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DETERMINATION OF PHENOLS BY LIQUID CHROMATOGRAPHY USING REDUCTIVE ELECTROCHEMICAL DETECTION VIA PRE-COLUMN DERIVATIZATION

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SUMMARY

A reductive amperometric detection method has been developed for the high-performance liquid chromatographic determination of phenols in aqueous samples. The phenols were derivatized to form the corresponding quinoneimines employing the 4-aminoantipyrine reaction prior to reversed-phase chromatographic separations. In contrast to the conventional oxidative detection of phenols with a high applied potential of over +0.95 V, a low potential of −0.20 V *vs.* Ag/AgCl was used successfully to detect the derivatized phenols with a glassy carbon electrode. The principal advantage of this method is that oxygen removal from the mobile phase is not required. This is because the applied potential is so low that oxygen reduction is not detectable at this potential. A linear dynamic range of concentrations between 10^{-7} *M* and 10^{-4} *M* was observed for some selected phenols.

INTRODUCTION

In the last few years, a wide variety of methods has been developed for the analysis of phenols in environmental and clinical samples at trace levels. Some of these new developments include chromatography[1–15], mass spectrometry[16,17], and flow-injection analysis[18]. The once popular colorimetry method of using 4-aminoantipyrine (4-AAP) to form colored derivatives with phenols[19] is now largely replaced by these new instrumentation methods. However, the classical 4-AAP reaction has been used successfully by Gasparič *et al.*[20,21] for derivatizing the phenols followed by paper and thin-layer chromatography analysis. More recently, the 4-AAP method was modified by Norwitz and Keliher[22] for the spectrophotometric determination of phenol after steam distillation of sample. The 4-AAP reaction was the basis for high-performance liquid chromatographic (HPLC) post-column derivatization with absorption detection at 470 or at 509 nm[12]. Ten priority pollutant phenols were quantified by Bigley and Grob[12] at ppm levels after solid phase extraction prior to reversed-phase separation with gradient elution[12]. Their method required a preconcentration step, which helped to enhance the sensitivity of detection.

For phenols of extremely low concentration, liquid chromatography with

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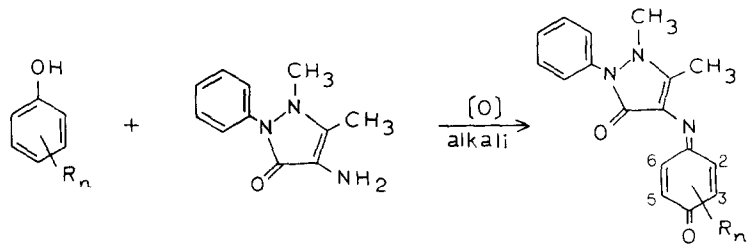
electrochemical detection (LC–ED) seems to be the method of choice. Using a glassy carbon thin-layer transducer, Shoup and Mayer[6] reported a detection limit of phenols in aqueous environmental samples at parts-per-trillion levels. Roston and Kissinger[5] used both single and dual-electrode transducers to identify nanomole quantities of phenolic constituents in alcoholic beverages. Detection of nanogram to picogram levels of phenolic compounds has been reported using a carbon-polyethylene electrode[2] and a graphite composite electrode[3,7]. Confirmation of chlorophenols in urine samples at ppb* levels has been accomplished using LC–ED detection[4]. More recently, MacCrehan and Brown-Thomas[15] developed an LC–ED method for phenols and naphthols in unrefined petroleum products. They reported detection limits of 100 ng/g of crude oil or below.

All previous LC–ED work of phenols employed an oxidation potential of around +0.95 V *vs.* Ag/AgCl or higher. In this investigation, we describe a scheme of determining derivatized phenols using a reductive LC–ED detection with a low applied potential of only −0.2 V *vs.* Ag/AgCl. The procedure of derivatizing the phenols, which is based on the 4-AAP reaction, was adopted from that used by Gasparič *et al.*[20,21] with slight modification.

In reductive LC–ED, dissolved oxygen in both mobile phase and sample solutions exhibits serious interferences at negative applied potentials[23]. The reduction of oxygen starts around −0.5 V *vs.* Ag/AgCl at a glassy carbon electrode, but around −0.1 V at a mercury-coated gold electrode. At −0.2 V no detectable oxygen reduction is observed on a glassy carbon electrode. Therefore, oxygen removal from the mobile phase by means of exhaustive degassing is not required if a glassy carbon electrode is used. Because of its relatively high oxygen overpotential, lower cost, and ready availability, the glassy carbon electrode was thus selected over mercury in this work.

The precolumn derivatization reaction of phenols used in this work can be shown as follows:



where R_n groups are substituents derived from the starting phenols. In a previous paper[24], we have reported the electrochemistry and HPLC behavior of 11 synthetically prepared quinoneimine dyes. The dye prepared from the unsubstituted phenol was named N-antipyryl-*p*-benzoquinoneimine (ABQI) and those prepared from the substituted phenols as the derivatives of ABQI. For example, *m*-cresol gives 2-methyl-ABQI; and *o*-chlorophenol gives 3-chloro-ABQI, etc. The structures of these quinoneimines proposed here were based on the NMR studies by Jones and Johnson[25] and the chromatographic investigations by Gasparič *et al.*[20,21]. Generally speaking, the reaction is positive only when the monohydric phenols have a free *para* position or

* Throughout the article the American billion (10^9) is meant.

with halogen, carboxyl, alkoxyl, or sulfonic acid group substituted at the *para* position.

EXPERIMENTAL

Apparatus

The LC system consisted of a Model 396 Instrument miniPump (Laboratory Data Control/Milton Roy, Riviera Beach, FL, U.S.A.), a Rheodyne Model 7010 valve injector with a 10-μl sample loop (Rheodyne, Cotati, CA, U.S.A.), a BAS TL-5A glassy carbon thin-layer cell, and a BAS LC-4B amperometric detector (Bioanalytical Systems, West Lafayette, IN, U.S.A.). All reversed-phase separations were carried out using either a Zorbax ODS column (DuPont, Wilmington, DE, U.S.A.) or an Econosphere C_{18} column (Alltech, Deerfield, IL, U.S.A.), both with 5-μm packing and a dimension of 15 cm $\times$ 4.6 mm I.D. The pressure was monitored with a Solfrunt pressure gauge. Coiled stainless-steel tubings (0.04 in. I.D.) were used between the pump and the precolumn, which was packed with 62 mesh silica gel. Capillary stainless-steel tubings (0.007 in. I.D.) were used between the precolumn and the valve injector and between the valve injector and the analytical column. Capillary PTFE connecting tube from Bioanalytical Systems, was used between the analytical column and the thin-layer transducer. All chromatograms were recorded on a Fisher Series 5000 Recordall strip chart recorder (Fisher Scientific, Pittsburgh, PA, U.S.A.), and peak integrations were done using an SP4270 chromatography integrator (Spectra-Physics, San Jose, CA, U.S.A.). Cyclic voltammetry experiments were run on a Bioanalytical Systems BAS-100A electrochemical analyzer.

Reagents

The phenols used in this investigation were purchased either from Fisher Scientific, Aldrich (Milwaukee, WI, U.S.A.) or from Eastman-Kodak (Rochester, NY, U.S.A.). All other chemicals, including 4-aminoantipyrine, were ACS Certified grade and were received from Fisher Scientific. The methanol used in the mobile phase was HPLC grade. The water was either HPLC grade or prepared in house by pumping distilled water through a NANOpure-A 4-holder system (Sybron/Barnsted, Boston, MA, U.S.A.). The mobile phase was filtered through a 0.8-μm polycarbonate membrane before use.

Analytical methodology

All phenols were derivatized via the 4-AAP method to form the corresponding quinoneimine dyes prior to the chromatographic runs. The scheme involved pipetting 25 ml of aqueous phenol samples, 1 ml of 0.1 *M* carbonate buffer of pH 10, 5 ml of 0.025 *M* of 4-AAP, and 1 ml of 0.060 *M* potassium ferricyanide into a 250-ml separatory funnel. After shaking the mixture for a few minutes, the resulting red quinoneimines were extracted by two aliquots of chloroform of 5-ml each into a small round bottom flask. The chloroform extract was then dried using a rotary evaporator. The dried sample was dissolved in methanol, quantitatively transferred into a 10-ml volumetric flask, and diluted to volume with methanol. The reconstituted solution was then chromatographed. All runs were carried out at room temperature in an air-conditioned laboratory. The glassy carbon electrode was resurfaced at least once

per week using alumina abrasives and soft polishing cloth followed by cleaning in an ultrasonic cleaner.

RESULTS AND DISCUSSION

The cyclic voltammograms of the synthetically prepared ABQI and the derivatized phenol obtained from the chloroform extract are compared in Fig. 1a and b. Both exhibit a cathodic wave near -0.2 V *vs.* Ag/AgCl and an anodic wave near $+0.1$ V. The analytically pure crystalline ABQI (m.p. 162°C) was prepared by following the literature procedure[25]. The red ABQI crystals were dissolved in the HPLC mobile phase prior to the voltammetric experiments. The chloroform extract was prepared by derivatizing the unsubstituted phenol after the procedure outlined in the *Analytical methodology* section and was reconstituted with the HPLC mobile phase for the voltammetric experiments. The results clearly demonstrate that the reconstituted chloroform extract did contain the expected ABQI, which has been formed from the unsubstituted phenol via derivatization. Similarly, the voltammograms of the derivatized *m*-cresol and *o*-chlorophenol (Fig. 1c and d) also exhibit the characteristic cathodic peak between -0.1 and -0.4 V and the anodic peak near $+0.1$ V. The electrode reactions of all ABQIs involve a single 2e, $2H^+$ step in a manner similar to that of the *p*-benzoquinoneimine–*p*-aminophenol redox couple[24,26].

In all cases, the anodic peaks of the derivatized phenols merge partially with a large background wave. By comparing with Fig. 1e, this background wave is attributed to 4-AAP, which we suspect was partially extracted into the chloroform layer. The voltammogram of 4-AAP clearly shows that there is no observable cathodic peak even at a potential as negative as -1.00 V. As a consequence, no chromatographic peak corresponding to 4-AAP was found; therefore, it does not interfere with LC–ED analysis.

Chloroform was chosen here as the extracting solvent because it has been used successfully by previous workers to extract the ABQI dyes formed in the antipyrine reaction[20,21]. It has high extraction efficiency and the extracts were found to be very stable, a real advantage for storing and preparing sample solutions prior to the chromatographic runs.

Effect of the amount of reagents

To determine how the yield of ABQI in the chloroform extract is affected by the quantities of 4-AAP and phenol used in the derivatization reaction, a study similar to the work by Ettinger *et al.*[27] was undertaken. In this study, the amounts of phenol (25.00 ml of $4.00 \cdot 10^{-5}$ *M*), carbonate buffer, and potassium ferricyanide were kept constant during the reaction while varying the amounts of 4-AAP. The sample preparation procedure was the same as outlined in the *Analytical methodology* section. The chloroform extract was chromatographed at an applied potential of -0.200 V *vs.* Ag/AgCl. The results are shown in Fig. 2. It can be seen that the peak heights (also peak areas, not shown in figure) reach a plateau value when the mole ratio of 4-AAP *versus* phenol exceeds approximately 10:1. In other words, the results have proven that phenol is the limiting reagent in the derivatization reaction as long as 4-AAP exists in large excess. No attempts were made to investigate the effect of the amount of oxidant on the yield of ABQI since Ettinger has already shown that the ferricyanide

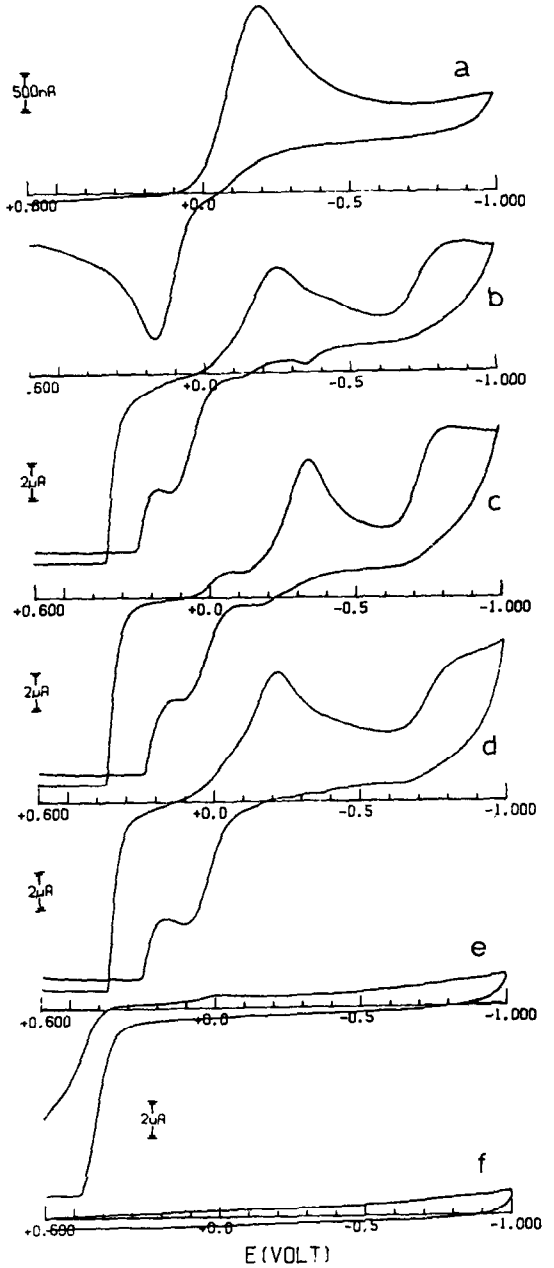


Fig. 1. Cyclic voltammograms of (a) synthetically prepared ABQI; (b) derivatized phenol; (c) derivatized *m*-cresol; (d) derivatized *o*-chlorophenol; (e) 4-aminoantipyrine and (f) background. Sample concentration: $2.00 \cdot 10^{-4}$ *M* each. Solvent: methanol–phosphate buffer (pH 5) (48:52). Working electrode: glassy carbon. Reference electrode: Ag/AgCl. Scan rate: 0.100 V/s.

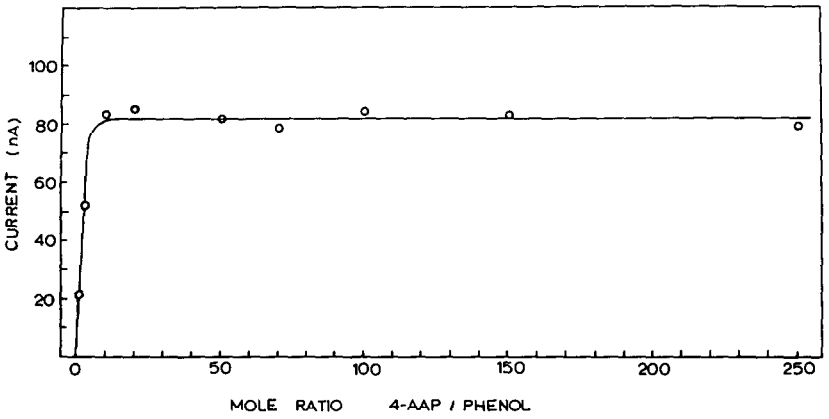


Fig. 2. Effect of the amount of 4-AAP reagent on the peak current of derivatized phenol.

concentration is not critical[27]. The reaction time of all trials during the derivatization step was less than five minutes at room temperature.

Chromatographic behavior

To determine the optimum applied potential for LC–ED of derivatized phenols, their hydrodynamic voltammograms were determined. All phenols (25.00 ml of $5.00 \cdot 10^{-5}$ *M*) were derivatized and extracted in the same manner as outlined in the *Analytical methodology* section. The methanol reconstituted chloroform extracts were chromatographed at different applied potentials. The resulting normalized hydrodynamic voltammograms are shown in Fig. 3. All derivatized phenols except thymol reached the limiting current at a potential less than −0.30 V. For reasons unknown, the derivatized thymol behave very sluggishly on the glassy carbon electrode.

From the hydrodynamic voltammograms, it seems that an applied potential of −0.40 V should be chosen for all derivatives studied. However, a potential of −0.20 V was selected instead as the optimum value. The rationale for choosing this value is that at this potential the currents due to impurities and oxygen in the mobile phase are negligibly small, thus exhaustive degassing of the mobile phase is not required. At this potential, the observed currents of all derivatized phenols except thymol have reached between 63% and 97% of their limiting values. Therefore, this low value does not seriously jeopardize the sensitivity. Another advantage is that a low applied potential also gives better selectivity[28]. Furthermore, a low applied potential usually results in lower background currents and faster decay to the steady background value. For example, we observed that using an applied potential of −0.20 V, it took less than 6 min for the cell current to decay to a steady value of about 0.7 nA as soon as the cell was switched on. On the contrary, it took more than 40 min for the cell current to decay to a much higher steady value of 3 nA at +0.6 V and more than 1 h to reach a steady value of 6.5 nA at +0.8 V.

The chromatographic data of individually derivatized phenols are summarized in Table I. Using a mobile phase of methanol–water (48:52) containing 0.04 *M* potassium chloride and 0.01 *M* phosphate buffer of pH 5, all derivatized phenols

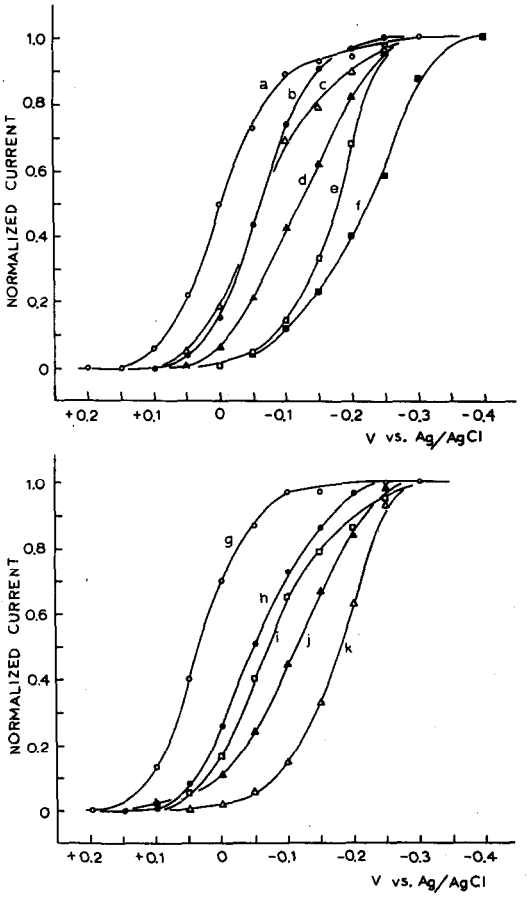


Fig. 3. Normalized hydrodynamic voltammograms of derivatized phenols. (a) Phenol; (b) *m*-chlorophenol; (c) 2,3-dimethylphenol; (d) guaiacol; (e) 2,5-dichlorophenol; (f) thymol; (g) *o*-chlorophenol; (h) 2,4,6-trichlorophenol; (i) 2,5-dimethylphenol; (j) *m*-cresol; (k) 2,3-dichlorophenol.

were eluted within 45 min on a C_{18} reversed-phase column. It should be noted that in addition to the listed phenols, *o*-nitro-, *p*-nitrophenol, and 4-hexylresorcinol were also tested, but they failed to give identifiable peaks. Fig. 4 shows the separation of a mixture of 11 derivatized phenols at an applied potential of −0.20 V using the same mobile phase. The aqueous phenol mixture containing $1.00 \cdot 10^{-5}$ *M* each was derivatized in the same manner as the individual phenols. It can be seen that eight derivatized phenols are eluted within 30 min, but severe overlap occurs for the di-and tri-substituted chlorophenols. No attempts were made to develop a better separation scheme to resolve these peaks.

Four phenols representing different substituent groups were selected to test the linear dynamic response. All original phenol solutions before derivatization were prepared in the range of 10^{-7} *M* to 10^{-4} *M*, which corresponds to 25 ppb to 13 ppm depending on the identity of the phenols. The results are summarized in Table II. The day-to-day reproducibility is good. For a period of 48 h, the peak height changes for

TABLE I
CHROMATOGRAPHIC DATA OF DERIVATIZED PHENOLS
Mobile phase: methanol–water containing 0.04 *M* potassium chloride, 0.01 *M* phosphate buffer (pH 5) (48:52).

Compound	*k'*
Phenol	6.1
Guaiacol	6.8
o-Cresol	9.9
m-Cresol	12.3
o-Chlorophenol	14.3
m-Chlorophenol	17.7
2,5-Dimethylphenol	20.9
2,3-Dimethylphenol	23.5
2,4,6-Trichlorophenol	36.2
2,5-Dichlorophenol	37.3
2,3-Dichlorophenol	37.9
Thymol	54.1

unsubstituted phenol were on the average less than 1%, but higher (*ca.* 7%) for other phenols with longer retention times. Better reproducibility can be achieved if the electrode is frequently polished and the mobile phase composition is kept constant. Excellent linear relationships (correlation coefficients >0.99) were found for the four phenols studied between $3 \cdot 10^{-7}$ *M* to $1 \cdot 10^{-4}$ *M*, a more than 300-fold variation in concentration. The dynamic range reported here was the range arbitrary chosen and studied. Our previous work[24] has shown that ABQI at a $1 \cdot 10^{-7}$ *M* level can still be

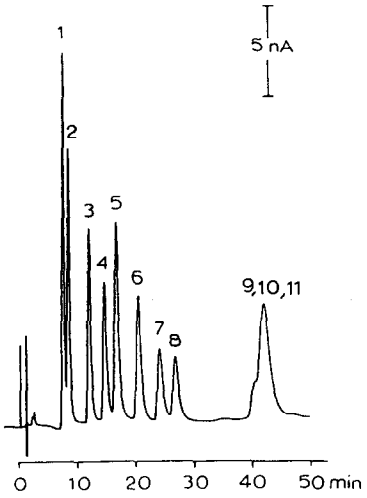


Fig. 4. Chromatogram of a mixture of derivatized phenols ($1.00 \cdot 10^{-5}$ *M* each) on a C_{18} column. 1 = Phenol; 2 = guaiacol; 3 = *o*-cresol; 4 = *m*-cresol; 5 = *o*-chlorophenol; 6 = *m*-chlorophenol; 7 = 2,5-dimethylphenol; 8 = 2,3-dimethylphenol; 9 = 2,4,6-trichlorophenol; 10 = 2,5-dichlorophenol; 11 = 2,3-dichlorophenol. Mobile phase; methanol–phosphate buffer (pH 5) (48:52). Flow-rate: 1.5 ml/min. $E_{applied} = -0.200$ V *vs.* Ag/AgCl on a glassy carbon electrode.

TABLE II
LINEAR REGRESSION ANALYSIS OF DERIVATIZED PHENOLS

Compound	*Range** *(ng)*	*Corr. Coef.*	*Regression Line** (slope ± S.D.)*	*Sensitivity*** (nA/μM)*	*R.S.D.§ peak ht.*
Phenol	0.26– 86	0.9978	1.098 ± 0.042	2.23	0.41
Guaiacol	0.37–124	0.9976	1.078 ± 0.043	1.87	0.85
o-Cresol	0.32–108	0.9999	1.030 ± 0.048	1.23	1.7
o-Chlorophenol	0.39–129	0.9920	1.050 ± 0.077	1.92	0.36

* Amount of derivatized phenols injected using a 10 μl sample valve. Calculated from each original phenol concentration by assuming 100% conversion to the corresponding ABQIs.

** Calculated from log current *vs.* log concentration plots.

*** Obtained from the slope of current *vs.* concentration plots.

§ Relative standard deviation calculated from at least four repetitive injections at each original phenol sample concentration of 10^{-5} *M*.

detected with ease. It is conceivable that the dynamic range could be improved at least three-fold, but vigorous testing at such low levels has not been attempted.

All four log peak currents *versus* log concentration calibration plots give a slope of nearly unity (Table II). This is an excellent indication that the observed current is, indeed, proportional to concentration. It should be noted that initial attempt of using technical-grade commercial *o*-chlorophenol to establish a calibration curve gave poorer linear response than the other three phenols. An excellent response was obtained after it was purified by drying *o*-chlorophenol over potassium sulfate followed by distillation. From the results of regression analysis in Table II, it can be seen that the sensitivity of this technique follows the order: phenol > *o*-chlorophenol > guaiacol > *o*-cresol. It is interesting to note that *o*-chlorophenol has higher sensitivity than either *o*-cresol or guaiacol despite its longer retention time. This observation is probably due to the fact that at −0.2 V, *o*-chlorophenol, being highly reversible at the glassy carbon electrode, has already reached its limiting current value; while *o*-cresol and guaiacol have only reached 85% and 83% of their maximum heights, respectively.

For unsubstituted phenol, the detection limit (based on a signal-to-noise ratio, S/N of 2) of this technique is estimated to be around $4 \cdot 10^{-8}$ *M*, which corresponds to 34 pg per injection if a 10-μl sample loop is used. It should be mentioned that direct injections of chloroform extract without reconstitution with methanol were also tried. Unfortunately, chloroform is also electroactive at −0.2 V; and it coelutes with the derivatized phenol using a mobile phase of methanol–water (48:52) (with phosphate buffer). A more polar mobile phase such as methanol–water (46:54) was needed to make chloroform to elute just prior to the phenol peak. The disadvantage is, of course, longer retention times are required for phenol samples.

The application of the reductive LC–ED detection is demonstrated with a waste water sample as shown in Fig. 5. The sample was obtained from a local waste water treatment plant. The silt and sludge in the sample were allowed to settle overnight, and the liquid portion of the sample was then filtered several times. No other pretreatment was performed. The filtered sample was then treated and chromatographed following the same procedure as described in the Analytical methodology section. The

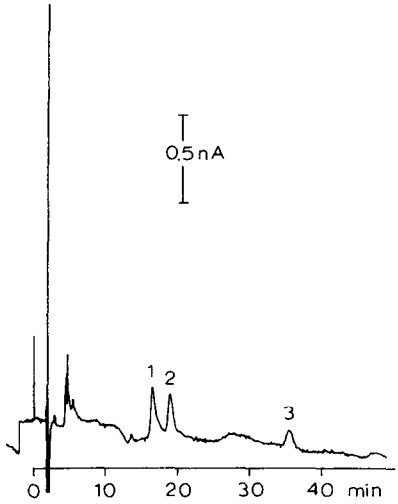


Fig. 5. Chromatogram of a waste water sample. Mobile phase: methanol–phosphate buffer (pH 5) (50:50). 1 = Phenol; 2 = guaiacol; 3 = *o*-chlorophenol. Flow-rate: 1.0 ml/min. $E_{applied} = -0.200$ V *vs.* Ag/AgCl on a glassy carbon electrode.

separation was performed on a 15 cm × 4.6 mm I.D. ODS column using a mobile phase of methanol–phosphate buffer (50:50) and a slower flow-rate of 1 ml/min. The sample was found to contain low levels of phenol (78 ppb), guaiacol (137 ppb), and *o*-chlorophenol (30 ppb). The small ill-defined peak between guaiacol and *o*-chlorophenol and peaks eluted after *o*-chlorophenol were not identified. It is interesting to note that the phenol levels detected in our sample are in the same order of magnitude as reported previously in the waste water samples of other regions of the country by LC–ED oxidative detection[2].

CONCLUSION

The chromatographic method described above has demonstrated that it is feasible to determine ppb levels of phenols via derivatization using low-potential (−0.2 V) reductive amperometric detection without exhaustive oxygen removal. Low potential detection has additional advantages, including lower background currents and potentially less interferences; because not many compounds are electroactive at −0.2 V. The conversion of phenols into quinoneimines (ABQIs) is rather straightforward and rapid. The precolumn derivatization procedure involves only two simple operations: mixing reagents in a separatory funnel at room temperature followed by extraction with chloroform and reconstitution of chloroform extract with methanol. The major drawback of the precolumn derivatization technique is, of course, the limitation of the 4-AAP reaction, which gives negative tests to certain *para*-substituted phenols and nitrophenols.

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