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Multisyringe flow injection analysis coupled to capillary electrophoresis (MSFIA–CE) as a novel analytical tool applied to the pre-concentration, separation and determination of nitrophenols

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ABSTRACT

For the first time, a multisyringe flow injection analysis capillary electrophoresis system is described. The potential of the hyphenation for sample treatment including analyte pre-concentration is demonstrated by its successful application to the determination of *mono*-nitrophenols (NPs) in different water samples.

The analytical system was used to automate in-line sample acidification, analyte pre-concentration, elution, hydrodynamic injection, electrophoretic separation, and detection as well as the maintenance and re-conditioning of the solid-phase extraction (SPE) column and the separation capillary.

A pre-concentration factor of better than 115 and detection down to 0.11 μmol L^{-1} were achieved. Detection was carried out at visible wavelength using a blue LED as a low baseline-noise light source. High repeatability was obtained each for migration times and for peak heights with relative standard deviations typically below 2.5 and 6% including the pre-concentration procedure, respectively.

Three injections per hour were achieved by running in parallel the pre-concentrating and the electrophoretic separation procedures. Instrumental control and data registration and evaluation were carried out with the software package AutoAnalysis, allowing autonomous operation of the analytical system.

1. Introduction

In the present work, the hyphenation of multisyringe flow injection analysis (MSFIA) [1] with capillary electrophoresis (CE) is firstly described. The flow system was used for solid-phase extraction (SPE) pre-concentration of *mono*-nitrophenols (NPs) from water samples on a reverse phase (C18) mini-column, elution, and injection in a home-made CE system [2] as well as for all re-conditioning and cleaning procedures.

CE is a powerful tool in biomolecular, pharmaceutical, and environmental analysis and one of the fastest-growing analytical technique nowadays. Its advantageous characteristics are excellent separation efficiencies with up to several 100,000 theoretical plates, a simple instrumentation, and its versatility and applicability even to neutral analytes due to a variety of operation modes and detection techniques developed up-to-now [3,4]. Since the first works on CE [5,6], considerable investigation work was done to overcome the relatively low sensitivity derived from small sample and detection volumes as a main drawback of this technique, which also limits its applicability for trace analysis. Although these efforts have led to ingenious on-capillary concentration techniques such as sample stacking, focusing or sweeping techniques [7,8], SPE presents one of the most applied techniques for analyte enrichment. This is due to the variety of commercially available SPE products, handling simplicity and the simultaneous removal of sample matrix components, which might affect the CE separation. However, the SPE procedures are labor-intensive, time-consuming and the cartridges are relatively costly.

Flow techniques such as flow injection analysis (FIA) [9], sequential injection analysis (SIA) [10], Lab-on-valve technique [11] or MSFIA have been multiply applied for the automation of SPE pre-concentration [12–19]. The ability of these techniques to handle small liquid volumes precisely and reproducibly allow the minimization of the required sorbent and solvent quantity and improvement of sample frequency and reproducibility. On-line coupling of flow techniques and CE is an excellent supplementation combining the benefits of both techniques [20]. Apart from the potential of sensitivity improvement by automated pre-concentration [21–23], coupled flow systems can be used for the automation of sampling and injection protocols [24–27], required sample pre-treatment as mixing with required additives [28], ana-

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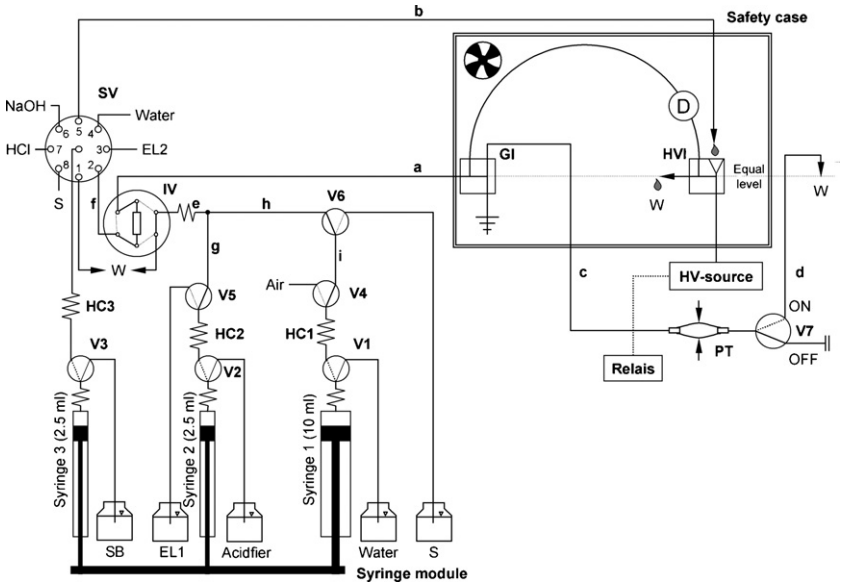

Fig. 1. Scheme of the MSFIA–CE system. GI: grounded interface, HVI: high-voltage interface, IV: injection valve with SPE column, SV: selection valve (Pos1: waste, Pos2: IV, Pos3: EL2, Pos4: water, Pos5: HVI, Pos6: HCl 10 mmol L^{-1}, Pos7: NaOH 10 mmol L^{-1}, Pos8: S, and V1–V7: solenoid valves with normally closed position (ON, activated, dotted) and normally open; position (OFF) straight; V3 and V7 of enhanced pressure stability, D: photometric detector cell, PT: pressure tube, and HC: holding coils (1: 500 cm, 1.5-mm i.d., 2: 150 cm, 0.8-mm i.d., 3: 175 cm, 0.8-mm i.d., a: tube 40 cm, 0.5-mm i.d., b: tube 50 cm, 0.5-mm i.d., c: tube 40 cm, 0.8-mm i.d., d: tube 20 cm, 0.8-mm i.d., e: 20 cm, 0.8-mm i.d., knotted, f and g: 10 cm, 0.8-mm i.d., h and i: PVC tubes 4 cm, 0.8-mm i.d., SB: separation buffer, W: waste, S: sample, EL1: 10 mmol L^{-1} NaOH with 40% MeOH, and EL2: 10 mmol L^{-1} NaOH with 10% acetonitrile.

lyte derivatization [29,30] or sample clean-up [31,32]. The fully automation of the analytical procedure using flow techniques further allows the application of CE for monitoring purposes [33]. A review of coupling flow techniques to CE has been published lately [34]. An overview about interfacing modes and resulting instrumental limitations can be found elsewhere [2].

MSFIA comprises advantages of SIA, such as a programmable syringe pump, high pressure and solvent robustness, low consumption of sample and reagents, and easy adaptation of the analytical procedure by software control as well as of FIA, such as multichannel manifolds, implementation of multicommutation using additional solenoid valves and a high-sample frequency due to parallel execution of flow operations. MSFIA instrumentation, flow-network configurations, and analytical applications have been reviewed lately [35].

Phenolic derivates such as NP are substances of considerable toxicity showing mutagenic, cyto- and phyto-toxic effects and are regarded as priority pollutants [36]. They are widely used in plastic, textile, pharmaceutical, armaments, paper, and dye-fabricating industry. Further anthropogenic sources are pesticide degradation and combustion processes [37,38]. They also present secondary pollutants generated by nitration of phenolic compounds in the atmosphere [39,40]. Consequently, they can be found in different environmental compartments such as atmosphere, precipitation, surface, and ground water or leaching water from land areas of former-mentioned industries [41]. Analytical techniques with the ability to monitor NPs including automated pre-concentration and quantification of the different species are therefore of high interest.

Former analytical flow technique applications for nitrophenols are based on multivariant regression using absorbance spectra data in order to achieve the quantification of the single compounds [42–44]. Although limits of detection (LOD) in the range of 0.5–0.04 μmol L^{-1} were achieved applying liquid–liquid extraction (LLE) or SPE for analyte pre-concentration and even down to 3 nmol L^{-1} applying reflectometry [45], the precision of species quantification of separation techniques can hardly be achieved.

With separation techniques such as HPLC and CE, a resolution between the analytes and absorbing matrix components is ideally achieved, by this allowing the application of less selective but more sensitive spectrometric detection at deep ultraviolet. In combination with CE using a capillary of either 75-μm i.d. [46] or 300-μm i.d. [47], including sample stacking [48] or SPE [49], or with HPLC with prior LLE [50], LOD in the range of 1.4 mg L^{-1}, 27, 0.7, and 2 μg L^{-1} were obtained, respectively. Electrochemical detection on HPLC in combination with SPE pre-concentration allowed the detection of even 10 ng L^{-1} [51].

In this paper we demonstrate the advantages of coupling MSFIA and CE as an alternative analytical tool to the former approaches for the fully automation of sample treatment (acidification, pre-concentration, and elution) and electrophoretic separation on the analytes NP with visible wavelength spectrometry.

2. Material and methods

2.1. Reagents

Distilled water and chemicals of analytical-reagent grade were used throughout. All stock solutions and water for dilution were filtered through 0.45 μm nylon membrane filters prior to use.

Stock solutions of *mono*-NP (each 600 mg L^{-1}) were prepared by accurate weighting using 10 mmol L^{-1} NaOH. An intermediate stock solution containing *p*-NP, *o*-NP, and *m*-NP in the concentrations of 30, 60, and 120 mg L^{-1}, respectively, was prepared and used for all experiments applying CE. Both stock solutions were stored in the dark. Standard working solutions were prepared daily by proper dilutions. For the optimization experiments on the pre-concentration and elution procedures applying a flow cuvette instead of the CE apparatus, a solution of *p*-NP of 0.3 mg L^{-1} was used.

All CE separations were carried out using a borate separation buffer (SB) of pH 9.7 of a final concentration of 40 mmol L^{-1} containing 10% (v/v) methanol as organic modifier. It was prepared daily from a stock solution of 1 mol L^{-1} sodium borate. HCl