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Short Communication

Capillary electrophoresis coupled on-line with flame photometric detection

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Abstract

Preliminary work indicates that capillary electrophoresis can be coupled on-line with a gas chromatographic detector such as a flame photometric detector. A test mixture containing low-nanogram amounts of three organophosphorus compounds has successfully been analysed.

1. Introduction

In analytical chemistry, the determination of more polar, and also ionic non-volatile or high-molecular-mass compounds often is a serious problem. Recent developments in the field of analytical chemistry favour the use of liquid-based separation techniques such as liquid chromatography (LC) and capillary electrophoresis (CE). However, a serious drawback is the lack of detectors that can match the sensitivity and selectivity of gas chromatographic (GC) detectors such as, for example, thermionic (TID) (N, P-selective) and flame photometric (FPD) (S, P-selective) detection systems. When using conventional (non-selective) LC detectors, off-line or on-line sample clean-up and/or trace enrichment are generally necessary. Besides, the compounds of interest do not always possess suitable

chromophores or fluorophores; that is, detection will create manifest problems. Solving these problems by combining LC and CE with GC-type detectors is an interesting alternative.

In recent years, we have extensively studied the on-line coupling of micro-column liquid chromatography (μ LC) and flame-based GC detectors for the trace-level determination of non-volatile compounds such as substituted phosphoric and phosphonic acids [1–6]. As a sequel to this work, we have now attempted to use the same interface for the direct on-line coupling of CE and FPD. The present paper describes the first results of this work, with methylphosphonic acid (MPA), which is the final breakdown product of several highly toxic chemical warfare agents, and two related compounds as test solutes. MPA does not have a chromophoric group and can therefore not be determined by UV detection. The coupling of CE with FPD will make it possible to separate and selectively detect phosphorus-containing compounds such as MPA.

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2. Experimental

2.1. Materials

Analytical-grade hexane, ethanol, acetic acid, phosphoric acid (PA) and 25% ammonia solution were purchased from Merck (Darmstadt, Germany). Analytical-reagent grade ammonium acetate was obtained from Aldrich-Chemie (Steinheim, Germany). MPA and triethyl phosphate (TEP) were synthesized at the Prins Maurits Laboratory.

All solvents and solutions were filtered prior to use over 0.45- μm pore size filter disks from Millipore (Bedford, MA, USA).

2.2. Instrumentation

For the CE–FPD set-up, a Prince CE system (Laurerlabs, Emmen, Netherlands) and an FPD system Model 380 (Fisons, Milan, Italy) were used. A Valco valve from VICI (Schenkon, Switzerland) was used. Fused-silica capillaries of different diameters were obtained from Polymicro Technologies (Phoenix, AZ, USA). A Knurl-Lok III polyether ether ketone (PEEK) tee and PTFE tubing of different diameters were obtained from Alltech (Deerfield, IL, USA). The on-line coupling of the separation and detection parts of the system is discussed below.

3. Results and discussion

The main difference between μLC and CE when coupled with a GC-type detector is that the former is a pressure-driven system and the latter an electroosmotically driven one. With a CE system care must be taken to avoid pressure differences in the separation part of the set-up. Furthermore, the electric field should be decoupled after the electrophoresis capillary in such a way, that no gases formed due to electrochemical reactions will enter the separation and/or the detection system and disturb either the electrical field or the introduction of the liquid into the detector.

Considering the above, the experimental set-

ups of Fig. 1 were built. The CE system of Fig. 1A was grounded via a piece of 0.3 mm I.D. \times 1/16 in. O.D. (1 in. = 2.54 cm) PTFE tubing that had been treated under high pressure with hexane, which slowly penetrates the tubing wall, and washed with ethanol and water. Coupling of the make-up flow to the interface was made via a modified Valco injection valve. The make-up liquid was pure water.

The CE system of Fig. 1B was grounded via the make-up liquid, which was 1% acetic acid. Care was taken that the first contact of the make-up liquid with metal would be in the bulk

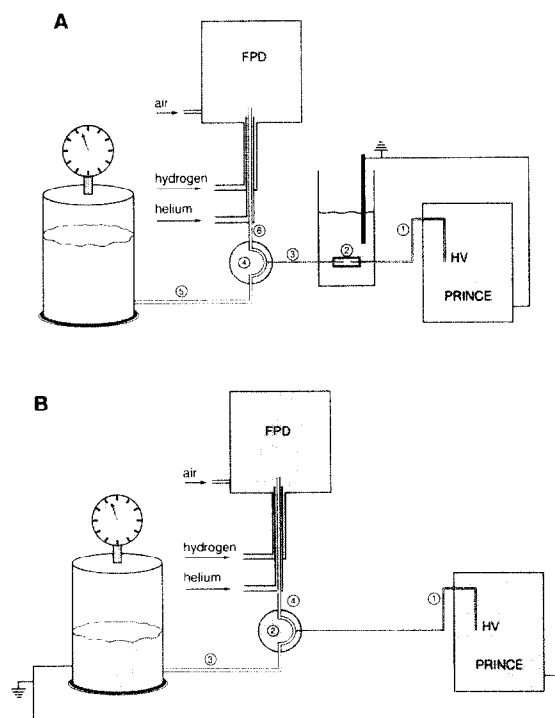


Fig. 1. Experimental CE–FPD set-ups. (A) 1 = Electrophoresis capillary, 75 cm \times 75 μm I.D. fused-silica capillary; 2 = modified PTFE tubing; 3 = coupling capillary, 5 cm \times 75 μm I.D. fused-silica capillary; 4 = modified Valco injection valve; 5 = hydrostatic make-up flow (pressure: 250 mbar); 6 = interface capillary, 35 cm \times 100 μm I.D. fused-silica capillary. (B) 1 = Electrophoresis capillary, 75 cm \times 75 μm I.D. fused-silica capillary; 2 = Knurl-Lok III PEEK tee; 3 = hydrostatic make-up flow, 0.8 mm I.D. PTFE tubing (pressure: 300 mbar); 4 = interface capillary, 40 cm \times 100 μm I.D. fused-silica capillary. Hydrogen flow-rate, 600 ml/min; air flow-rate, 300 ml/min; helium flow-rate, 40 ml/min. All capillary outlets in set-ups A and B were at the same height.

liquid, so that any gas bubbles formed would not enter the make-up tubing and disturb the electric field.

For both set-ups the make-up flow was induced by a hydrostatic pressure in order to have a constant, and relatively low, pressure rather than a constant flow at the end of the CE capillary. The pressure can then be counterbalanced at the inlet of the capillary. The required pressure was calculated from the length and diameter of the interface capillary by means of Poiseuille's law for laminar capillary flow, for a make-up flow-rate of *ca.* 10 $\mu\text{l}/\text{min}$. During injection, no make-up pressure was applied.

As regards the grounding via the modified PTFE tubing, its efficiency was tested by comparing the electric current through the electrophoresis capillary at the same electric field with and without the modified PTFE tubing inserted. This showed the tubing to be permeable for the electric current. When a solution of MPA was injected into the coupled CE–FPD system, the same peak height was registered as for an injection into the system without the modified PTFE tubing. In other words, no significant loss of analyte occurred due to sorption into and/or permeation through the modified tubing. We do realise that the performance of this grounding device has to be studied in more detail. However, for preliminary work where frequent modification of a system is required, it has the distinct advantage of being inexpensive and easy to exchange.

Both experimental set-ups could be used successfully. As an example, Fig. 2 shows the electropherogram of an on-line CE–FPD analysis performed using the set-up shown in Fig. 1B: a 15-nl injection was made of a mixture of 0.4 mg/ml TEP, 0.8 mg/ml MPA and 1.3 mg/ml PA in water, with 0.05 M ammonium acetate (adjusted to pH 9.3) as eluent. Obviously, the coupling is successful and a limit of detection of, *e.g.*, 1–2 ng MPA can be achieved. Actually, the experimental plate height of this test solute is $2 \cdot 10^4$ as against a theoretical plate height of $4 \cdot 10^5$ ($D = 1 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$). The rather large difference may well be due to the use of a liquid junction instead of a coaxial coupling of the CE

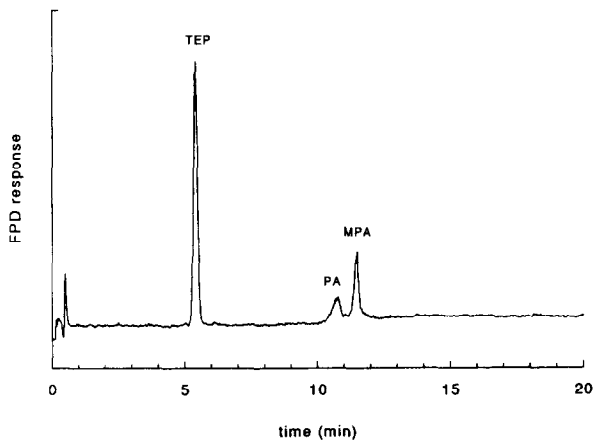


Fig. 2. CE–FPD analysis of a test mixture containing 0.8 mg/ml MPA, 0.4 mg/ml TEP and 1.3 mg/ml PA, injection 0.05 min at 50 mbar (15 nl); electrophoresis eluent: 0.05 M ammonium acetate adjusted to pH 9.3; 20 kV; 25°C; 300 mbar.

eluent with the make-up flow to the interface capillary [7]. Besides, a commercially available tee was used, which introduced a relatively large dead volume. Furthermore the electrophoretic conditions were not optimized for these compounds. It is to be expected therefore that the rather poor concentration sensitivity can be distinctly improved by optimizing these parameters and by minimizing band broadening due to dead volume. In addition, preconcentration techniques already developed for CE can be used (*e.g.* refs. 8 and 9). Further work will therefore be devoted to designing a coaxial coupling of the CE eluent and the make-up flow.

Finally, the liquid introduction into the detector is currently under investigation. By improving this introduction, *e.g.* by using electrospray introduction or inductive heating [10], the detector performance should be improved as a result of a reduction of the detector noise.

4. Conclusions

Our first attempts show that the on-line coupling of CE and FPD can be carried out using principles similar to those of μLC –FPD. This is a rather rewarding result because the use of CE

with its high separation efficiency in combination with the selective and sensitive detection provided by FPD is of distinct interest as an alternative method of analysis for polar and non-volatile phosphorus-containing ionic compounds that can not be determined by UV detection.

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