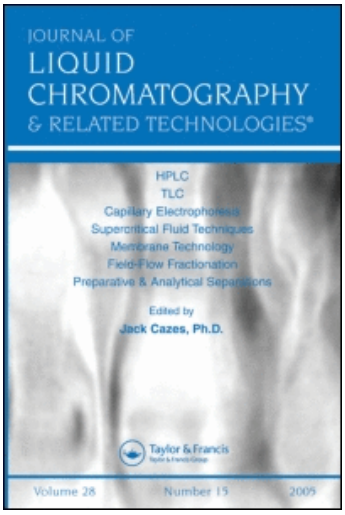

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HPLC Method for Determination of Phenol in River and Waste Water

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HPLC METHOD FOR DETERMINATION OF PHENOL IN RIVER AND WASTE WATER

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ABSTRACT

A method is proposed for the determination of phenol in river and waste water using electrochemical detection HPLC. An octadecyl silica solumn was used with a gradient of methanol in water from 40 % to 100 %. With preconcentration unit (guard C 18 column) on line and ampermetric detection (+1.1 V), detectability limit at 30 ppt was achieved. The method has been applied for the control of the performance of the purification plant.

INTRODUCTION

Phenol is common water pollutant because it is the product of many industrial processes (for example, the manufacture of dyes, plastics, drugs and antioxidants). Phenol has been found to be toxic to most aquatic organisms /1/ and has an adverse effect on the taste and odour of both water and fish even at very low concentrations (less than 1 ppb) /2/. Therefore, legal requirements of many countries are increasing, making it necessary to determine phenol at very low levels. Environmental samples can have very complex matrices; therefore detection and separation methods are prefered for the determination of

phenol. Various techniques have been applied to the measurement of phenol in water. The most widely used methods are HPLC with UV detection /1, 3 - 7/ and GC /8 - 10/. Recently, LC methods with electrochemical detection have been described /11, 12/.

Renie and Mitchel proposed a method involving dual-electrode electrochemical detection without preconcentration, with a detection limit of $3.6 \cdot 10^{-10}$ mol/l for phenol /13/. Borra at al. combined preconcentration on a graphitized carbon black cartridge column and UV detection at 280 nm /14/. A reaction method was also proposed for the determination of phenol /15, 16/.

This paper discusses the application of electrochemical detection to the analysis of phenol in river and waste water. The LC method was combined with a on-line preconcentration method. The aim was to establish a simple method for the analysis of phenol at ppb and ppt levels and to apply this to real samples.

EXPERIMENTAL

The scheme of the LC system is shown in Figure 1. The system consisted of two pumps (Waters Model 501), a chromatographic column (0.32 x 15 cm) packed with 5/um Separon C 18 (Tessek, Prag CSFR) and an electrochemical detector (Waters Model 460). The preconcentration pump was a Model HP 5000 (CSFR) at a flow rate 1 ml/min. On-line preconcentration was carried out using a precolumn (0.32 x 3 cm) packed with 5/um particles Separon C 18 (Tessek, Prag, CSFR).

Before introduction of the sample the preconcentration column was washed with twice distilled water. The sample is then injected via a 1.0 ml loop and pumped through the preconcentration column. After flushing phenol is desorbed to the analytical column with a gradient of methanol in water eluent. The mobile phase was prepared by mixing two solutions according to Table 1. Electrochemical detection was performed with ampermetric detector using carbon electrode.

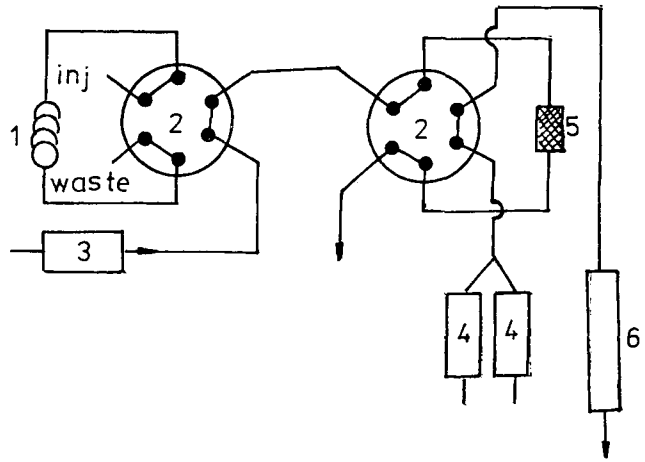

Figure 1. Schematic diagram of the apparatus
1 - injection loop; 2 - valve; 3 - pump;
4 - LC pump; 5 - preconcentration precolumn;
6 - analytical column

Table 1. Gradient of methanol in mobile phase

time /min/	composition % A	% B
0	100	0
10	100	0
15	0	100 (linear)
19	0	100

A - 40 % methanol in water
B - methanol

The applied potential with respect to calomel electrode (as reference) was + 1.1 V. River or waste water was filtered over a 0.5 μm membrane filter (millipore type AA), acidified with glacial acetic acid and adjusted to pH 4.0 by addition of sodium hydroxide solution. For the recovery experiment the river water was spiked with phenol up to concentration of 20 ppb. Water solutions for calibration experiments were made starting from a 30 ppt to 100 ppb. Preconcentration of at least 2 ml was found possible on 3 x 0.32 cm I.D. preconcentration precolumn without breakthrough.

RESULTS AND DISCUSSION

Initial investigations into the change in the capacity factor of phenol with pH of eluent, and the percentage of methanol showed that for the desorption of phenol from precolumn the pH should be kept in a range 3.8 to 4.1 and gradient of methanol from 40 % to 100 % to overcome the problem of the irreversible adsorption of some less polar compounds which can be found in river or waste water.

The composition of the mobile phase can influence the background current as well as the optimum detection potential. Phenol can be oxidized more easily at higher pH /17/ but on the other hand the shape of the chromatographic peak is not symetrical at higher pH of mobile phase. For RP chromatography, aqueous mobile phases are used that are able to form enough ions to provide sufficient ionic strenght. All solvents and the modifiers should be as clean as possible. The flow rate was only 0.5 ml/min because the lower flow rate has the lower noise level at the electrochemical detection /12/.

Figure 2 shows the gradient chromatogram of a river sample spiked with 20 ppb phenol and Figure 3 represents chromatogram of river water (40 ppt, without the addition of phenol). The large bands in the later part of both chromatograms must probable be attributed to less polar compounds which are preconcentrated too.

The above procedure is also suitable for the determination of phenol in waste water. The sample can be taken before

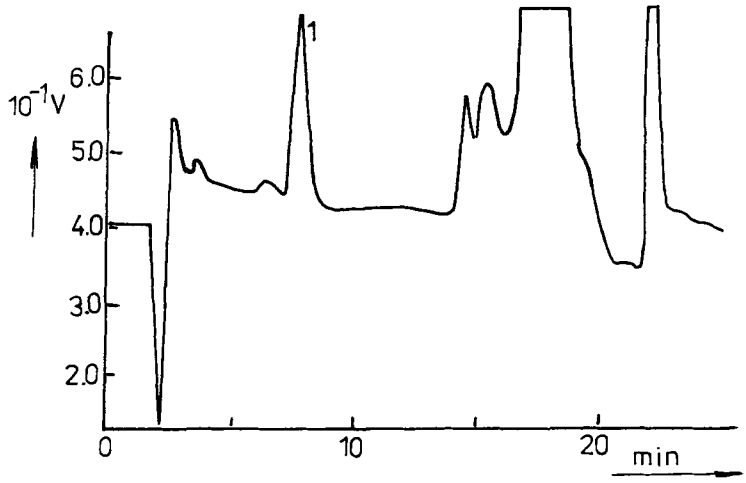

Figure 2. Determination of phenol. Preconcentration of 1 ml of river water spiked with 20 ppb phenol (peak 1) LC conditions : analytical column (0.32 x 15 cm packed with 5/um particles. Separon C 18; pre-column (0.32 x 3 cm) packed with 5/um particles Separon C 18; mobile phase, gradient of methanol in water (see Table 1) pH = 4.0; flow rate; 0.5 ml/min; electrochemical detection + 1.1 V. For sample pre-treatment, see Experimental section.

the inlet into the cleaner of waste water as well as during their outlet so that it might be possible to control the performance of the purification plant for phenol at very low concentration. Figure 4 presents the chromatogram of the sample before the inlet into the cleaner and Figure 5 presents the chromatogram of the sample after the outlet.
By the comparison of these chromatograms the performance of the purification plant can be calculated. In this case it was about 68 %. The amount of phenol was determined by linear least-squares fitting of the curves of the amount of phenol injected against peak area. The concentration of the standard solutions were 30 ppt - 100 ppb of phenol in water, and

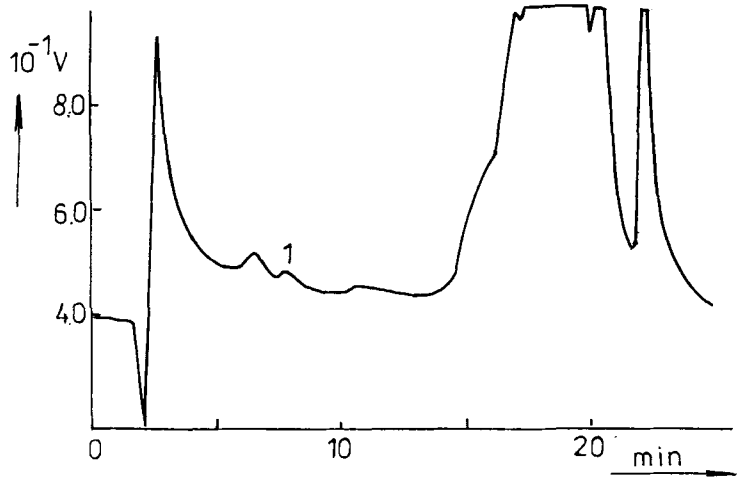

Figure 3. Determination of phenol (40 ppt). Preconcentration of 1 ml of river water (1 - phenol). For LC conditions, see Figure 2.

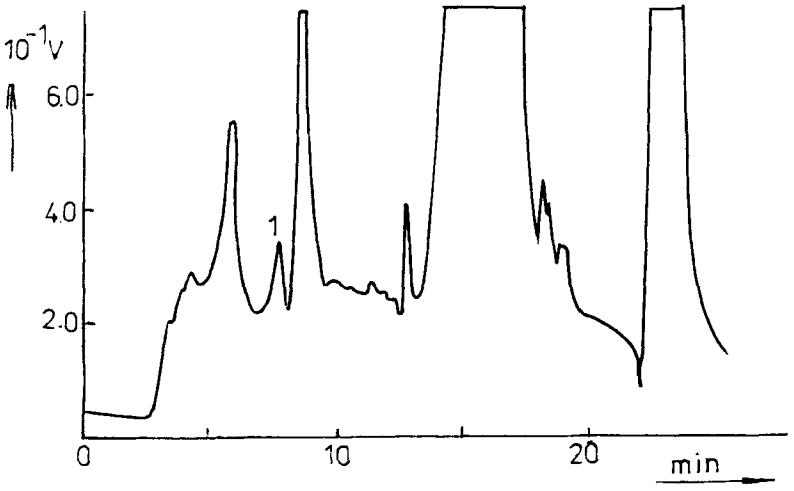

Figure 4. Determination of phenol in waste water before the inlet into the purification plant (1 - phenol) For LC conditions, see Figure 2.

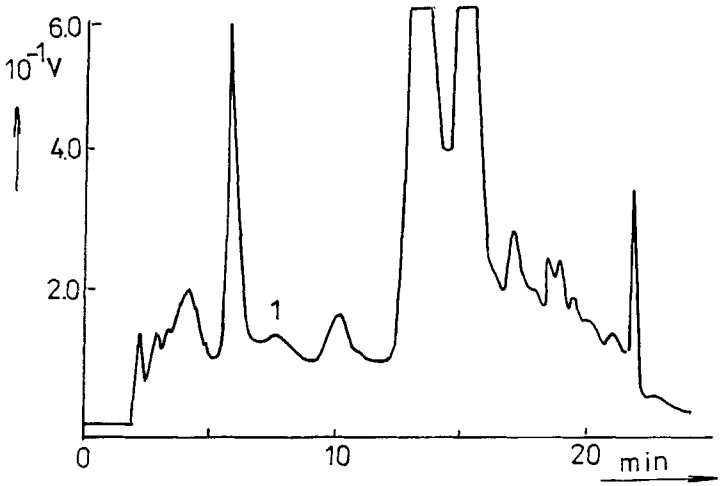

Figure 5. Determination of phenol in waste water after the outlet from the purification plant (1 - phenol). For LC conditions, see Figure 2.

the calibration graph was linear. The selectivity of the pre-concentration system allows the LC analysis to be performed within about 25 minutes with a detection limit of 30 ppt.

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