

Note

On-line extraction and preconcentration of solid samples in equilibrium sandwich chambers for thin-layer chromatography

Analysis of ink from ball-point pens

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The extraction of small samples requires special miniaturized extractors; the use of Soxhlet-type extractors operated at elevated temperatures increases the risk of decomposition of heat-sensitive sample components. Therefore, it would be advantageous to combine the extraction and elution steps in one operation.

Several earlier attempts to incorporate small solid samples into the adsorbent layer have been made (*cf.*, ref. 1, Ch. 4.2). It was found that on-line extraction can readily be carried out in equilibrium sandwich chambers for thin-layer chromatography equipped with glass distributors^{2–4} (for a review see ref. 5). This technique is suitable for porous or powdered samples well penetrated by the solvent.

The chamber, a modification of the Brenner–Niederwieser (BN) chamber, is shown in Fig. 1. The distributor is a strip of glass glued underneath the smaller cover plate; the 0.4-mm slit between the distributor and the margin of the carrier plate rates up the eluent from the container and distributes it across the layer.

The principle of the method is shown in Fig. 2. The small sample is placed between the distributor of the chamber and the layer of adsorbent. The distributors are typically 5–6 mm wide and are suitable for small samples, for instance bits of paper or small amounts of powdered materials, *e.g.*, dried and powdered plants. For larger samples a wider, *e.g.*, 10 mm, distributor can be used.

The complete extraction may require the passage of several volumes of solvent through the sample so that the resulting spots are too large for direct development. Therefore, the extract must be preconcentrated as described earlier^{6,7}. The procedure can thus be summarized as follows:

(1) The sample (porous or powdered) is placed between the distributor and the layer of adsorbent as shown in Fig. 2a (the tray of the chamber is covered only with the small cover plate). A volatile solvent of high extraction and elution strength relative to the analytes ($R_F = 1$) is introduced under the distributor from a micro-pipette or an all-glass syringe. The solvent penetrates the sample and then is absorbed by the layer.

(2) The sample is removed from the chamber (Fig. 2b). The large spot is concentrated by elution under the small plate with a volatile eluent, *e.g.*, acetone–methanol (1:1). Due to the evaporation of the solvent the extract migrates with the solvent

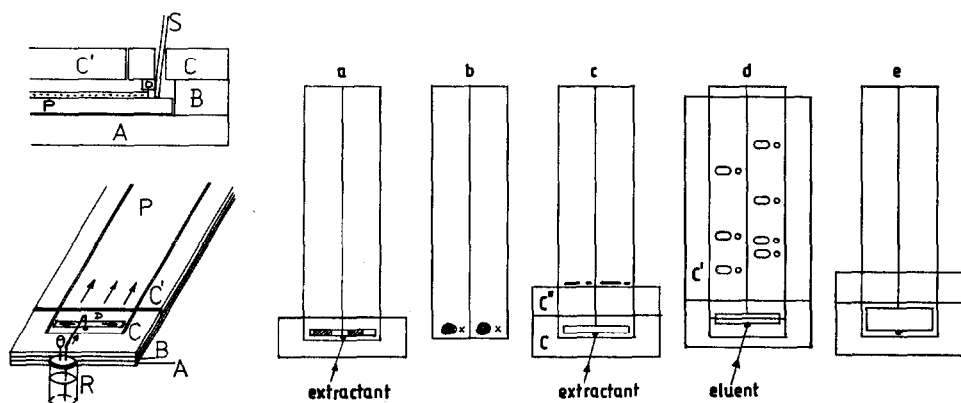


Fig. 1. Cross-section and perspective view of an equilibrium sandwich chamber equipped with a glass distributor: A = bottom plate; B = spacing frame; C, C' = small and large cover plates, the former with an orifice for the capillary siphon (S) and with a strip of glass (distributor D) welded underneath; P = carrier plate with adsorbent layer; R = eluent container.

Fig. 2. (a) Extraction of two 10×5 mm bits of paper. (b) Evaporation of extractant and direct spotting of reference samples (\times). (c) Preconcentration of extracted and directly applied samples. (d) Elution in closed chamber. (e) Use of larger distributors for larger samples. Lower part of chamber (tray) not shown. C = Small cover plate with distributor; C' = large cover plate; C'' = additional cover plate.

beyond the cover plate (Fig. 2c). If the adsorbent underneath is contaminated with sample components, *e.g.*, strongly polar solutes, resins, etc. it should be scraped off the carrier plate. After evaporation of the solvent, the small cover plate is placed over the tray with the distributor over the margin in the distance of about 1 cm before the preconcentrated zone. The large cover plate is also placed on the tray.

(3) The distributor is connected to the eluent container, a siphon effect being achieved by slight overpressure and the coverplate moved forward so that the eluent makes contact with the layer (Fig. 2d).

(4) The chromatogram is developed in the usual way^{2-4,6}. Short bed-continuous development⁸ and gradient elution^{5,9} are especially suitable.

This technique was investigated for the analysis of organic inks from ball-point pens which permitted direct observation of the degree of extraction and the process of preconcentration of the extract. The microanalytical problem is of interest in forensic investigations.

EXPERIMENTAL

Flat horizontal sandwich chambers²⁻⁵, (modification of Brenner-Niederwieser chambers^{10,11}) from Polish Reagents POCh (Lublin, Poland) were used. The following Merck (Darmstadt, F.R.G.) materials were used: HPTLC Alufolien, silica 60 F 254 or precoated glass plates for high-performance thin-layer chromatography, silica 60 F 254 for larger concentrations of the ink. On-line extraction and preconcentration was carried out using acetone-methanol (1:1). The same mixture was applied for the subsequent development of the chromatogram.

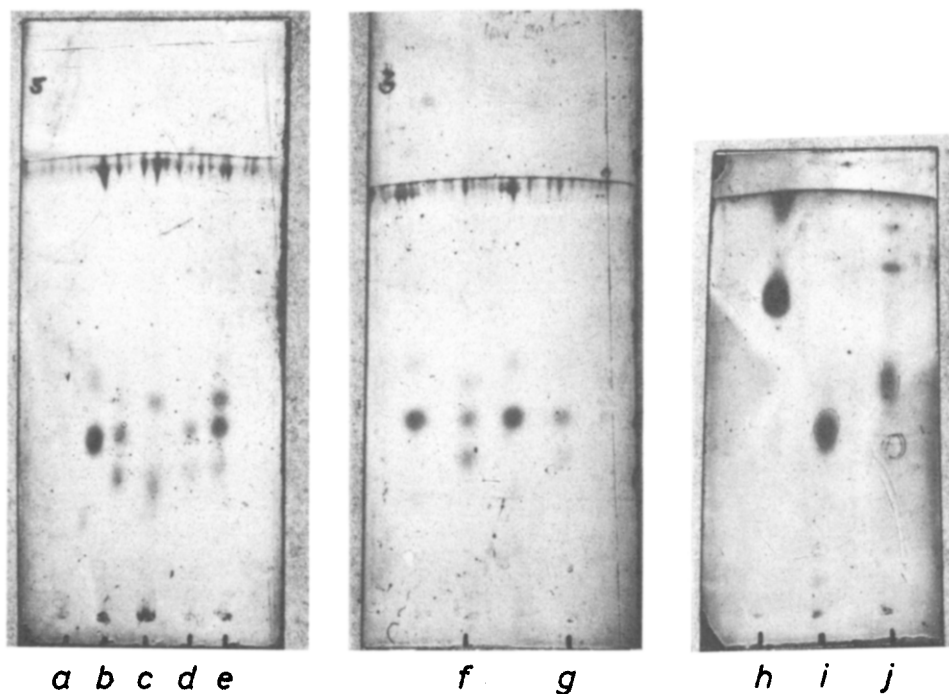


Fig. 3. Chromatograms of inks a–g from ball-point pens spotted directly precoated aluminium foil by making dots with the pens (eluent: acetone–methanol, 1:1) and chromatograms of inks from felt-tip pens, h (green), i (black), and j (blue) (eluent: 1% acetic acid in methanol).

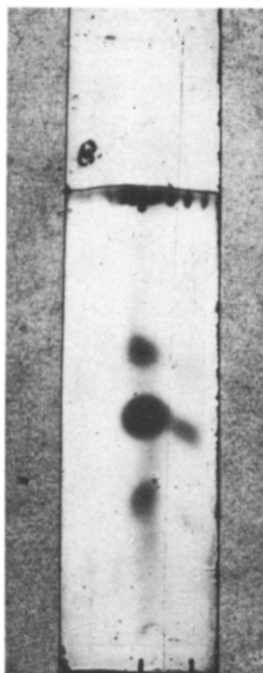
Dark blue inks from ball-point pens from various sources are denoted by letters a–g; the colours produced by felt-tip pens (Inco, Warsaw, Poland) are denoted by the letters h (green), i (black) and j (blue). The ink samples were applied directly by making a 0.5-mm dot on the start line or by extraction of a dot or a dash from white letter paper.

RESULTS AND DISCUSSION

Fig. 3a–g shows the chromatograms of inks a–g obtained on precoated foil (85 × 35 mm) developed with acetone–methanol (1:1). In some cases an additional spot due to a strongly adsorbed component ($R_F = 0$) was observed. The spots were somewhat diffuse, especially for higher sample sizes; this effect is probably caused by the viscous diluent of the ink and was less pronounced for 0.5-mm layers of silica due to the larger capacity of the system. The inks from the felt-tip pens chromatographed in the system silica–1% acetic acid in methanol resulted in regular chromatograms (Fig. 3h, i, j) with differentiated R_F values.

In Fig. 4 the sample (E) obtained by on-line extraction from a 4 × 4 mm bit of letter paper is compared with a reference sample (D) applied directly on the layer. After parallel preconcentration and elution, regular chromatograms were obtained.

Comparison of freshly written text samples with those obtained from three-week old samples revealed no differences in the appearance of the chromatograms.



E_a D_a

Fig. 4. Parallel chromatograms of a preconcentrated extract (E) and a directly applied reference sample (D) of ink "a" on precoated aluminium foil. Solvents: extraction and preconcentration, acetone-methanol (1:1); elution, ethyl acetate-methanol (1:1).

The extraction, preconcentration and development stages are quite rapid; the total analysis takes about 30–40 min. It seems that the rapid and efficient on-line extraction (the bits of paper did not contain any significant traces of ink after extraction) is suitable for microanalytical work.

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