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Note

Simultaneous determination of phenol, cresols and xylenols in workplace air, using a polystyrene–divinylbenzene column and electrochemical detection

EEVA NIEMINEN* and PIRJO HEIKKILÄ
Uusimaa Regional Institute of Occupational Health, Arinatie 3 A, SF-00370 Helsinki (Finland)
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Phenol, cresols and xylenols are of analytical interest as general environmental and urban air pollutants, as important raw materials in industrial processes, and as notable ingredients in products derived from coal tar. In workplace air they are significant pollutants in plants that apply insulation lacquers to copper wires. Occupational exposure can also occur during impregnation of wood with creosote oils and handling of freshly impregnated wood.

Existing methods for the measurement of phenol and cresol vapours in workplace air[1,2] do not provide for the analysis of other alkylphenols and are not very sensitive. Encouraged by a study at our institute on the hazardous vapours released during impregnation of railway ties with creosote oils and later handling of ties[3], we have developed a selective and sensitive method for the simultaneous determination of phenol, cresols and xylenols in workplace air.

The method is based on high-performance liquid chromatography (HPLC), the superior method for the analysis of phenol compounds[4–8], with use of a polystyrene–divinylbenzene resin-based reversed-phase column. This column is stable over the pH range 1–13. A mobile phase of alkaline pH was used, which provided an easy separation of phenol and the isomers of cresols and xylenols.

Use of polystyrene–divinylbenzene columns for the determination of phenol compounds is not entirely new[9–11]. Of special interest is the study of Pietrzyk and Hu[12,13], which dealt with the influence of pH on the elution of organic acids.

The amperometric electrochemical detector used in quantification provided excellent sensitivity. This is apparently the first use of this detector in alkaline conditions.

UV detection was examined too, and the sensitivity was significantly better in alkaline than in conventional acidic conditions.

EXPERIMENTAL

Chromatographic apparatus

The chromatographic system included an Altex Model 110 A pump, a Rheodyne Model 7120 injector with a 20-μl loop, and an electrochemical detector with an LC-4A amperometric controller (Bioanalytical Systems, West Lafayette, U.S.A.) and

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an EA 1096 detector cell (Metrohm, Herisau, Switzerland). The detector cell was equipped with a glassy carbon working electrode and a silver–silver chloride reference electrode. The separations were carried out using a Hamilton PRP-1 column (150 mm × 4.1 mm I.D.) with particle diameter 10 μm.

Another liquid chromatograph, consisting of a Varian Model 5000 pump, a Rheodyne Model 7120 injector with a 50-μl loop, a Knauer Model variable-wavelength monitor No. 87.00 and a Hewlett-Packard 3390A integerator, was used to study the UV detection of the phenol mixture.

Air sampling and sample preparation

Air was drawn through an Amberlite XAD-2 (SKC) tube[14] at a rate of 0.2 l/min, or alternatively through an impinger bottle filled with 15 ml of 0.1 *M* sodium hydroxide sampling solution at 1–2 l/min[1]. Sampling times varied between 10 and 60 min.

Phenols were desorbed from the Amberlite by shaking with 4 ml of acetonitrile for 30 min. Water was added to acetonitrile (1:1) before injection into the chromatograph to get better peak shapes. Where a stronger concentration was needed, a portion of the acetonitrile was carefully evaporated to a smaller volume (not to dryness, which causes the phenols to evaporate) and water was then added (1:1).

Standards

Phenol, cresols and xylenols were combined in a 10^{-2} *M* stock solution in acetonitrile–water (1:1). All reagents were p.a. grade.

Chromatographic conditions

Two different electrolyte-based mobile phases of alkaline pH were used: one a mixture of acetonitrile with 0.1 *M* sodium acetate and the other a mixture of acetonitrile with 0.06 *M* disodium hydrogen phosphate. In each case the pH was adjusted to 11.5–11.6 with 1 *M* sodium hydroxide. A mixture of 0.1 *M* sodium acetate and acetonitrile with pH 5–5.5 was used as acidic eluent. pH values were measured with a glass electrode and are apparent.

The acetonitrile in the mobile phase varied from 17 to 30%, and the flow-rate was regulated to 2 ml/min. A potential of +0.6 V was applied with the alkaline mobile phases, and potentials of +1.0–1.05 V with the acidic mobile phase. UV detection was performed at 280 nm.

RESULTS AND DISCUSSION

The alkaline eluents provided easy and good separation of phenol, cresols and xylenols (Fig. 1a and b). Even *meta*- and *para*-cresols were easily distinguished, the separation of which is impossible with conventional reversed-phase methods. Both phosphate- and acetate-based eluents were tested.

The phosphate-based eluent was chosen for further study because passivation of the glassy carbon electrode surface was slower than with the acetate-based eluent. Adjustment of the pH to values between 11.4 and 11.6 was important, since at pH values over 12 no retention was achieved and at values under pH 11 the resolution was poor.

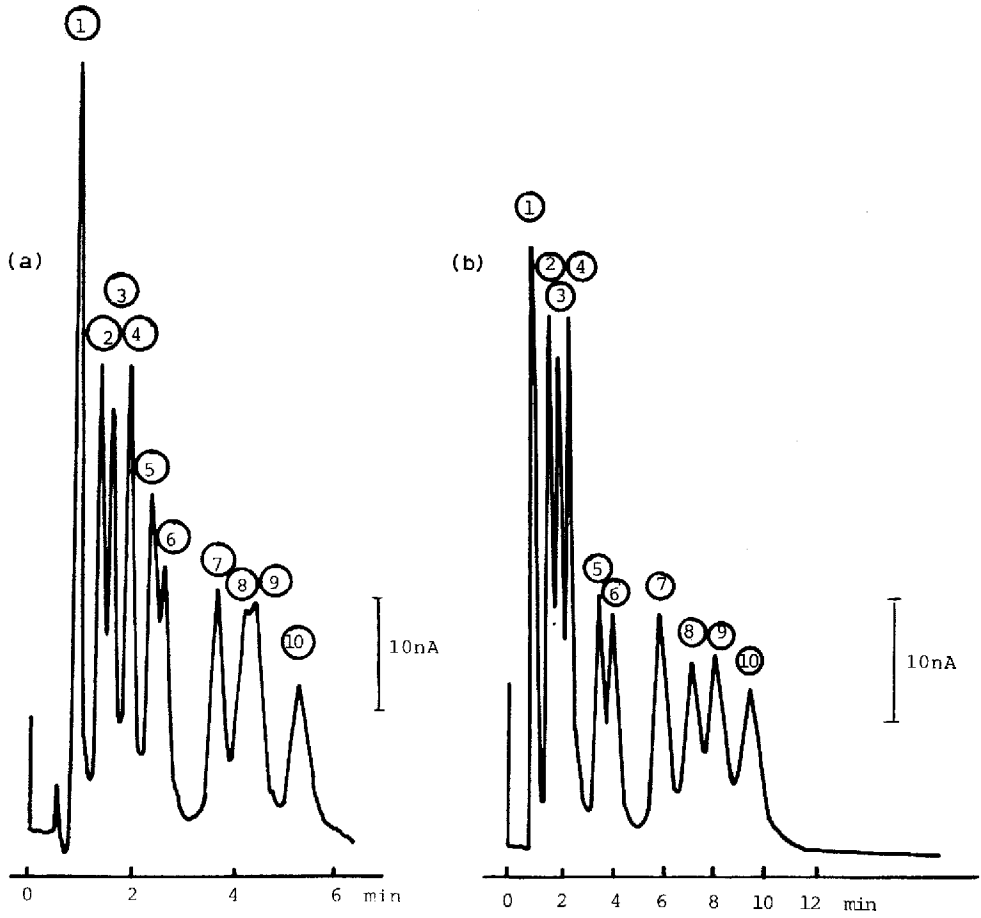

Fig. 1. Chromatographic separation of phenols using alkaline mobile phases. (a) 0.06 *M* disodium hydrogen phosphate and acetonitrile (70:30), pH 11.6; (b) 0.1 *M* sodium acetate and acetonitrile (83:17), pH 11.6. Flow-rate of eluent, 2 ml/min; applied potential of electrochemical detector +0.6 V (sensitivity 50 nA). Peaks: 1 = Phenol; 2 = *m*-cresol; 3 = *p*-cresol; 4 = *o*-cresol; 5 = 3,5-xylenol; 6 = 3,4-xylenol; 7 = 2,5-xylenol; 8 = 2,3-xylenol; 9 = 2,4-xylenol; 10 = 2,6-xylenol (*ca.* 20 ng each).

TABLE I

DISSOCIATION CONSTANTS OF PHENOL, CRESOLS AND XYLENOLS IN AQUEOUS SOLUTION

The variation in pK_a values is due to the different methods of measurement.

Compound	pK_a
Phenol	9.82– 9.99
m-Cresol	10.01–10.10
p-Cresol	10.14–10.26
o-Cresol	10.14–10.28
3,5-Xylenol	10.02–10.25
3,4-Xylenol	10.25–10.32
2,5-Xylenol	10.21–10.3
2,3-Xylenol	10.42–10.6
2,4-Xylenol	10.45–10.61
2,6-Xylenol	10.5 –10.59

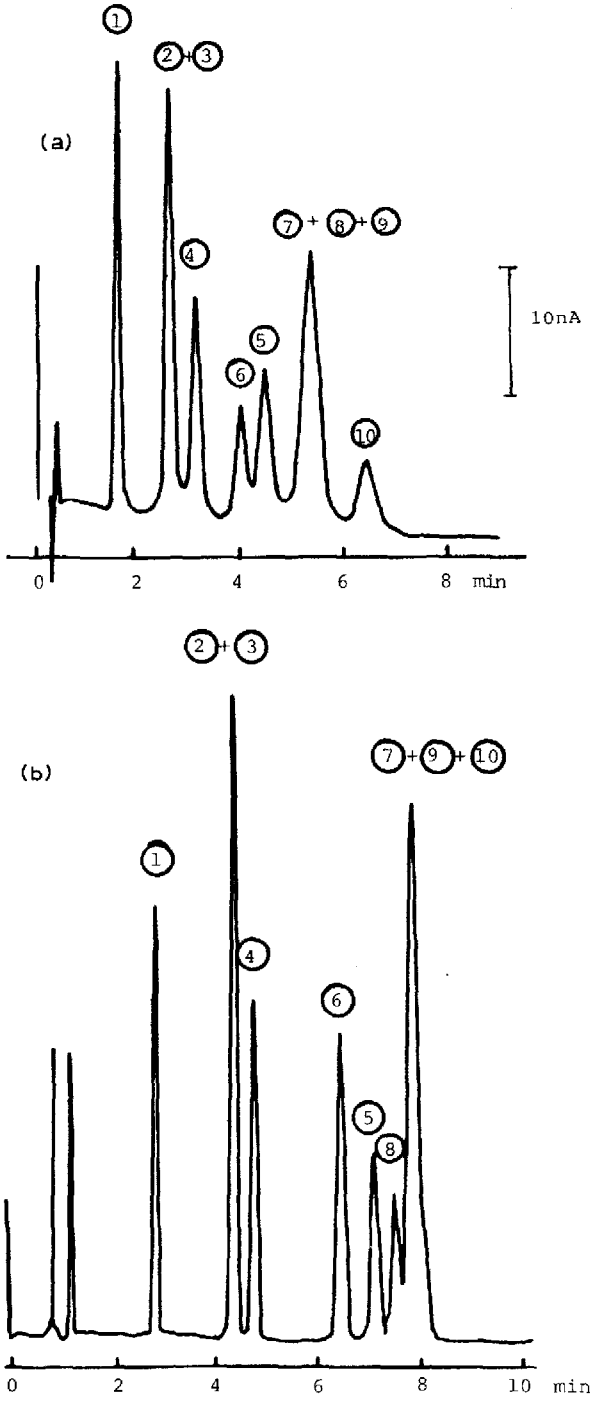

Fig. 2. Chromatographic separation of phenols using acidic mobile phase: 0.1 *M* sodium acetate–acetonitrile (73:27), pH 5.2. (a) PRP-1 column; electrochemical detector with applied potential +1.05 V (sensitivity 50 nA) (concentration of analytes *ca.* 20 ng); (b) ODS column (25 cm, 5-μm particle diameter); UV detection at 280 nm. Peaks as in Fig. 1.

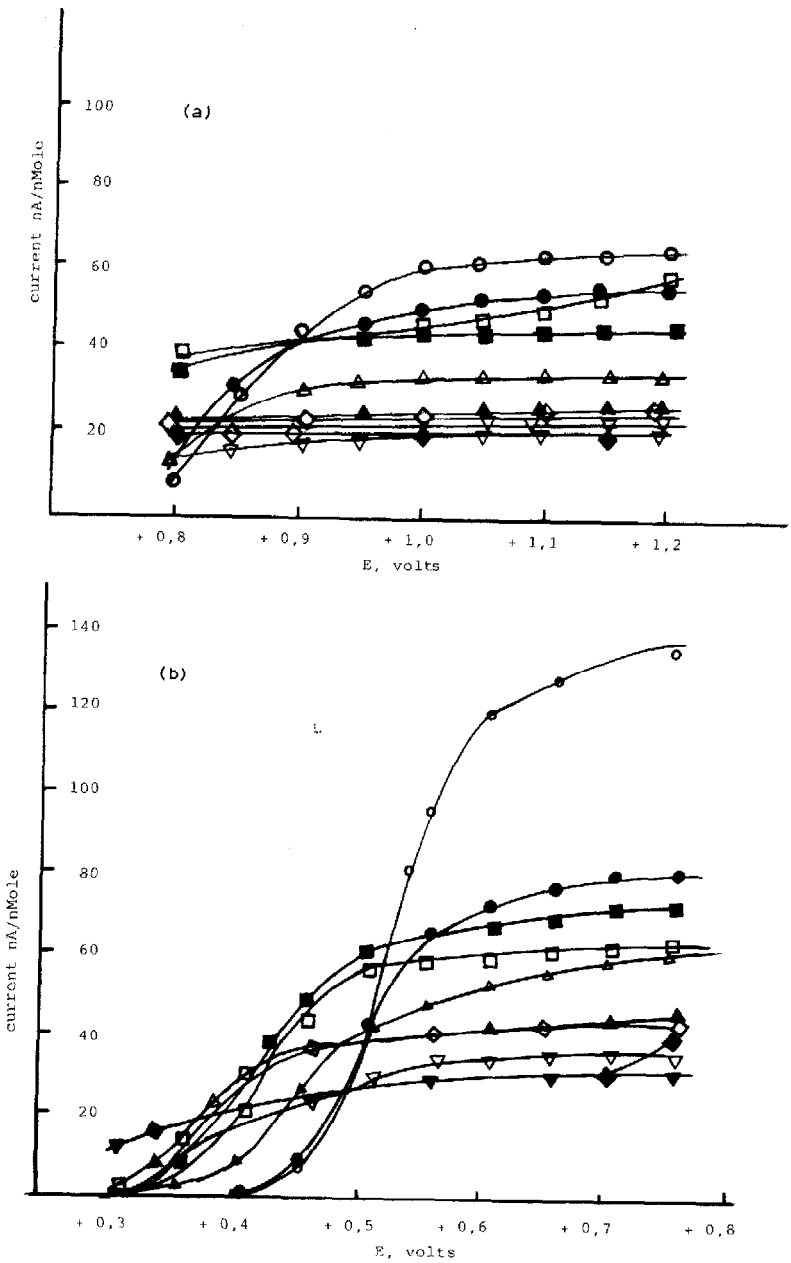

Fig. 3. Hydrodynamic voltammograms of phenol, cresols and xylenols in acidic and alkaline conditions, derived from chromatographic data on a PRP-1 column, with a flow-rate of eluent 2 ml/min. (a) Acidic eluent: 0.1 *M* sodium acetate–acetonitrile (70:30), pH 5.5; (b) alkaline eluent: 0.06 *M* disodium hydrogen phosphate–acetonitrile (70:30), pH 11.6. Phenol (○), *m*-cresol (●), *p*-cresol (□), *o*-cresol (■), 3,5-xylenol (△), 2,5-xylenol (▲), 3,4-xylenol (◇), 2,4-xylenol (◆), 2,3-xylenol (▽), 2,6-xylenol (▼).

Phenol, cresols and xylenols, being weak acids, are predominantly in ionic form (as phenolates) when the eluents are in the pH range 11.4–11.6. The pK_a values are given in Table I[15].

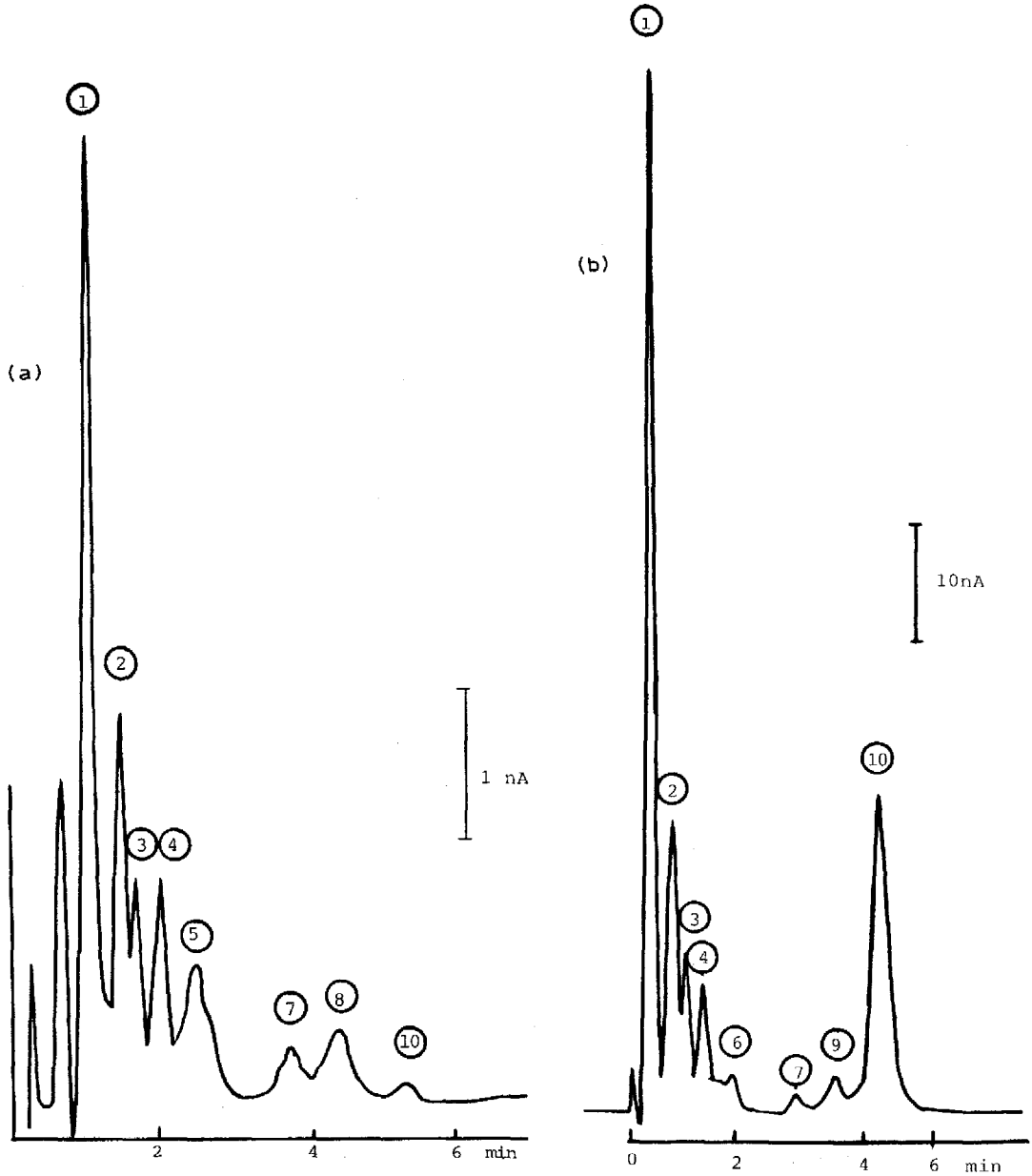

Fig. 4. (a) Chromatogram from an air sample collected in XAD-2 tube during the loading onto a ship of timber impregnated with creosote oil. (b) Air sample collected in 0.1 *M* sodium hydroxide during lacquering of copper wires. Conditions: phosphate-based alkaline eluent; flow-rate, 2 ml/min; electrochemical detector potential +0.6 V.

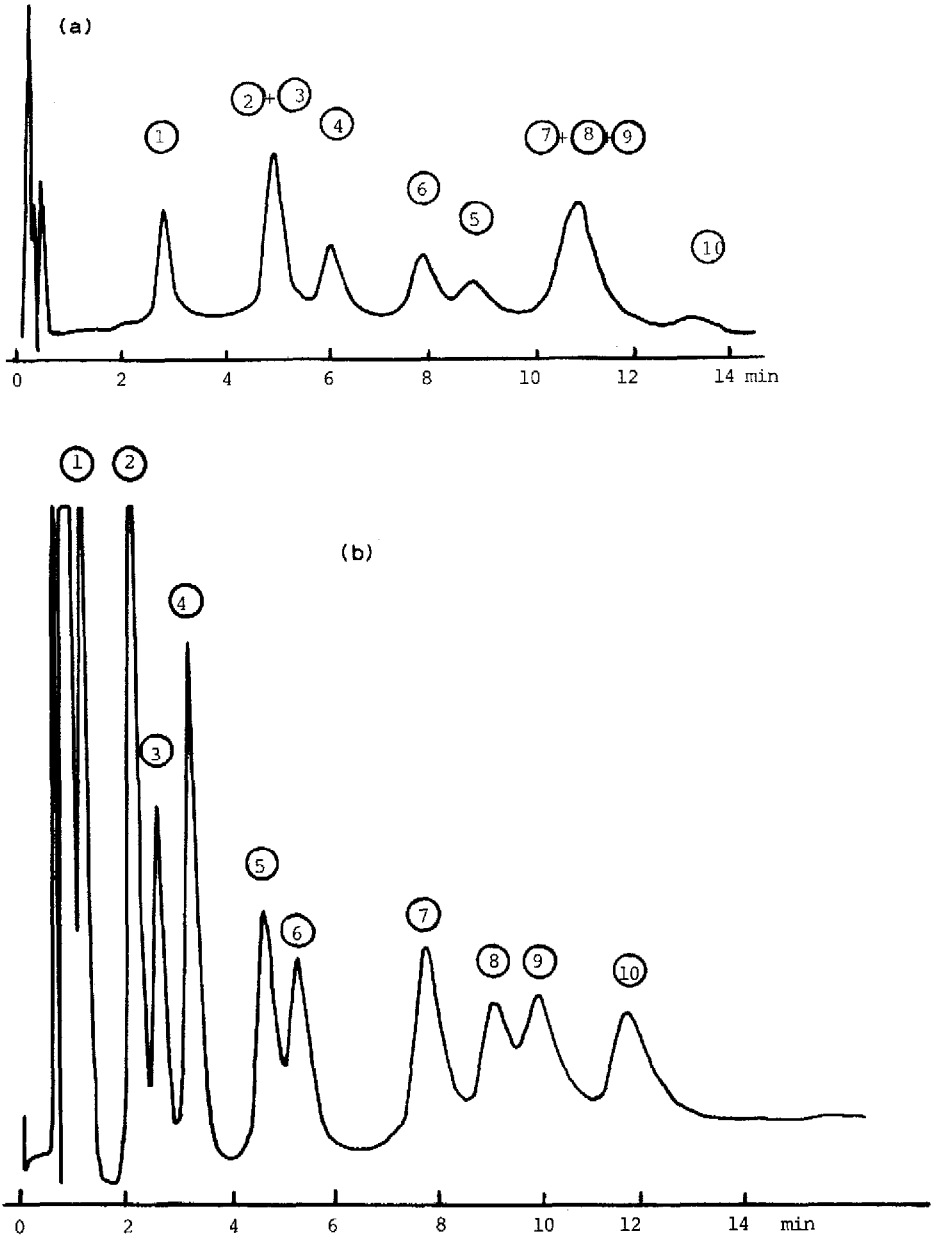

Fig. 5. UV detection of phenol, cresols and xylenols at 280 nm; 0.004 a.u.f.s.; concentration *ca.* 50 ng each. (a) With acidic eluent, pH 5.2; (b) with alkaline eluent, pH 11.6.

The pK_a values are too similar to indicate how they influence the elution order. But in any case it is the molecular size of the phenol compound that is important, with the alkaline as well as the acidic eluent. Phenol elutes first and then the cresols and xylenols, but with the sequence of cresol and xylenol isomers being different in

acidic and alkaline conditions (Figs. 1 and 2). The sequence in acidic conditions appears more clearly with the ODS column (Fig. 2b).

Pietrzyk *et al.*[16] have suggested a different orientation of ionizable solutes with the copolymer surface in ionized form (basic conditions) and neutral form (acidic conditions). Their theory could explain the differences in the elution order, as well as the partially pK_a independent behaviour of phenolate ions observed in our study.

The sensitivity and selectivity achieved with the electrochemical detector were very good. Although several publications on HPLC methods for phenols mention the use of such a detector in acidic conditions[8,17–19], ours is apparently the first use in alkaline conditions.

Oxidation of phenols occurred at much lower potential under alkaline (0.4–0.6 V) than under acidic conditions (0.8–1.2 V). Hydrodynamic voltammograms for phenol mixtures under acidic and alkaline conditions are presented in Fig. 3a and b.

The detection limits were *ca.* 0.5 ng with the alkaline phosphate–acetonitrile eluent of pH 11.6 and electrode potential +0.6 V, and slightly better than the limits achieved with the acidic eluents at electrode potential +1.05 V.

Accordingly, detection limits for the air samples were *ca.* 8 $\mu g/m^3$ with 12 l of air drawn through Amberlite XAD-2 or 60 l of air collected in 0.1 *M* sodium hydroxide solution. Sensitivity could be improved for the sample collected by XAD-2 tube by concentrating the desorption solvent.

Typical chromatograms of air samples collected during the loading of timber impregnated with creosote oil into a ship and during lacquering of copper wires are shown in Fig. 4a and b.

The sensitivity of the UV detector set at the conventional 280-nm wavelength was significantly better in alkaline than in acidic conditions (Fig. 5a and b), but still *ca.* 20 times lower than that achieved with the electrochemical detector.

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