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Capillary electrophoresis and sample stacking in non-aqueous media for the analysis of priority pollutant phenols

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Abstract

Non-aqueous capillary electrophoresis was applied to the separation of phenol derivatives included in the US Environmental Protection Agency list of priority pollutants and European Union directive 76/464/EEC concerning dangerous substances discharged into the aquatic environment. Best results were obtained with 60 m*M* ammonium acetate solution in acetonitrile–0.1 *M* KOH methanolic solution–acetic acid (74:25:1) as running buffer. A significant sensitivity enhancement was observed when field-amplified sample stacking in non-aqueous media was assayed for the study of low concentrated samples.

Keywords: Non-aqueous capillary electrophoresis; Sample stacking; Phenols

1. Introduction

The use of organic solvents as modifiers in capillary electrophoresis (CE) is a well-known alternative for the analysis of two basic classes of solutes: (a) sparingly water-soluble compounds, (b) compounds that show very similar electrophoretic mobility in aqueous media. The introduction of organic solvents extends the range of application of CE; one would have wider ranges of dielectric constant, polarity, density, viscosity and acid/basic properties to choose from.

Non-aqueous capillary electrophoresis (NACE), however, is a recently developed field. Walbroehl and Jorgenson [1] were the first in describing a CE application in a pure non-aqueous solvent for the separation of quinoline-like compounds in acetonitrile. Since then, interest in research into the possibilities offered by CE in non-aqueous systems has increased considerably.

The use of non-aqueous solvents for CE of small molecules has proven very beneficial for obtaining high selectivity using only simple electrolytes. Changing one organic solvent for another results in different solvation state of solutes, different total mobility and eventually, different separation selectivity [2]. Chemical and physical properties of non-aqueous solvents are much different from those of water and can be exploited in the optimization of CE separation. In CE, selectivity is based on differences in the effective charge–hydrodynamic ratios of analytes. This means that selectivity can only be achieved in solvents that are able to solvate charged compounds. Depending on the solvent, pK_a values of chargeable compounds can vary dramatically and different selectivity can be obtained by adjusting analyte acid–basic properties [3]. Even small differ-

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ences in the pK_a value of the compounds can be the basis of separating closely related molecules.

Other advantages of organic media for CE include reduced interaction of hydrophobic compounds with the negatively charged capillary wall, ion-pairing capabilities and the ability to invoke various forms of chemical equilibrium in order to place a charge on compounds, hence making them amenable to CE analysis [4]. Finally, the use of organic solvents results in very low currents and Joule heating compared to typical aqueous buffers, allowing much higher electric field strengths for theoretically faster and more efficient separations [5].

Increasingly, reports are being published on the use of CE for industrial and environmental applications, some of them focussed on phenol and substituted phenols determination. These reports include priority pollutant phenols determination with common aqueous buffers [6,7], sensitivity enhancement strategies for phenols determination at low concentration levels [8–10], and the use of buffer additives for improving resolution of phenols [11,12].

The presence of phenol and substituted phenols is not significant in natural waters because they are only present as a result of the decomposition of some types of vegetation [6]. They only increase if wastewater from industrial or mineral processes in which phenol and substituted phenols are used is not properly treated [13]. These compounds can persist under environmental conditions, depending on the temperature and pH, in ground water and even at low concentrations are detrimental on the taste and odor of water. Phenols have been found to be toxic to most aquatic organisms and most of them are listed in the European Union directive 76/464/EEC concerning dangerous substances discharged into the aquatic environment [14] and in the US Environmental Protection Agency (EPA) list of priority pollutants [15–17].

Routine analysis of phenols can be performed using chromatographic and electrophoretic methods such as GC, HPLC, supercritical fluid chromatography, capillary zone electrophoresis (CZE) and isotachophoresis. The major drawback of CE is the high detection limit for the usually involved on-column UV detection (ppm range) which is a serious limitation for its application to environmental analysis [8].

Without modification of the instrument, the low concentration sensitivity can be overcome using electrokinetic sample concentration, also referred to as sample stacking [18]. Procedures for stacking of anions, cations and electrically neutral analytes in CZE in aqueous media [19–23] and micellar electrokinetic chromatography [24–27] have been developed.

In this paper a capillary electrophoresis method in non-aqueous media for rapid analysis of phenolic compounds included in priority pollutants lists of the European Union and the EPA is presented. A sample stacking methodology in organic media for high sensitive phenols determination was assayed too.

2. Experimental

2.1. Chemicals

Acetonitrile (Merck, Darmstad, Germany) and methanol (Scharlau, Barcelona, Spain) were HPLC grade and used as received. Acetic acid, 2-methyl-4,6-dinitrophenol and 2,4-dichlorophenol were obtained from Merck. Ammonium acetate, phenol, 2-chlorophenol, 2,6-dichlorophenol, 2,4,5-trichlorophenol, pentachlorophenol, 4-nitrophenol, 4-chloro-3-methylphenol, 3-methylphenol, 2,4-dimethylphenol, 2-nitrophenol, 2,4-dinitrophenol, 2-amino-4-chlorophenol, 3-chlorophenol, 2,3,5-trichlorophenol and 4-chlorophenol were obtained from Aldrich (Madrid, Spain), 2-methylphenol and 4-methylphenol were from Fluka (Buchs, Switzerland).

Dinoseb was obtained from Sigma (Madrid, Spain); 2,3,4,5-tetrachlorophenol was from Supelco (Bellefonte, PA, USA); 2,3,4,6-tetrachlorophenol, 2,4,6-trichlorophenol, 2,3,4-trichlorophenol, 2,3,6-trichlorophenol and 2,3,5,6-tetrachlorophenol were from Riedel-de Haën (Seelze, Germany). Potassium hydroxide was obtained from Carlo Erba and sodium hydroxide was from BDH (Poole, UK). Ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Apparatus

Capillary electrophoresis was performed using a HP^{3D} system (Hewlett-Packard, Waldbronn, Ger-

many) equipped with an on-column diode array detection (DAD) system. A detection wavelength of 210 nm (direct UV detection) was used for all samples unless otherwise stated.

Composite uncoated narrow-bore silica capillaries (supplied by Tecnokroma, Barcelona, Spain) with an inner diameter of 75 μm, a total length of 70 cm and effective separation length of 62,5 cm were used. The capillary was thermostated to 18.5°C. A Techne RB-5A external water bath was used for thermostating the sample tray to 18.5°C.

Samples were injected by applying a pressure of 50 mbar for 2 s unless otherwise stated. The applied voltage for separation was 30 kV (either positive or negative).

New capillaries were rinsed with 1 *M* sodium hydroxide for 20 min. Before each injection, capillaries were conditioned by washing them with 0.1 *M* sodium hydroxide for 3 min, water for 5 min, organic solvent corresponding to the electrophoresis medium for 2 min and 5 min with the separation electrolyte. Between runs, capillaries were flushed for 5 min with water.

All solutions were filtered before use through a membrane of 0.22 μm pore size.

2.3. Sample preparation

Stock solutions of each phenol derivative were prepared at 1000 μg/ml. Chemical standards were dissolved in the solvent or solvent mixture corresponding to the electrophoresis medium, except in the case of stacking injections as detailed in the results and discussion section. All solutions were refrigerated and protected against daylight. Prior to injection, stock solutions were diluted 10 times with the running buffer for using them as working solutions

3. Results and discussion

In previous work [10], the separation of the EPA priority pollutant phenols by CE in aqueous buffers was studied with emphasis on buffer pH selection. The pK_a values in water of these phenols range from 4 to 10.6, this means that at alkaline pH they all are probably at least partially dissociated, ready for CE analysis. However, the direct comparison of separations in aqueous buffers and in organic solvents is difficult for many reasons: attending to the chemical and physical properties of organic solvents, the experimental conditions are very different compared with aqueous media electrophoresis. Non-aqueous electrolyte also leads to shifts in the dissociation constants for both acidic and basic compounds. The solute pK_a may change for different solvents by many orders of magnitude. Then, we cannot use pH values of aqueous buffers in the optimization of NACE separations, so previous works about CE separations of phenols with aqueous buffers were almost useless for choosing the starting experimental conditions.

Capillary characteristics (diameter and length) and conditioning sequence were chosen as follows: separation complexity dictates the appropriate capillary length; it is recommended to use a capillary of 50–60 cm for 11–50 analytes and for best UV detection limits, 50–100 μm inner diameter (I.D.) must be used [28]. According to the complexity of sample under study (a mixture of 26 compounds in our case), a 70 cm×75 μm I.D. fused-silica capillary was chosen.

On the other hand, the appropriate treatment of the capillary wall is critical to ensure a consistent and repeatable electroosmotic flow (EOF). As described in Section 2, for capillary conditioning we follow a simple sequence, similar to that used in aqueous systems: 0.1 *M* NaOH, water, pure organic solvent (corresponding to buffer solvent) and electrolyte. The conditioning process involves aqueous and organic phases, and special care was taken about the compatibility of these phases inside the capillary; many inorganic ions are poorly soluble in organic solvents, and precipitated buffer crystals can block the capillary. In this sequence, the capillary was rinsed with water after the 0.1 *M* NaOH step. Then, water is eliminated by flushing the capillary with pure organic solvent, prior to final conditioning step with electrolyte solution.

Before choosing the electrolyte solution, acidic/basic properties of phenols derivatives must be considered in order to ensure solute dissociation and electrolyte solubility in the particular organic solvent selected. One of the most important features of organic solvents to be used in NACE is the protolytic

behavior. Acetonitrile, a very weak base as well as a very weak acid is a good differentiating solvent for acidic and basic solutes. Due to its good UV transparency and low viscosity, acetonitrile is the first choice solvent for NACE.

Due, however, to its aprotic characteristics, acetonitrile seems to be a less suitable solvent for most of the common electrolyte salts. By adding some hydrogen-bond donor, e.g., acetic acid, the solubility of salts can be considerably enhanced thus overcoming this drawback. In a recent paper by Hansen et al. [2], ammonium acetate, which is soluble in many organic solvents, has been considered one of the most suitable electrolyte for NACE.

Buffer concentration depends on separation requirements: high ionic strengths must be used for closely related analytes or numerous analytes. In this case, with a 75-μm I.D. capillary, a good first choice is 25–50 m*M* [28]. Ammonium acetate, however, has limited solubility in pure acetonitrile; for preparing relatively concentrated solutions addition of acetic acid is needed. First experiments were carried out using 25 m*M* ammonium acetate and 1 *M* acetic acid in acetonitrile [3].

3.1. Analysis of complex mixtures: normal hydrodynamic injection

In order to obtain a first estimation about system performance, individual solutions of 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol and a mixture of them (all diluted in electrolyte solution) were injected.

In first runs, capillary temperature was set at 25°C (sample tray temperature was not controlled). At this temperature, it was demonstrated that acetonitrile, a relatively volatile solvent, under the separation voltage (30 kV) may reach its boiling point and the bubbles alter the electric continuity inside the capillary, leading to current drops. This is the reason it was necessary to control the temperature of capillary and sample tray at 18.5°C. Under controlled temperature conditions, the results were successful concerning peak shape and analysis time. In the mixture, all three components were resolved in approximately 12 min (electropherograms not shown). Fig. 1 shows the electropherogram corresponding to the analysis of a mixture of all compounds in the study (26 phenol derivatives) diluted with electrolyte solution. The electropherogram only shows nine peaks including two not baseline resolved. Three levels of ionic strength were assayed: (a) 0.5 *M* acetic acid–25 m*M* ammonium acetate, (b) 2 *M* acetic acid–50 m*M* ammonium acetate and (c) 4 *M* acetic acid–100 m*M* ammonium acetate. The results indicated (electropherograms not shown) that slightly better resolution can be attained on increasing buffer concentration (systems b and c), but the analysis time becomes too long. As the nature of the organic solvent or solvent mixture used for the electrophoresis medium may have a strong influence on the separation selectivity, acetonitrile–methanol combinations were also assayed as electrolyte solvent.

Methanol has favorable properties for NACE, such as dielectric constant, viscosity and a useful UV range for detection. Moreover, being an appropriate solvent for most common electrolyte salts, methanol allows the preparation of buffers with higher ionic strength [29].

Electrolyte solutions for first runs were prepared with equivalent volumes of acetonitrile (MeCN) and methanol (MeOH), and three levels of ionic strength were evaluated: (a) 20 m*M*, (b) 40 m*M* and (c) 60 m*M* of ammonium acetate, all dissolved in MeCN–MeOH–acetic acid (49:50:1).

Improved resolution (compared with previous best results) was obtained with system (c) (see Fig. 2a). This change in selectivity is probably due to the influence of methanol in the solvation process of solutes: both solvated ionic radius of the solute ion and pK_a values are altered when switching between solvents. This leads to increased differences in mobility because structural differences are now more important. Further improvements in selectivity (See Fig. 2b) were obtained using 60 m*M* ammonium acetate in MeCN–MeOH–acetic acid (74:25:1) as running buffer (20 and 40 m*M* ammonium acetate were evaluated too). The MeCN–MeOH (75:25) mixture has the lowest viscosity [30] even compared to each pure solvent and it may explain the results. Jansson and Roeraade [31] showed that the efficiency by time unit depends on the electrolyte ϵ^2/η ratio because both electrophoretic and electroosmotic mobilities are functions of ϵ^2/η. Then, in principle, solvents exhibiting high ϵ^2/η ratios should provide higher efficiencies. It is also evident from this

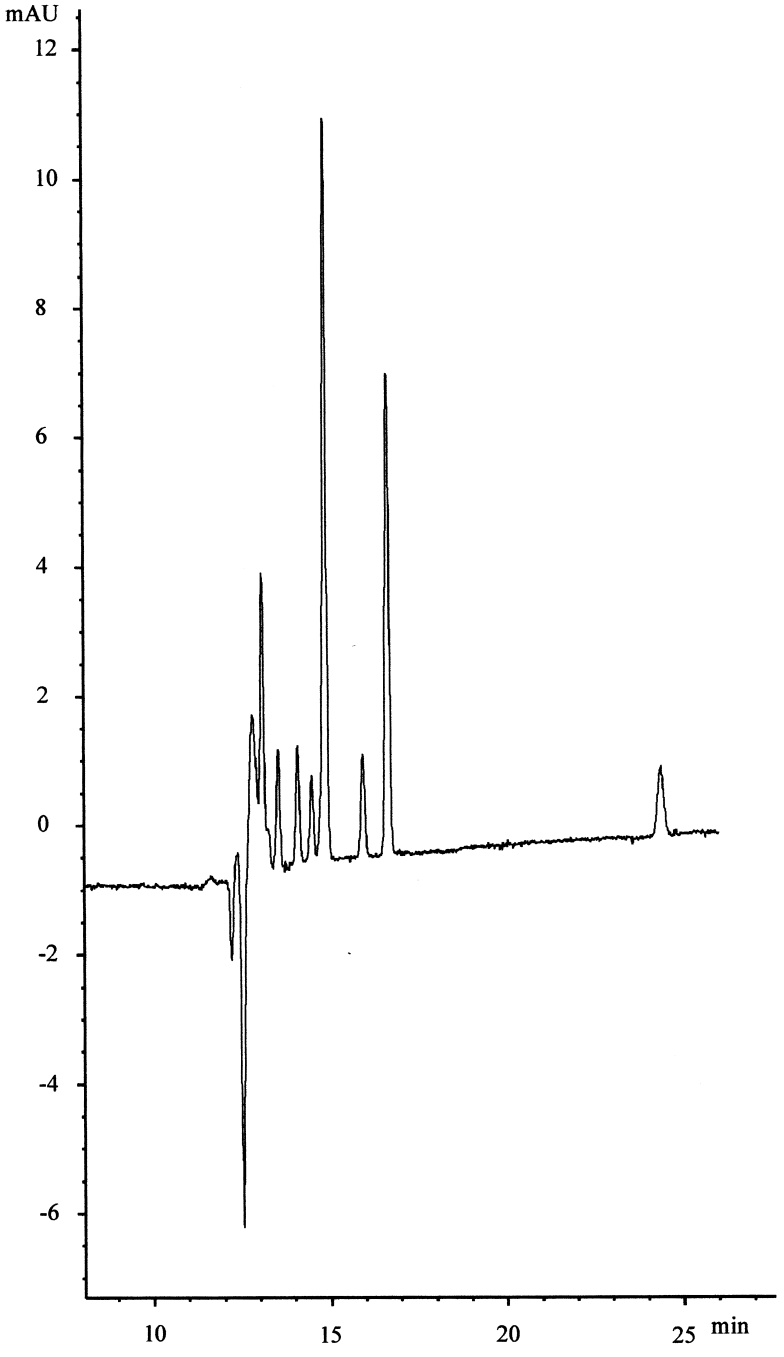

Fig. 1. Electropherogram corresponding to the mixture of 26 phenols in study diluted with electrolyte. Injection, hydrodynamic (50 mbar by 2 s); running buffer, 25 m*M* ammonium acetate and 1 *M* acetic acid in acetonitrile; capillary, 70 cm×75 μm I.D.; applied voltage, 30 kV; detection, 210 nm.

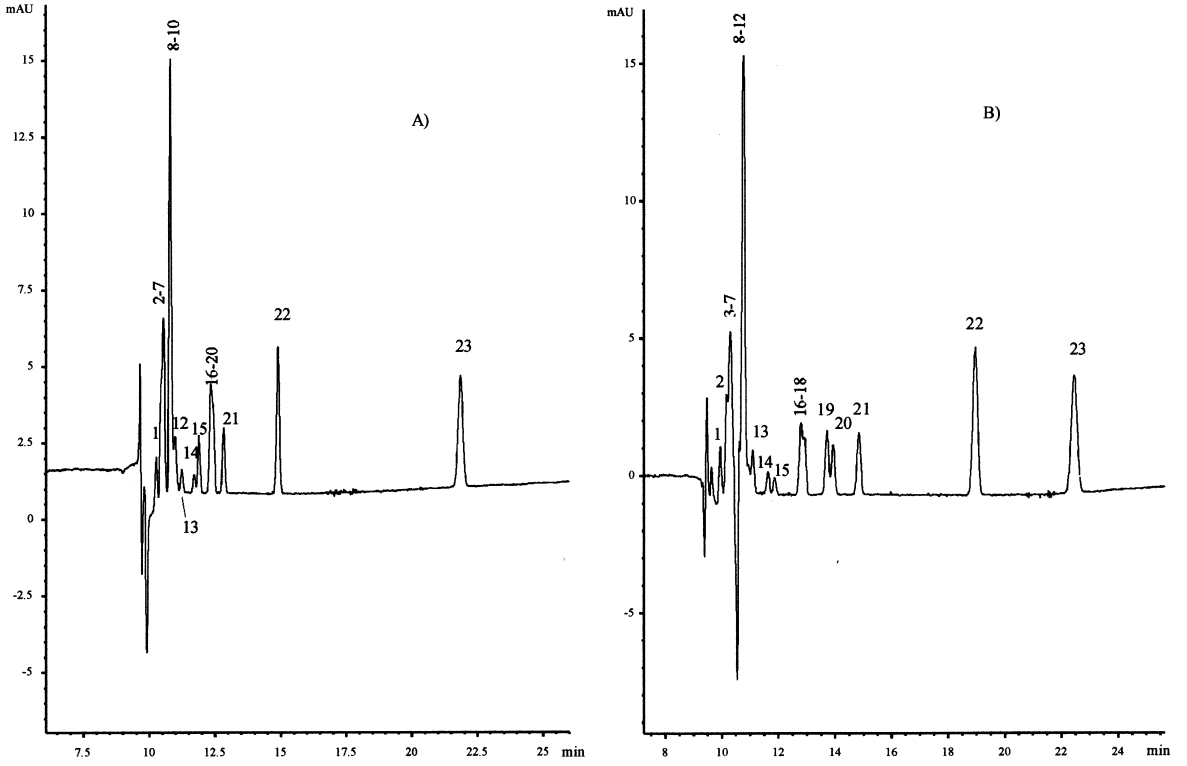

Fig. 2. Electropherograms of the mixture of 26 phenols in study diluted with electrolyte. Injection, hydrodynamic (50 mbar by 2 s); capillary, 70 cm×75 μm I.D.; applied voltage, 30 kV; detection, 210 nm. (A) Running buffer, 60 m*M* ammonium acetate in acetonitrile–methanol–acetic acid (49:50:1); (B) running buffer, 60 m*M* ammonium acetate in acetonitrile–methanol–acetic acid (74:25:1).

relationship that the lower the solvent viscosity (being ϵ constant), the better the efficiency attainable.

With this running buffer (MeCN–MeOH–acetic acid, 74:25:1), however, compounds that migrate close to EOF (at lowest migration times) are not properly resolved; probably the buffer is unable to dissociate them. New attempts were carried out substituting methanol by 0.1 or 0.05 *M* potassium hydroxide methanolic solutions. Both systems provided enhanced resolution of almost all above-mentioned peaks that previously appeared partially overlapped (see Fig. 3 corresponding to 0.1 *M* potassium hydroxide methanolic solution). By carrying out individual injections of each investigated phenol it was demonstrated that *o*-cresol, *m*-cresol, *p*-cresol and 2,6-dichlorophenol have very similar mobility, giving one peak in the electropherogram. The same happens with 2-chlorophenol, 2-amino-4-chlorophenol and 4-chloro-3-methylphenol, which originate only one peak. KOH concentrations higher than 0.1 *M* produced increasingly higher currents, poor resolution between peaks and noisy baselines.

Besides that, in positive polarity (cathodic detection) 2-methyl-4,6-dinitrophenol, 2,4-dinitrophenol and dinoseb migrate to the anode and make its detection impossible. This observation can be explained considering that the magnitude of EOF might be not enough to overcome the intrinsic mobility of corresponding phenolates towards the anode. All three compounds can be readily analyzed in negative polarity (anodic detection), as shown in Fig. 4.

3.2. Sample stacking injections

Once a suitable system performance was reached for non-aqueous electrophoretic separation of a complex mixture of phenols (60 m*M* ammonium

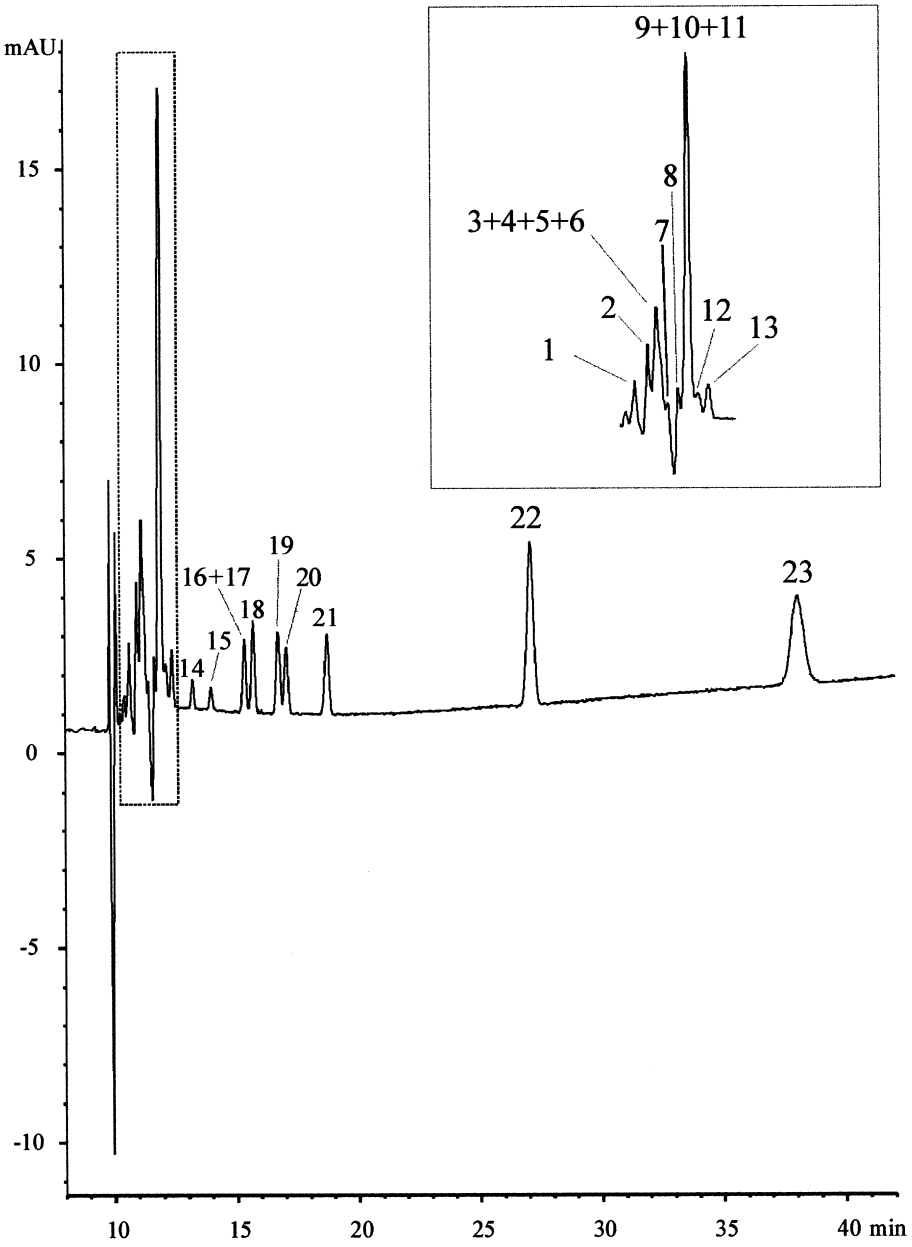

Fig. 3. Electropherogram of the mixture of 26 phenols in study diluted with electrolyte. Injection, hydrodynamic (50 mbar by 2 s); running buffer, 60 m*M* ammonium acetate in acetonitrile–0.1 *M* KOH methanolic solution–acetic acid (74:25:1); capillary, 70 cm×75 μm I.D.; applied voltage, 30 kV; detection, 210 nm. Compounds: (1) 2-nitrophenol (35 μg/ml); (2) 2,4-dimethylphenol (70 μg/ml); (3) *o*-cresol (117 μg/ml); (4) *m*-cresol (47 μg/ml); (5) *p*-cresol (117 μg/ml); (6) 2,6-dichlorophenol (117 μg/ml); (7) phenol (117 μg/ml); (8) pentachlorophenol (234 μg/ml); (9) 2-chlorophenol (56 μg/ml); (10) 2-amino-4-chlorophenol (117 μg/ml); (11) 4-chloro-3-methylphenol (47 μg/ml); (12) 4-chlorophenol (24 μg/ml); (13) 3-chlorophenol (24 μg/ml); (14) 2,4-dichlorophenol (24 μg/ml); (15) 2,4,6-trichorophenol (70 μg/ml); (16) 2,3,5,6-tetrachlorophenol (141 μg/ml); (17) 2,3,4-trichlorophenol (24 μg/ml); (18) 2,3,6-trichlorophenol (141 μg/ml); (19) 4-nitrophenol (70 μg/ml); (20) 2,4,5-trichlorophenol (24 μg/ml); (21) 2,3,5-trichlorophenol (24 μg/ml); (22) 2,3,4,5-tetrachlorophenol (47 μg/ml); (23) 2,3,4,6-tetrachlorophenol (47 μg/ml).

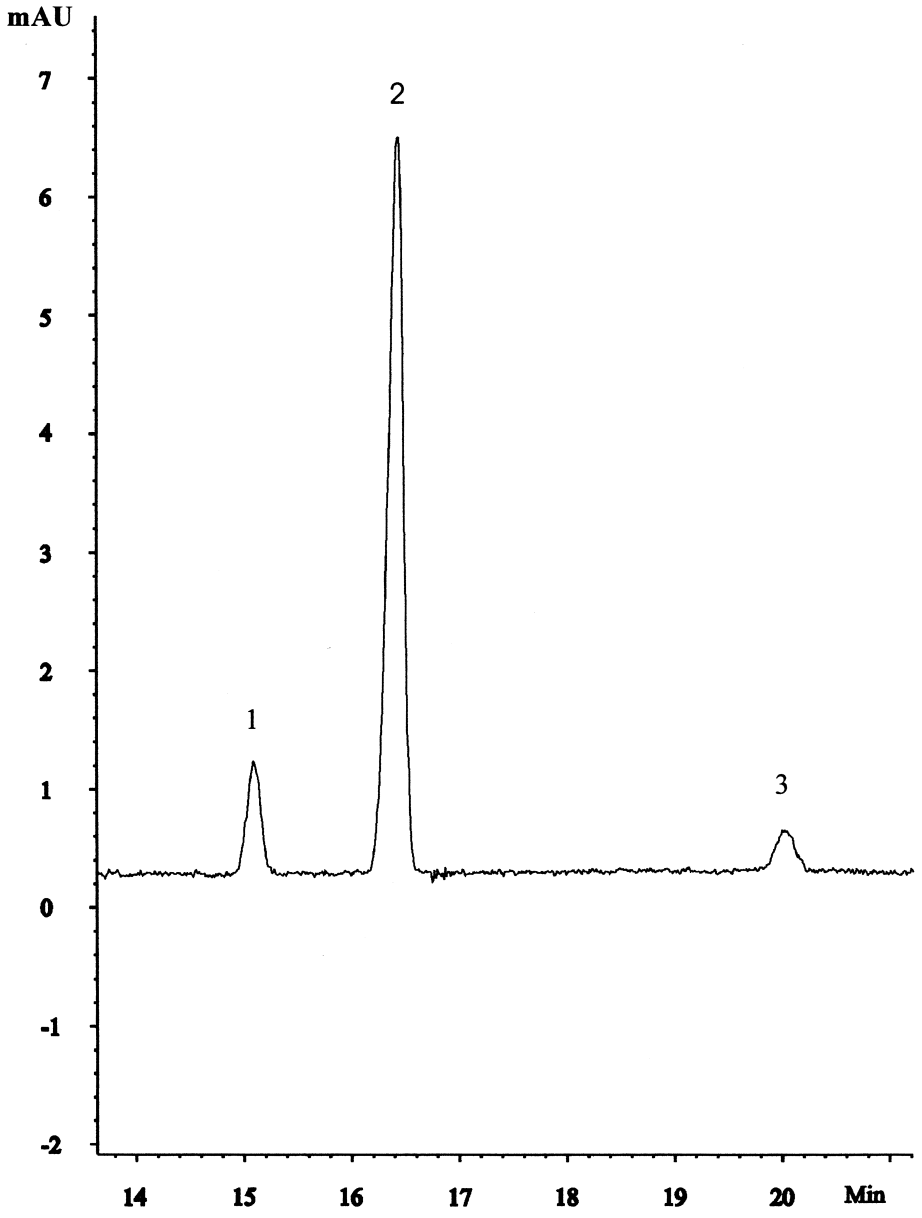

Fig. 4. Separation of a mixture of (1) 2,4-dinitrophenol (12 μg/ml), (2) 2-methyl-4,6-dinitrophenol (3 μg/ml) and (3) 2-*sec*.-butyl-4,6-dinitrophenol (3 μg/ml) diluted with electrolyte in negative polarity. Injection, hydrodynamic (50 mbar by 2 s); running buffer, 60 m*M* ammonium acetate in acetonitrile–0.1 *M* KOH methanolic solution–acetic acid (74:25:1); capillary, 70 cm×75 μm I.D.; applied voltage, −30 kV; detection, 370 nm.

acetate in MeCN–0.1 *M* KOH methanolic solution–acetic acid, 74:25:1), the next challenge was to try analyte enrichment strategies for low concentration sample analysis. If all analytes are stacked completely, electrostacking is the most promising way for on-column sample enrichment. This process involves the injection of large low conductivity sample volumes. At negative polarity the analytes migrate towards a high conductive buffer zone and the sample zone is simultaneously removed from the

capillary by the EOF (opposite direction). When the capillary is refilled with the buffer (at 95% of the buffer conductivity), the analytes have been focused into a small zone at the injection end of the capillary and electrophoretic separation is started with positive polarity.

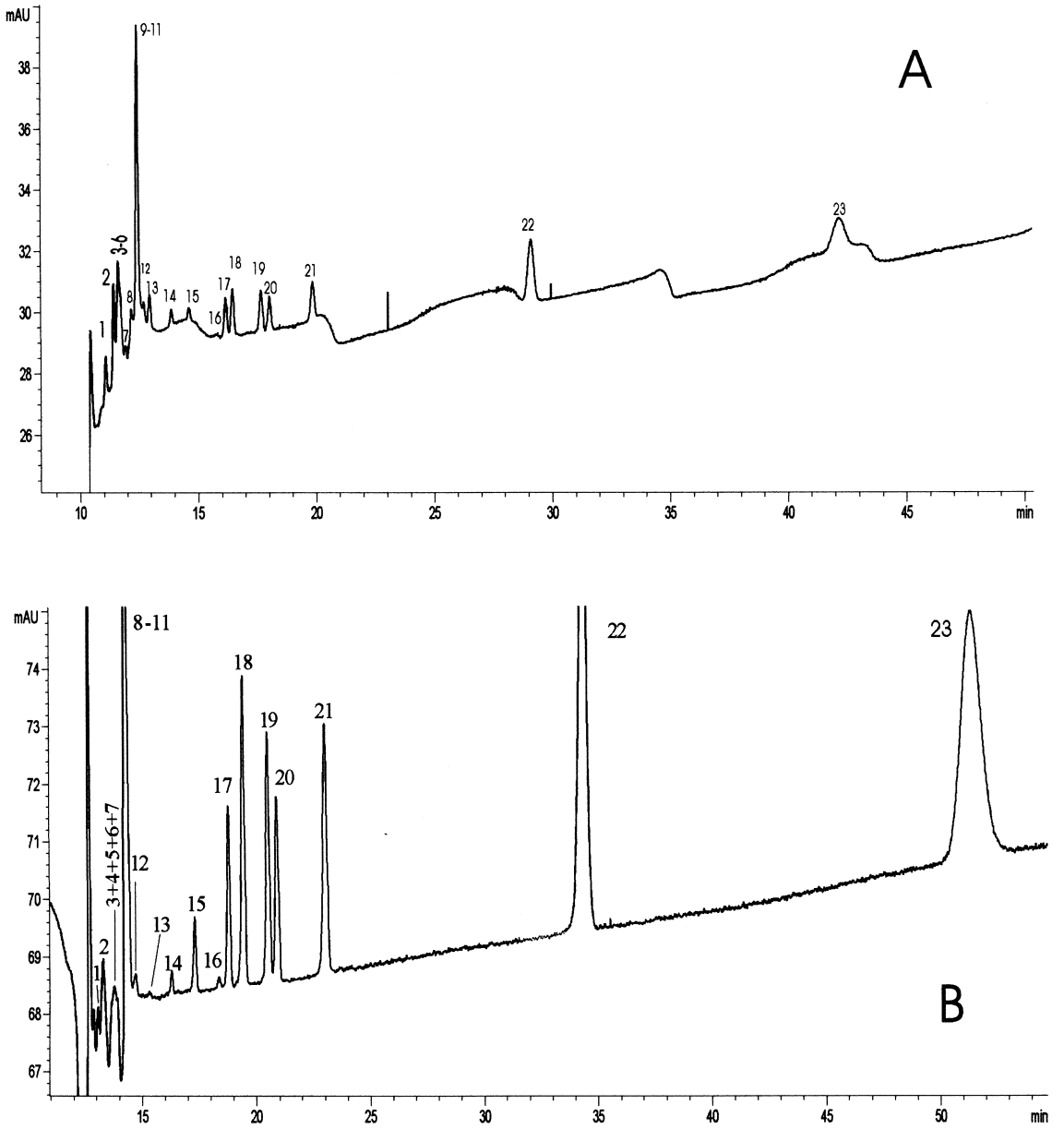

Fig. 5. Electropherograms corresponding to (A) a mixture of all compounds diluted 10 times (as compared to Fig. 3), in the running buffer; hydrodynamic injection (50 mbar by 2 s) and (B) the same mixture, diluted 400 times (compared to Fig. 3) in acetonitrile, sample stacking injection (50 mbar by 300 s). Running buffer, 60 m*M* ammonium acetate in acetonitrile–0.1 *M* KOH methanolic solution–acetic acid (74:25:1); capillary, 70 cm×75 μm I.D.; applied voltage, −30 kV for removing the matrix and 30 kV in the separation step; detection, 210 nm.

It is obvious that for the stacking of a large sample zone, a considerable difference in the conductivity of sample and buffer has to be created. In the case of phenols, to achieve high analyte mobility for the electrostacking process, all of them should be dissociated. The high pH needed leads to high conductivity in the sample zone, which represents a disadvantage for the stacking efficiency. Thus, in order to have a low conductivity solution for a large volume injection, pure MeCN, pure MeOH, MeOH–water mixtures and pure water were tried as sample solvent.

In all cases, long time hydrodynamic injections of samples diluted with water or MeOH–water combinations failed at the start of the separation step due to current drop once polarity was switched after matrix removing. In the case of pure MeOH, excessively high currents and noisy baselines were observed. For samples dissolved in pure acetonitrile the electrostacking in a non-aqueous system took place as it does in aqueous media: after a first step with negative polarity for matrix elimination the positive polarity was restored, starting then the separation process.

The sensitivity improvement achieved by the sample stacking was evaluated by comparing normal hydrodynamic injections (50 mbar by 2 s) and sample stacking injections (50 mbar by 300 s) of mixtures of phenolic derivatives dissolved in the running buffer (normal hydrodynamic injections) and in pure acetonitrile (stacking injections). Solutions used in normal injections were diluted close to the determination limit ($S/N=10$) (see Fig. 5a). Departing from this concentration level, the solutions subjected to sample stacking were successively diluted in order to evaluate the limit of determination attainable by this technique. Fig. 5b depicts an electropherogram of a solution diluted 40 times as compared to the one depicted in Fig. 5a. Notice the differences in the graph scales. In Table 1 the estimated values for the limits of determination in both techniques have been summarized for comparative purposes.

As can be seen in Fig. 5 and Table 1, the

Table 1
Enhancement of the limit of determination for peaks resolved in positive polarity through sample stacking

Compound	Peak number (as in figures)	Limit of determination (μg/ml) (normal hydrodymanic injection)	Limit of determination (μg/ml) (sample stacking injection)
2-Nitrophenol	1	2.0	0.08
2,4-Dimethylphenol	2	3.5	0.07
o-Cresol	3	11.7	0.3
m-Cresol	4	4.7	0.1
p-Cresol	5	11.7	0.3
2,6-Dichlorophenol	6	11.0	0.5
Phenol	7	12.0	0.9
Pentachlorophenol	8	24.0	3.0
2-Chlorophenol	9	5.6	0.5
2-Amino-4-chlorophenol	10	11.8	0.06
4-Chloro-3-methylphenol	11	4.7	0.02
4-Chlorophenol	12	2.4	0.03
3-Chlorophenol	13	1.2	0.06
2,4-Dichlorophenol	14	1.0	0.02
2,4,6-Trichorophenol	15	3.5	0.03
2,3,5,6-Tetrachlorophenol	16	7.0	0.08
2,3,4-Trichlorophenol	17	2.4	0.05
2,3,6-Trichlorophenol	18	3.5	0.02
4-Nitrophenol	19	1.5	0.01
2,4,5-Trichlorophenol	20	0.8	0.008
2,3,5-Trichlorophenol	21	0.6	0.003
2,3,4,5-Tetrachlorophenol	22	0.3	0.001
2,3,4,6-Tetrachlorophenol	23	0.4	0.001

detectability increase as a consequence of the stacking for those compounds that migrate close to EOF (shortest migration time) is lower than the one obtained for the other compounds studied. Something similar has been reported in the electrostacking of phenolic compounds with water-based buffers [10]. This behavior have been explained by assuming that during the stacking phase the EOF itself not only causes the matrix to be removed, but also the loss of some molecules of these compounds as a consequence of its low intrinsic mobility against the anode.

4. Conclusions

Non-aqueous CZE appears a useful alternative for the determination of most phenolic compounds included in the EPA and European Union/Directive lists of priority pollutants. Seventeen of the 26 compounds considered can be separated in positive polarity mode, while the other three can be easily resolved and analyzed in negative polarity mode.

As expected, the selectivity can be enhanced or manipulated by varying the type and amount of organic solvent used in the running buffer preparation. In the case of phenolic pollutants best results were achieved with the system ammonium acetate (60 m*M*) in acetonitrile–0.1 *M* KOH methanolic solution–acetic acid (74:25:1) as running buffer. The applicability of field-amplified sample stacking as an on-line enrichment technique in non-aqueous media has been proven by the electrostacking of large volumes of samples dissolved in pure acetonitrile.

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