

This article was downloaded by:

On: 17 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

Capillary Electrophoretic Analysis of Organic Anions in Tannery Wastewater Including High Contents of Chloride and Sulfate

O. Fiehn^a; G. Wegener^a; M. Jekel^a

^a Technical University of Berlin, Berlin, Germany

To cite this Article Fiehn, O. , Wegener, G. and Jekel, M.(1998) 'Capillary Electrophoretic Analysis of Organic Anions in Tannery Wastewater Including High Contents of Chloride and Sulfate', *International Journal of Environmental Analytical Chemistry*, 69: 3, 257 – 271

To link to this Article: DOI: 10.1080/03067319808032591

URL: <http://dx.doi.org/10.1080/03067319808032591>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

CAPILLARY ELECTROPHORETIC ANALYSIS OF ORGANIC ANIONS IN TANNERY WASTEWATER INCLUDING HIGH CONTENTS OF CHLORIDE AND SULFATE

O. FIEHN*, G. WEGENER and M. JEKEL

*Technical University of Berlin, Sekr. KF 4, Dept. of Water Quality Control, Str.d.17.
Juni 135, 10623 Berlin, Germany*

(Received 23 February 1997; In final form 30 April 1997)

A new sample preparation method for capillary electrophoresis is presented to analyze organic anions in industrial wastewater which is highly contaminated with inorganic salts. Chloride and sulfate can be completely removed by use of strong cation exchangers in their Ag- and Ba-form. Good recoveries were found for 10 small organic acids out of spiked pure water after removal of up to 2 g/L for both, chloride and sulfate. Recoveries of oxalic acid were decreasing from 92 to 47% with increasing salt contents. Using tannery wastewater samples, irreversible adsorption of the organic load onto the cation exchangers could be minimized by an additional washing step. Included in these samples, 17 peaks could be identified by spiking 46 organic and inorganic compounds. The alteration of the organic anions present in the wastewater samples could be characterized along a biological treatment pilot plant. Some of these anions proved to be persistent to biological degradation.

Keywords: Industrial wastewater; capillary electrophoresis; environmental analysis; sample preparation; organic anions

INTRODUCTION

Since a couple of years, methods using capillary electrophoresis (CE) have gained much attention for the separation of complex mixtures of inorganic and organic analytes, and some reviews have been published.^[1,2] Aliphatic anions such as fatty acids are analyzed most frequently,^[3] but there are also reports on the separation of aromatic sulfonates^[4] or even hydrophobic organics such as chlorophenols.^[5] Therefore, a broad variety of target analytes can be determined.

*Corresponding author. Fax: +49-30-424 16 85, E-mail: O.Fiehn@T-online.de

Reliable separations and quantifications may be a problem in CE due to inadvertent hydrodynamic flow and diffusion effects,^[6] but method development and optimizations can be done quite systematically.^[7] Usually, CE-methods require higher analyte concentrations caused by the small internal diameters of the capillaries. Therefore, there are few reports using CE-techniques for environmental analysis^[8,9] in general. Even less publications deal with CE-methods for industrial wastewaters^[10] as these samples are usually accompanied by high organic and inorganic loads.

Dolník and Dolníková have investigated the influence of chloride on the CE-separation of small organic anions.^[11] Due to inhomogenities of the local electric field strength, sample self-stacking effects occurred and some anions were lost in the chloride zone. Anions were migrating slower and a pH-decrease was stated in the chloride zone in comparison with the operational electrolyte. Concluding, separation of target organics and baseline stability can be severely hampered as it was also reported by Boden.^[12]

Tannery wastewater is known to exhibit extraordinary contents of both, organic and inorganic compounds, and concentrations may enormously vary from day to day. DOC-values normally reach 600–4500 mg/L, chloride may be present between 1000–5000 mg/L and sulfate between 600 – 8000 mg/L.^[13] Some compound classes in tannery effluents have been investigated in detail such as benzothiazoles,^[14] sulphonated polyphenols^[15] or phenols.^[16] However, in total less than 10% of the DOC included in these samples could be identified using various HPLC- and GC-methods.^[17] CE is often seen as a complementary tool to these methods. Therefore, we report here on the use of capillary electrophoresis for the determination of small organic acids such as oxalate or formiate in tannery wastewater. It is shown how to overcome separation problems caused by the high salt contents, and the resulting electropherograms are qualitatively characterized.

EXPERIMENTAL

Chemicals

Standards for the spiking tests, triethanolamine and all solvents were purchased from Merck (Darmstadt, FRG). Hexamethoniumbromide (HMB_r), 2,6-naphtalenedicarboxylic acid (NDC), 1,2,4,5-benzenetetracarboxylic acid (PMA), sulfosalicylic acid (SSA) and tetradecyltrimethylammoniumbromide (TTAB) were obtained from Aldrich (Steinheim, FRG). Hexadimethrinbromide, 2,6-pyridine-

dicarboxylic acid (DPA) and 1,2,4-benzenetricarboxylic acid (TMA) were provided by Fluka (Neu-Ulm, FRG).

Samples

Removal of chloride was done by OnGuard-Ag cartridges and sulfate was precipitated by OnGuard-Ba cartridges (both Dionex, Sunnyvale, CA). Sample pH-values did not exceed pH 7 to avoid formation of Ag_2O . All cartridges were conditioned using 5 mL pure water. 6.5 mL sample volume was sucked through the cartridges with 1–2 mL/min., and the first 3 mL were rejected.

Standard mixtures containing 12 small organic acids (see result section), each at 10 mg/L, were prepared by spiking aliquots of the corresponding stock solutions to pure water. These mixtures were used for the optimization of the buffer systems and for the recovery tests using OnGuard-cartridges.

Two streams of tannery wastewater were investigated. Stream I included wastewater of all steps for the preparation of the cattle hides, the so-called beamhouse wastewater. Stream II contained wastewater of all following processing steps (tanning, dyeing, fatliquoring, etc.), the tan-yard wastewater. The first wastewater stream was subjected only to aerobic treatment, and the second stream was anaerobically pretreated with subsequent aerobic treatment. Some samples have been ozonated to test DOC-losses at increasing amounts of small organic anions. The tannery wastewater treatment pilot plant^[18] and the ozonation procedure^[13] are described elsewhere.

Analysis

The dissolved organic content was determined using an AstroLiqui-TOC 2001-MB analyzer (Foss-Heraeus, Hanau, FRG).

Capillary electrophoresis was carried out on a Dionex CES I instrument (Sunnyvale, CA). A 45/50 cm \times 75 μm i.d. uncoated Dionex capillary was used, and samples were injected in the hydrostatic mode (10 s, 50 mm). Buffers were filtered using 0.2 μm esterified cellulose filters (Schleicher&Schuell, Dassel, FRG). The optimal buffer/flow modifier system is given in the result section. Indirect UV detection was chosen, and all signals were reverted electronically to obtain electropherograms similar to usual HPLC- or GC-chromatograms.

TABLE I Optimized conditions of 5 EOF/BGE-systems for the separation of 12 small organic anions. For abbreviations: see text.

<i>electroosmotic flow modifier</i>	<i>background electrolyte</i>	<i>pH</i>	<i>voltage [kV]</i>	λ_{det} [nm]	<i>signal-to-noise ratio</i>	
					<i>oxalate</i>	<i>glutarate</i>
0.001% (w/w) polybrene	5 mM SSA	11	10	210	95	89
0.75 mM HMBr + 1.6 mM triethanolamine	2.25 mM PMA	7.7	20	250	45	24
0.6 mM TTAB	6 mM NDC	10.15	10	285	27	33
1 mM TTAB	3 mM TMA	10	10	245	52	39
1 mM TTAB	5 mM DPA	10	10	270	16	33

RESULTS AND DISCUSSION

Optimization of the CE-separation Conditions

Analyses of aliphatic acids are mostly done by indirect UV detection using background electrolytes (BGE)^[19,20] but these buffers regularly cause high noise levels.^[21] Hence, the separation of these acids was first tested using 12 highly hydrophilic organic anions, some of which were already known as dead-end products for biodegradation:^[22] oxalate, malonate, succinate, glutarate, adipinate, formiate, acetate, fumarate, maleinate, tartrate, malate and citronate. Five different systems of background electrolytes (BGE) and electroosmotic flow modifiers (EOF) were optimized: tetradecyltrimethylammoniumbromide (TTAB) in combination with 2,6-naphthalenedicarboxylic acid (NDC), trimellitic acid (TMA) and dipicolinic acid (DPA), respectively. Two other EOF-modifiers were tested: hexamethoniumhydroxide (HMBr) combined with pyromellitic acid (PMA) and, at last, polybrene (hexadimethrinbromide) with sulfosalicylic acid (SSA). Signal-to-noise ratios were calculated for each system for oxalate and glutarate. Results of the optimization are given in Table I.

Without cooling, noise is somewhat higher due to the Joule's heating effect.^[23] Unfortunately, irreproducible spikes occurred when simultaneously TTAB was used and the capillaries were cooled. This effect might be due to the low solubility of TTAB and, thus, the TTAB-systems had to be tested without cooling. Therefore, highest signal-to-noise ratios were obtained with use of polymeric surfactants, i.e. polybrene.

No system could separate all 12 anions in one run. However, in addition to the excellent signal-to-noise values, separation performed best using the polybrene/SSA-system. Unfortunately, baseline was highly unstable when waste-

TABLE II Reproducibility (relative standard deviations, $n = 10$) and detection limits of some small anions using the TTAB/NDC-system. n.d. = not determined

<i>anion</i>	<i>migration time r.s.d. [%]</i>	<i>peak area r.s.d. [%]</i>	<i>detection limits [mg/L]</i>
sulfate	0.21	7.89	1.83
oxalate	0.22	1.80	0.24
sulfite	0.23	4.44	0.74
formiate	0.18	0.83	0.12
hydrogencarbonate	0.19	13.15	n.d.
acetate	0.19	2.56	0.39
glycolate	0.19	1.66	0.23
glyoxalate	0.19	2.72	0.34
lactate	0.20	3.78	0.51

water samples were analyzed, and use of this EOF/BGE-system had to be rejected. The HMBr/PMA-system caused bad peak shapes, and some unknown contamination peaks occurred. The mobility of TMA seemed to be too high to obtain good separations for four of the slower anions. Similar separation results were observed for the DPS/TTAB-system, and the signal-to-noise ratios were the worst of all. The remaining NDC/TTAB-system has been described as a very suitable background electrolyte for organic anions before.^[24,25] In fact, 10 of the 12 standard compounds could be separated at least partially. After a ten-fold injection of the standard mixture, the separation proved to be highly reproducible (Table II).

Peak areas, however, were somewhat less stable. For sulfate, quantification was difficult since there was a huge baseline dip just before the sulfate peak front. In all analyses, an additional system peak occurred which we could identify as hydrogencarbonate. For quantification of hydrogencarbonate, we were able to abolish this system peak by applying a 10 kV voltage for 3 min. directly before the injection^[26] (Figure 1). Assumably, rests of the system peak caused the high deviation (r.s.d. = 13.2%) found for the determination of hydrogencarbonate.

No baseline instability was observed when complex ozonated batch samples^[27] were analyzed. Therefore, this system was chosen for routine analyses. Baseline separation of the remaining two unseparated analytes, formiate and tartrate, could be achieved by addition of methanol^[28] or *i*-propanol (but not by acetonitrile) to the buffers (Figure 2). However, the separation of slow migrating anions got worse, and thus, two runs were needed for the reliable identification of formiate in the wastewater samples (see result section 3.).

Removal of Chloride and Sulfate

Separation of the standard mixture was harshly disturbed in the presence of each 2000 mg/L chloride and sulfate (Figure 3). Hence, the major inorganic anions chloride and sulfate had to be removed before CE-separations of organic anions

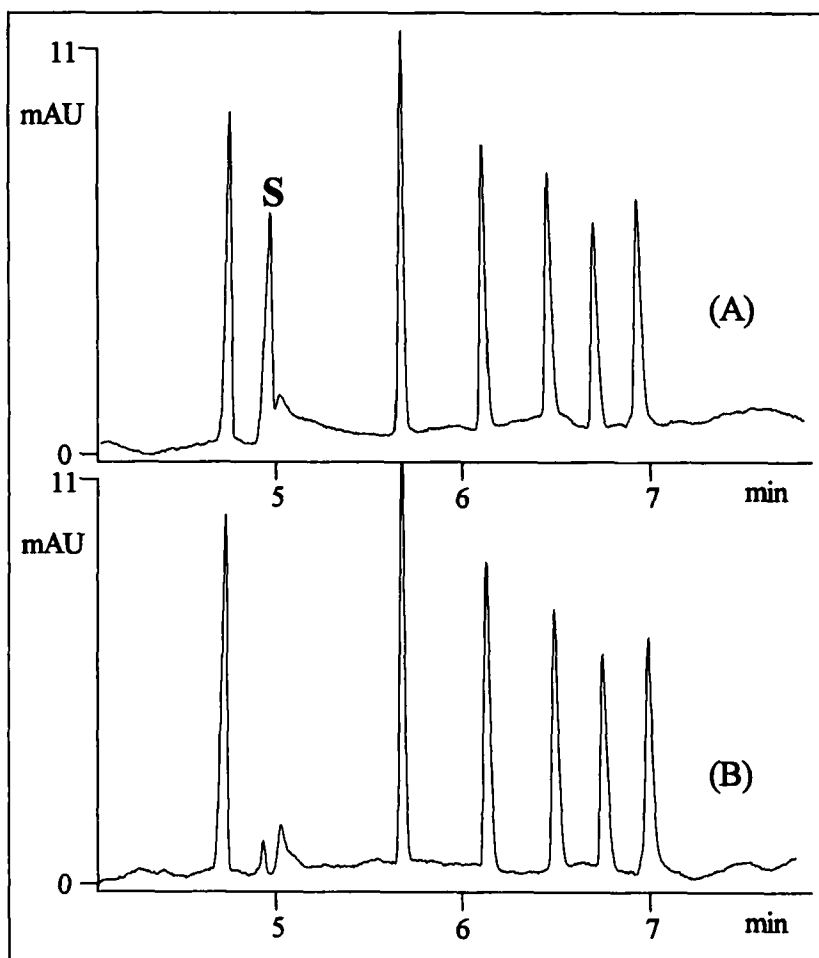


FIGURE 1 CE-separation of the $C_1 - C_6$ aliphatic acids using the NDC/TTAB-system without (A) and with (B) abolishing the system peak S (hydrogencarbonate)

in real tannery wastewater samples were possible. Precipitation reactions using $AgNO_3$ or $BaCl_2$ were forbidden due to the simultaneous addition of inorganic anions. Use of strong anion exchangers was expected to be accompanied by the removal of organic anions. However, use of strong cation exchangers in their Ag- and Ba-form might exclude chloride and sulfate from the samples without severe co-adsorption of organic anions. Thus, the standard mixture of the 12 small organic acids was spiked with increasing amounts from 0–4000 mg/L of a) sulfate and b) chloride and phosphate. Results are given in Table III. We refrained from separating formiate and tartrate by addition of organic solvents,

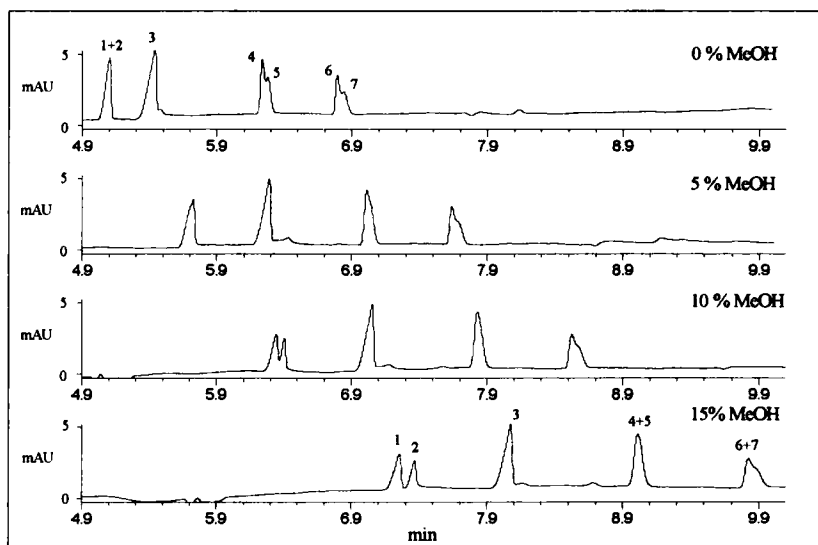


FIGURE 2 CE-separation of formiate and tartrate with increasing addition of methanol to the NDC/TTAB-system. Peak no. 1 = formiate, 2 = tartrate, 3 = system peak, 4 = acetate, 5 = glycolate, 6 = propionate, 7 = lactate

and additionally, the system peak hydrogencarbonate was not abolished by voltage application before the separations. Therefore, the adipinate peak was overlaid by the system peak, and assumingly, it was underestimated. Phosphate has been included in these tests, since it was regularly added to improve the biodegradation processes in our tannery wastewater treatment pilot plant. However, in contrary to informations given by the cartridge manufacturers, it could not be removed at all by precipitation of Ag_3PO_4 . This might be explained by the known ease of back-dissolution of its precipitates. Therefore, baseline separation of the formiate/tartrate, malate and succinate peaks was deteriorated. Quantifications of these anions could not be made at PO_4^{3-} -contents exceeding 10 mg/L (n.d.).

In general, it can be seen that small organic acids nearly quantitatively pass the cation exchanges, with or without additional precipitation of chloride and sulfate. With increasing amounts of sulfate up to 4000 mg/L, recovery of oxalate was reduced from 92 to 47%, whereas recoveries of all the other compounds were not affected. For this test, mean recoveries are given in Table III. These recoveries have also been gained with addition of all three anions, chloride, sulfate and phosphate, to the spiked water samples.

Chloride was completely removed up to 4000 mg/L. Sulfate removal was somewhat incomplete, and certain, but small amounts were still detectable in

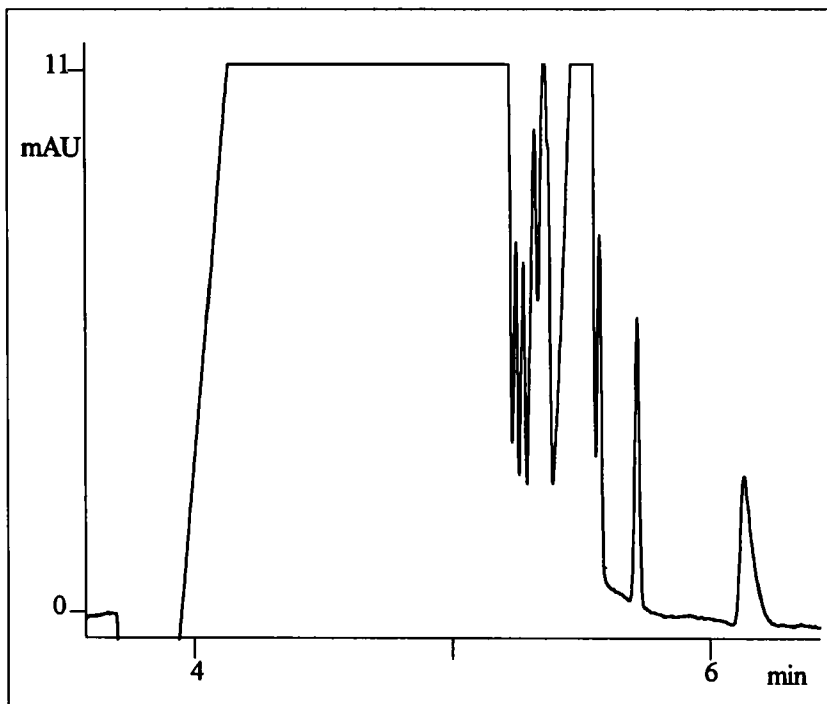


FIGURE 3 Unsuccessful separation of a standard mixture of 12 small organic acids at 10 mg/L using the NDC/TTAB-system in the presence of each 2000 mg/L chloride and sulfate

the electropherograms. However, when first the Ba- and secondly the Ag-exchanger was applied, sulfate was fully abolished. This effect is not fully understood, but it was supposed to be very suitable for the sample pretreatment of tannery wastewater.

Application on Tannery Wastewater

Recovery rates of individual compounds could not be investigated using tannery wastewater samples because the complexity of the organic load was much too high. Thus, we further studied DOC-losses after passing first the Ba- and second the Ag-cation exchanger using different tannery effluents (Table IV). DOC-coadsorption was between 8 and 67%. It is assumed, that the polymeric surface of the cation exchangers especially adsorbed non-ionic and cationic compounds, but maybe also anionic organic analytes including a hydrophobic part in their molecular structure. Some samples showed extraordinary chloride contents of up to 17 g/L, accompanied by sulfate with 8 g/L. For these samples,

TABLE III Recoveries of 10 ppm-solutions of 12 small organic acids after passing strong cation exchangers and removal of chloride and sulfate. For increasing sulfate contents, mean recoveries and relative standard deviations are given (n = 5), n.d. = not determined (see text)

anion	recovery [%] using a Ba-exchanger with		increasing contents of SO_4^{2-}	recovery [%] using an Ag-exchanger with	
	no inorg. anions	100 mg/L SO_4^{2-}		no inorg. anions	each 100 mg/L Cl^- and PO_4^{3-}
oxalate	92	83	decreasing	94	90
malonate	99	95		97	102
citrate	102	104	98 ± 12	101	98
maleate	94	96	111 ± 10	93	93
fumarate	85	89	106 ± 11	89	76
formiate/tartrate	94	93	93 ± 6	93	n.d.
malate	98	106	92 ± 7	103	n.d.
succinate	91	90	104 ± 5	97	n.d.
glutarate	94	78	97 ± 9	85	94
adipinate	59	53	86 ± 7	57	105
acetate	98	103	58 ± 4	95	95
			102 ± 9		

TABLE IV DOC-losses of tannery wastewater samples along the removal of chloride and sulfate

<i>wastewater sample</i>	DOC [mg/L] <i>original</i>	Loss of DOC [%] after		DOC-recovery [%] in <i>the desorption step</i>	Total loss of DOC [%]
		2 exchangers	4 exchangers		
beamhouse	untreated	2279	68	8	60
	aerobically treated ozonated	1558 2332	41 67	17 15	65 15
tan-yard	untreated	997	20	13	7
	anaerobically treated	435	37	13	24
	untreated	2710	44	7	33
	aerobically treated ozonated	913 3842	8	5 22	26 23

the cation exchanging capacities were overloaded and two Ag- and Ba-cartridges each had to be employed. The DOC-amounts were further reduced resulting in severe losses of 20–82%. A total removal of some organic anions was very likely. To minimize these losses, an additional desorption step has been introduced into the sample preparation procedure. When both Ag- and Ba-cartridges were washed using 10 mL of a 0.1 m NaOH-solution, between 5–22% of the original DOC-content could be recovered. It is assumed that the rest predominately consisted of hydrophobic compounds which could only be eluted by organic solvents. Another part might be due to irreversible adsorption, but a detailed investigation was beyond the scope of this study. However, it can be stated that a remarkable part of the organic load might be lost during the removal of chloride and sulfate. It seems that neither the kind of tannery wastewater stream nor the step of biological treatment directly indicate the amount of DOC-losses. Careful recovery tests should be included when analyses of organic anions of special interest are requested.

In CE-analyses, no separation of the tannery wastewater samples could be achieved without removal of chloride and sulfate (Figure 4, A). Some authors dilute samples to avoid matrix effects,^[29] but in fact, concentrations of most anions in tannery wastewater were below the detection limits, afterwards (B). However, after removal of chloride and sulfate, a clear separation of about 45 anionic compounds was achieved (C), and some of them showed additional shoulders. Many of these anions can be characterized as compounds with a comparatively low mobility, indicating large molecules with a low charge density. When additional cation exchangers are used to remove excess inorganic anions (D), most of these slowly migrating organic compounds have also been adsorbed. This finding supports the hypothesis that the DOC-losses might be due to hydrophobic adsorptions or to π - π -interactions with the polymeric material of the cation exchangers. Besides, there are remarkable shifts in the migration times of some anions. Therefore, migration times are obviously depending on matrix effects.

Additionally, the NaOH-desorption solutions of the cation exchanges were compared to the corresponding wastewater samples (Figure 5). It is shown that high amounts of anionic compounds could be recovered from the cation exchangers. Regarding the peak patterns, nearly all peaks in the desorption solution were also present in the electropherogram of the wastewater sample. For quantitative analysis of target analytes, the desorption solutions should be combined with the wastewater filtrates. However, this was not necessary for our aim of a qualitative characterization of wastewater electropherograms.

Compound identifications have been carried out in detail only for some wastewater samples. Generally, it has been found in our studies that identifications

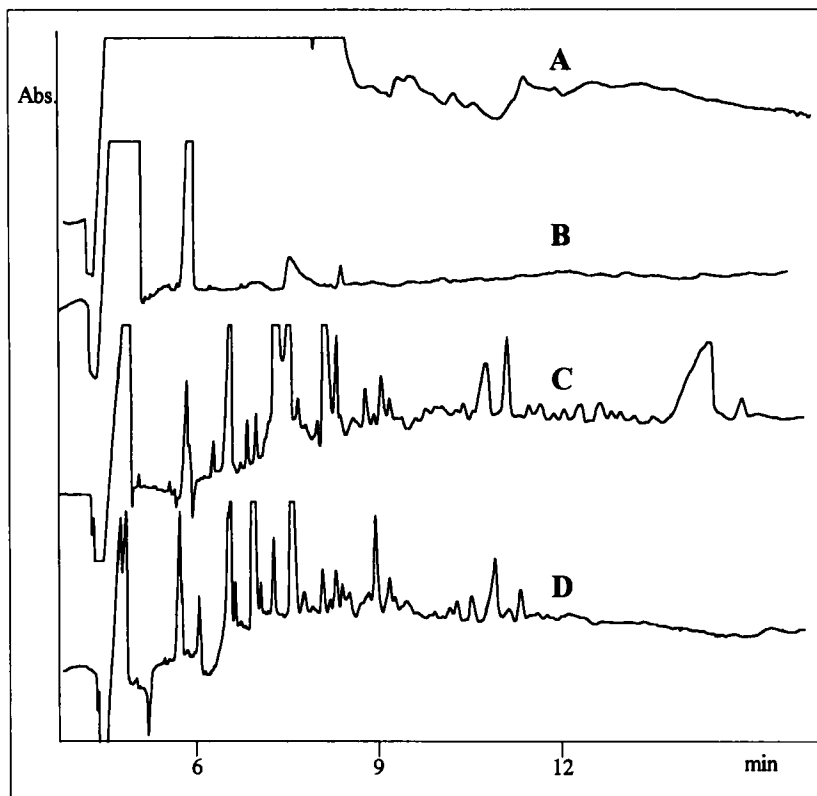


FIGURE 4 Comparison of the CE-analyses of an untreated beamhouse wastewater sample (all scaled from 0–11 mAU). A: without cation exchangers (original), B: without cation exchangers (1:20 diluted) C: after one Ba- and one Ag-exchanger, D: after two Ba- and two Ag-exchangers

cannot be carried out by comparison with external standard compounds, but only by spiking tests. In sum, 35 organic and 11 inorganic anions have been spiked sequentially to a beamhouse wastewater before and after the aerobic treatment and an aerobically cleaned tan-yard effluent (Figure 6). For some analytes, calibration curves have been worked out, and quantitative results of the identified compounds are given in parentheses. Although identifications were only assessed positive when the migration times of the spiked sample exactly matched the mobility and the peak form of an unknown peak, these spiking tests remain somewhat tentatively since there might be a variety of compounds with identical mobilities. However, some results are quite interesting. Lactate, for example, was not expected to be present at contents as high as 47 mg/L in the beamhouse wastewater, and it could not be found after the biological treat-

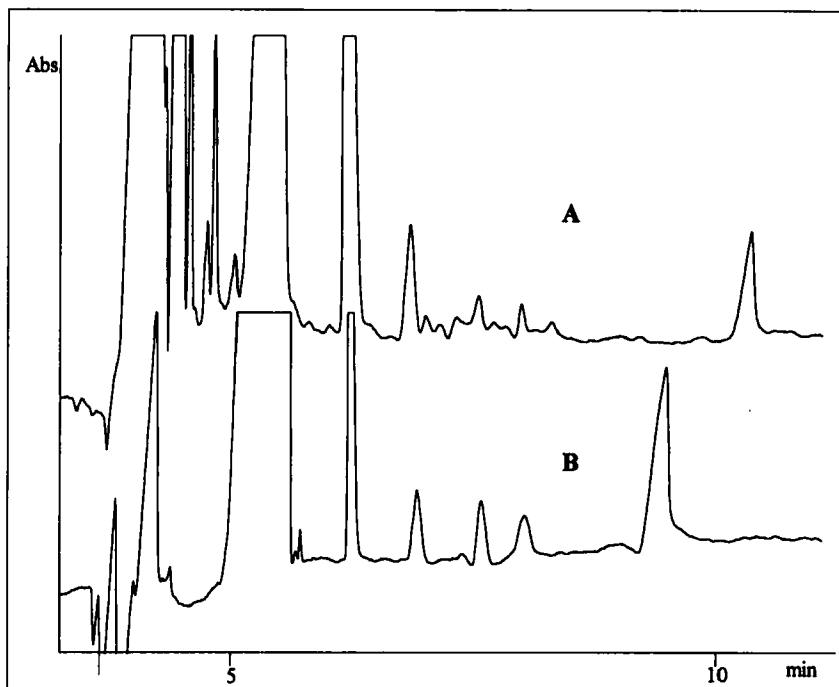


FIGURE 5 Comparison of the CE-pherograms of an untreated tan-yard wastewater sample after four cation exchangers (A) with its corresponding desorption solution (B)

ment. Instead, high amounts of propionate were detected after the aerobic treatment step, and possibly, lactate might have been directly transformed to propionate. Astonishingly, oxalate was only present in low amounts in one sample. Regarding the results of the recovery tests, oxalate might have been partially lost during the removal of chloride and sulfate. At least, it can be stated that oxalate was not present in high amounts in the wastewater samples. Acetate, propionate and butyrate have been found in aerobically treated samples of both tannery wastewater streams. Additionally, some slowly migrating compounds such as the unknown peaks u have been proven to be persistent to biological treatment. An evaluation of the environmental impact of these anions cannot be given without knowing their identities. For an identification of these unknown and poorly degradable organics, a reliable CE-MS interface with low detection limits would be very helpful.

CONCLUSION

With the help of strong cation exchangers in their Ag- and Ba-form, high contents of chloride and sulfate can be removed for subsequent capillary electrophoretic analyses. This pretreatment step only takes 15 min per sample.

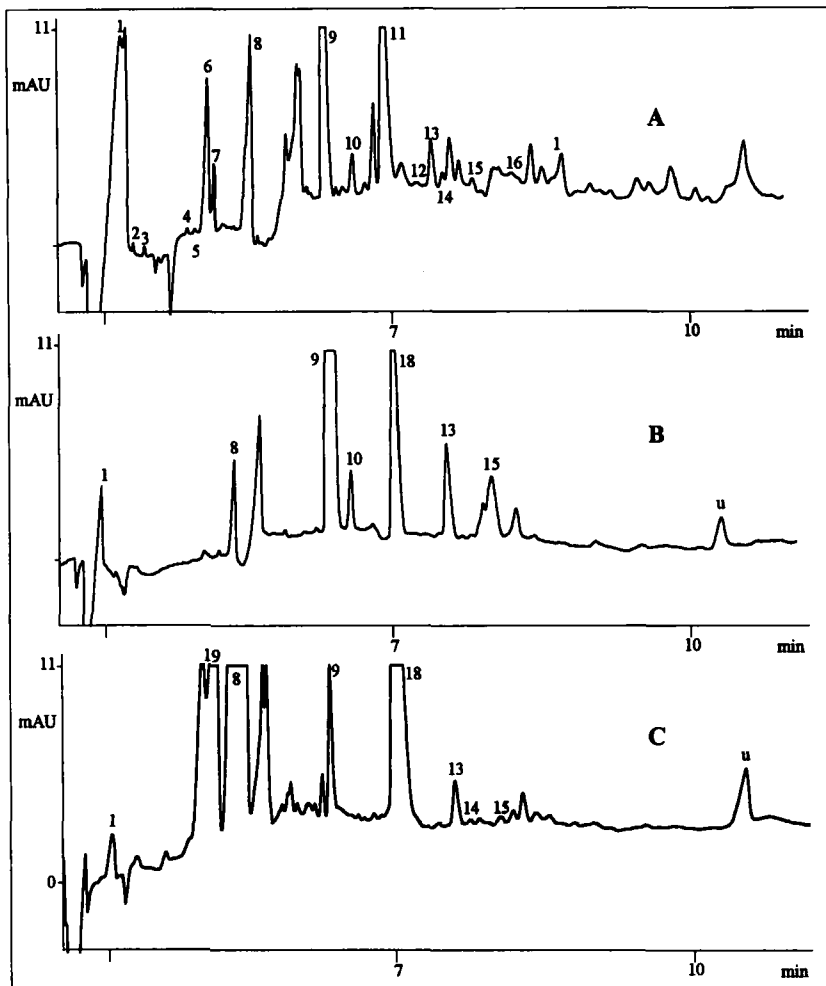


FIGURE 6 Tentatively identified anions in an untreated [A] and an aerobically treated beamhouse wastewater [B] as well as in an aerobically cleaned tan-yard wastewater sample [C] after four cation exchangers. 1 fast inorganic anions, 2 oxalate [A: 0.4 mg/L], 3 disulfite, 4 maleate, 5 fumarate ([A] 0.2 mg/L), 6 formiat ([A] 14 mg/L), 7 succinate, 8 carbonate, 9 acetate ([A] 27, [B] 8, [C] 33 mg/L), 10 glyoxalate ([A] 4, [B] 3 mg/L), 11 lactate ([A] 47 mg/L), 12 benzenesulfonate, 13 butyrate, 14 benzoate, 15 phenylacetate, 16 capronate, 17 indene-3-acetate, 18 propionate, 19 phosphate. For peaks u, see text.

Therefore, samples with extreme complexities such as tannery effluents have been made accessible for environmental analysis using capillary electrophoresis. Target analytes may be determined quantitatively, and degradation processes can be characterized by comparing corresponding electropherograms. For reliable

identification purposes, however, further developments of CE-interfaces and detectors are required.

Acknowledgements

We owe the company Schering AG, Berlin, a debt of gratitude for lending us a capillary electrophoresis instrument. The financial support by the German Research Council (DFG, Bonn) through SFB 193 "Biological treatment of industrial wastewater" project A8 is gratefully acknowledged.

References

- [1] M. L. Marina and M. Torre, *Talanta*, **41**, 1411–1433 (1994)
- [2] C. A. Monnig and R. T. Kennedy, *Anal. Chem.*, **66**, 280R–314R (1994)
- [3] R. Roldan-Assad and P. Gareil, *J. Chromatogr. A*, **708**, 339350 (1995)
- [4] S. J. Kok, E. H. M. Koster, C. Gooijer, N. H. Velthorst, U. A. Th. Brinkman and O. Zerbini, *J. High Resol. Chromatogr.*, **19**, 99–104 (1996)
- [5] Y.-C. Chao and C.-W. Whang, *J. Chromatogr. A*, **663**, 229–237 (1994)
- [6] E. V. Dose and G. Guiochon, *Anal. Chem.*, **64**, 123–128 (1992)
- [7] M. Jimidar, Q. Yang, J. Smeyers-Verbeke and D. L. Massart, *Trends Anal. Chem.*, **15**, 91–102 (1996)
- [8] W. C. Brumley, *J. Chromatogr. Sci.*, **33**, 670–685 (1995)
- [9] G. Dinelli, A. Vicari and P. Catizone, *J. Chromatogr. A*, **733**, 337–347 (1996)
- [10] C. D. Gaitonde and P. V. Pathak, *J. Chromatogr.*, **514**, 389–393 (1990)
- [11] V. Dolník and J. Dolníková, *J. Chromatogr. A*, **716**, 269–277 (1995)
- [12] J. Boden, M. Darius and K. Bächmann, *J. Chromatogr. A*, **716**, 311–317 (1995)
- [13] J. Jochimsen and M. Jekel, *Water Sci. Tech.*, **33**, (in press) (1997)
- [14] T. Reemtsma, O. Fiehn, G. Kalnowski and M. Jekel, *Environ. Sci. Technol.*, **29**, 478–485 (1995)
- [15] T. Reemtsma and M. Jekel, *J. Chromatogr.*, **660**, 199–204 (1994)
- [16] O. Fiehn and M. Jekel, *J. Chromatogr. A* (in press) (1997)
- [17] T. Reemtsma and M. Jekel, *Water Res.* (in press) (1997)
- [18] H. Schenk and W. Hegemann, *GWF Wasser/Abwasser*, **136**, 465–470 (1995)
- [19] W. M. F. Nielen, *J. Chromatogr.*, **588**, 321–326 (1991)
- [20] W. Buchberger, S. M. Cousins and P. R. Haddad, *Trends Anal. Chem.*, **13**, 313–318 (1994)
- [21] T. Wang and R. A. Hartwick, *J. Chromatogr.*, **607**, 119–125 (1992)
- [22] Y.-T. Wang, *Water Environ. Res.*, **64**, 268–273 (1992)
- [23] I. Z. Atamna, H. H. Issaq, G. M. Muschik and G. M. Janini, *J. Chromatogr.*, **588**, 315–320 (1991)
- [24] E. Dabek-Zlotorzynska and J. F. Dlouhy, *J. Chromatogr. A*, **685**, 145–153 (1994)
- [25] G. W. Tindall, D. R. Wilder and R. L. Perry, *J. Chromatogr.*, **641**, 163–167 (1993)
- [26] G. A. Ross, *J. Chromatogr. A*, **718**, 444–447 (1995)
- [27] O. Fiehn, G. Wegener, J. Jochimsen and M. Jekel, *Water Res.* (subm.)
- [28] M. Chiari and E. Kandler, *J. Chromatogr. A*, **716**, 303–309 (1995)
- [29] C. H. Wu, Y. S. Lo, Y. H. Lee and T. I. Lin, *J. Chromatogr. A*, **716**, 291–301 (1995)