Teflon-coated steel funnel, Teflon tubing and precipitation sensor for the collection of rainwater only (i.e. without dry deposition) was used. Samples were collected within 12 h following the event during which formic and acetic concentrations did not change [29]. Rain samples were placed in 30 mL Teflon vials, preserved with chloroform, and stored in a refrigerator (4°C) immediately after collection to stop biological activity [30]. Chloroform blanks showed no organic contamination. Samples were mailed to the laboratory and immediately after reception, samples were stabilized by filtration through a Millipore 0.45 μm HA membrane filter, 1 mg L^{-1} of butyric acid used as internal standard was added and samples were stored at 4°C before analysis. The obtained solutions were directly injected in the capillary electrophoresis system. All the samples were analyzed within 3 months during which no significant concentration changes occurred [31].

Electrophoretic Conditions

Capillary Column Conditioning

In order to obtain a stable baseline, the capillary was daily conditioned by washing it according to the following cycle: 0.1 M NaOH for 5 min followed by ultra pure water for 10 min and finally the carrier electrolyte for 10 min.

Separation

The operation conditions were as following. Separation was performed at room temperature, the applied voltage was –20 kV, and the current intensity achieved under these conditions was 18 ± 1 μA. Isomigration mode was used making constant the current intensity to 18 μA for 120 s. Hydrostatic mode injection at 10 cm for 30 s was employed. Detection was performed by direct UV at 185 nm. The running time for the analysis was 6 min.

RESULTS AND DISCUSSION

Optimization of CE Separation

The background electrolyte (BGE) was optimized in a previous work [21]. Five different electrolytes were evaluated (phthalic acid, benzoic acid, sorbic acid and phosphate based electrolyte) for the analysis of five organic acids present in wine samples. All the conditions that affected the electrophoretic separation were studied (pH, concentration of BGE, concentration of electroosmotic flow modifier, presence of an organic solvent).

CE separation for the organic acids object of this study were carried out using an electrolyte that contained 10 mM phosphate and 0.5 mM MTAB at pH 6.5. Direct UV detection at 185 nm was used. Organic acids were well separated and sharp symmetrical peaks were observed. The solutes migrated in the order of formic, acetic and butyric acid (IS). The precision within a day of migration time and peak area was studied by injecting ten times a standard solution that contained 5 mg L^{-1} of each organic acid studied and expressed as the relative standard deviation (RSD). As can be seen in the results summarized in Table I, the method showed good precision with RSD of 1.02 (acetic acid) and 1.81% (formic acid) for peak area, and 0.46 and 1.11% for migration time–IS migration time for acetic and formic acid respectively. In addition, the in-between day precision was evaluated by injecting a standard solution containing 5 mg L^{-1} of each organic acid studied during six different days. The RSD obtained in this case were 0.86 and 2.08% for peak area and 0.57 and 1.55% for migration time–IS for acetic and formic acid respectively.

TABLE I pKa values for the species studied and analytical figures of merit

Compound		*Formic acid*	*Acetic acid*
pka*		3.75	4.76
Migration time (min)		3.40	4.63
Precision migration time	Within a day	1.11	0.46
($n = 10$) (RSD) (%)	In-between day	1.55	0.57
Precision peak area	Within a day	1.81	1.02
($n = 10$) (RSD) (%)	In-between day	2.08	0.86
Detection limit (mg L^{-1})		0.042	0.055
Linearity (Correlation coefficient)		0.9999	0.9999
Linear range (mg L^{-1})		Up to 5	Up to 5
Recovery (%)		99 ± 1.2	101 ±2.5

*Data of pKa values from [32].

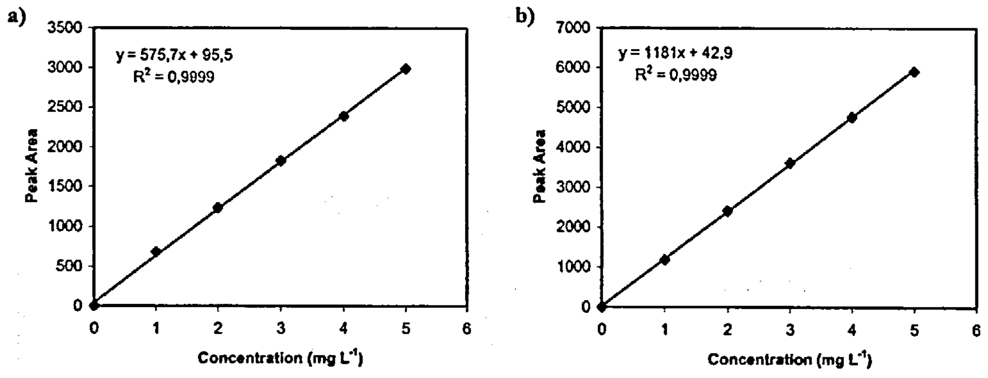

FIGURE 1 Calibration lines for the organic acids studied: (a) formic acid; (b) acetic acid.

The linearity of the method was evaluated by injecting various concentrations up to 5 mg L^{-1}. The calibration lines obtained by plotting peak area *vs* the concentration of the test acids produced correlation coefficients (r^2) of 0.9999 (Fig. 1).

The detection limits calculated using signal-to-noise ratios of 3:1 were formic acid, 0.04 mg L^{-1} and acetic acid, 0.05 mg L^{-1}. Recovery of the method was studied using a rainwater sample spiked with the organic acids under analysis. The recoveries, shown in Table I, were satisfactory, ranging from 99 to 101%.

Analysis of Real Samples

Considering the importance of the determination of organic acids in environmental samples the proposed method was applied for the analysis of organic acids in rain water under the optimized conditions. Only the addition of the internal standard and a subsequent filtration of the sample were necessary before direct injection into the capillary electrophoresis system. Analyses were performed in triplicate. An example of the electropherogram obtained in the analysis of a rainwater sample is presented in Fig. 2.

The results obtained for the determination of organic acids studied are presented in Table II. Mean concentrations of formic and acetic acid were 2.39 and 1.65 mg L^{-1} respectively.

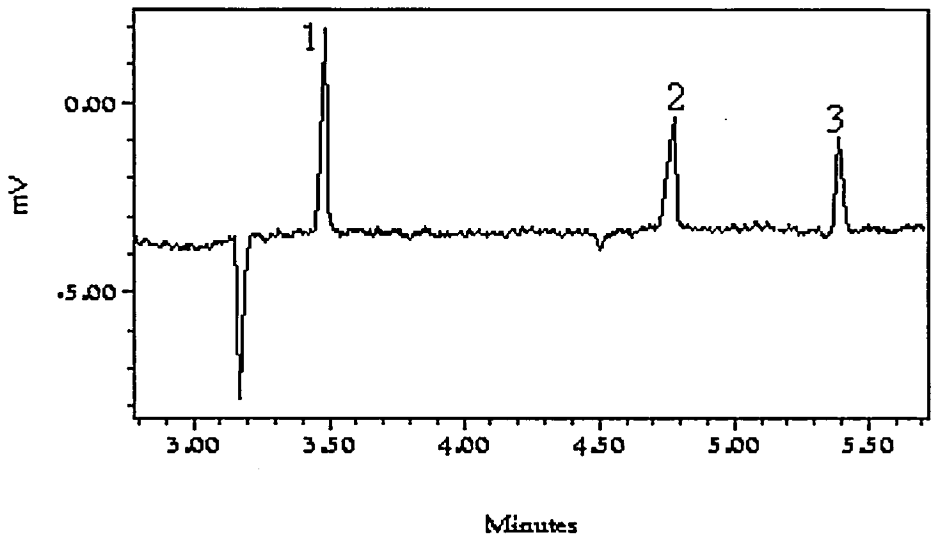

FIGURE 2 Electropherogram corresponding to a rainwater sample. Peak identification: 1 – formate; 2 – acetate; 3 – internal standard (butyrate).

TABLE II Concentrations (mg L^{-1}) of organic acids in the rainwater samples

Sample code	*Formic acid*	*Acetic acid*	*Sample code*	*Formic acid*	*Acetic acid*
2524/00	3.92	0.46	446/01	0.67	2.73
2525/00	1.55	1.29	669/01	2.36	n.d.
2526/00	11.00	1.09	664/01	0.42	4.50
2527/00	4.23	0.87	612/01	0.91	1.00
2528/00	3.83	1.04	605/01	1.80	0.86
2529/00	1.82	0.89	587/01	1.51	1.03
2530/00	0.54	1.46	316/01	n.d.	1.64
2531/00	1.79	1.30	600/01	0.35	0.88
2532/00	0.84	0.98	584/01	2.82	0.93
2533/00	0.81	1.18	609/01	4.72	1.65
2534/00	10.90	3.49	604/00	1.00	0.83
2535/00	1.12	1.05	590/01	3.52	1.89
2537/00	3.44	0.92	586/01	3.86	1.61
2538/00	7.03	n.d.	603/01	1.58	0.92
2555/00	12.76	1.92	588/01	2.42	2.35
2556/00	0.66	2.22	666/01	0.20	2.86
2557/00	2.28	1.99	445/01	0.23	3.16
2559/00	0.78	2.80	2521/00	1.47	0.83
2560/00	0.63	2.93	602/01	1.60	0.95
2561/00	1.67	2.07	2554/00	1.19	2.97
2562/00	1.58	2.66	606/01	0.20	1.15
592/01	1.88	1.43	607/01	0.85	0.95
663/01	1.21	2.76	608/01	4.92	1.63
665/01	1.33	3.58	667/01	0.39	3.40
591/01	3.08	1.54	2519/00	2.64	0.59
1380/00	2.84	1.35	585/01	3.96	1.30
595/01	n.d.	1.26	593/01	1.30	1.04
614/01	0.20	0.97	594/01	0.36	0.79
613/01	0.69	0.94			

n.d.: not detected.

CONCLUSIONS

A simple CE method with UV detection for the determination of organic acids in rain water, which can be used as an alternative to other chromatographic techniques, is described. The use of phosphate as a BGE provided a well-resolved and reproducible electrolyte system. The proposed method was successfully applied in the analysis of two organic acids with environmental interest. The determination was performed in rain water samples in less than 6 min with a very simple sample pre-treatment. Thus, the described procedure is able to complement other methods commonly used for the determination of organic acids in this kind of samples.

Acknowledgments

This work was supported in part by the Local Government of Galicia (Xunta de Galicia), Spain. Research Project code PGIDT99MA26201.

References

[1] J. Ludwig and O. Klemm, *Tellus, Ser. B*, **40B**, 340–347 (1988).
[2] A. Chebbi and P. Carlier, *Atmos. Environ.*, **30**, 4233–4249 (1996).
[3] W.C. Keene and J.N. Galloway, *Atmos. Environ.*, **20**, 1508 (1986).
[4] J. Palassis, *American Industrial Hygiene Association Journal*, **39**, 731–736 (1978).
[5] R.W. Talbot, A.S. Vijgen and R.C. Harris, *J. Geophys. Res. [Atmos.]*, **97(D15)**, 16531–16543 (1992).
[6] C.R. Deng, *Sepu*, **15**, 505–507 (1997).
[7] H. Haila, J. Kumpulainen, U. Hakkinen and R. Tahvonen, *J. Food Compos. Anal.*, **5**, 100–107 (1992).
[8] D.G. Hu, J.S. Cheng and Y. Zhu, *Sepu*, **12**, 265–267 (1994).
[9] M.W. Dong, *LC-GC*, **16**, 1092–1097 (1998).
[10] R. Vonach, B. Lendl and R. Kellner, *J. Chromatogr. A*, **824**, 159–167 (1998).
[11] C. Linget, C. Netter, D. Heems and E. Verette, *Analusis*, **26**, 35–39 (1998).
[12] A. Escobal, J. Gonzalez, C. Iriondo and C. Laborra, *Food Chem.*, **58**, 381–384 (1997).
[13] E. Falque-Lopez and E. Fernández-Gómez, *J. Chromatogr. Sci.*, **35**, 254–257 (1996).
[14] Y. Zhu, X.D. Zhang and W.J. Niu, *Mikrochim. Acta*, **127**, 189–194 (1997).
[15] M.Y. Ding, Y. Suzuki and H. Koizumi, *Analyst*, **120**, 1773–1777 (1995).
[16] M. Lourdes, A. Gustavo and A.M. Troncoso, *J. Chromatogr. A*, **822**, 45–51 (1998).
[17] Z. Chen, C. Tang and J. Yu, *J. High Resol. Chromatogr.*, **22**, 379–385 (1999).
[18] J. Sádecká and J. Polonský, *J. Chromatogr. A*, **880**, 243–279 (2000).
[19] J.P. Landers, *Handbook of Capillary Electrophoresis*, Chap. 6, pp. 156–483. CRC Press, Boca Raton (1997).
[20] M.G. Khaledi, *High Performance Capillary Electrophoresis, Theory, Techniques and Applications*, Part IV, pp. 637. Wiley, New York (1998).
[21] A Castiñeira, R.M. Peña, C. Herrero and S. Garcia, *J. High Resol. Chromatog.*, **23**, 647–652 (2000).
[22] J.W. Jorgenson and K.D. Lukacs, *J. Chromatogr. A*, **216**, 209–216 (1981).
[23] J.W. Jorgenson and K.D. Lukacs, *Anal. Chem.*, **53**, 1298–1302 (1981).
[24] S. Turcat, P. Masclet and T. Lissolo, *Sci. Total Environ.*, **158**, 21–29 (1994).
[25] G. Kiss, A. Gelencsér, Z. Krivácsy and J. Hlavay, *J. Chromatogr. A*, **774**, 349–361 (1997).
[26] J. Dahlén., J. Hagberg and S. Karlsson, *Fresenius J. Anal. Chem.*, **366**, 488–493 (2000).
[27] D.H. Craston and M. Saeed, *J. Chromatogr. A*, **827**, 1–12 (1998).
[28] D. Orta, P.D. Mudgett, L. Ding, M. Drybread, J.R. Schultz and R.L. Sauer, *J. Chromatogr. A*, **804**, 295–304 (1998).
[29] G.B. Avery Jr., J.D. Willey and C.A. Wilson, *Environ. Sci. Technol.*, **25**, 1875–1879 (1991).
[30] W.C. Keene and J.N. Galloway, *Atmos. Environ.*, **18**, 2491–2497 (1984).
[31] Y. Tang, Masters Thesis, University of North Carolina at Wilmington, (1998).
[32] D.R. Lide and H.R. Frederiske, *Handbook of Chemistry and Physics*, 80th Edn., Section 8, pp. 46–47. CRC Press, Boca Raton (1999).