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A HIGHLY SENSITIVE TECHNIQUE FOR THE LIQUID CHROMATOGRAPHIC ANALYSIS OF PHENOLS AND OTHER ENVIRONMENTAL POLLUTANTS

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SUMMARY

This paper describes a highly sensitive technique for the analysis of phenols and other environmental pollutants by high-speed liquid chromatography. The system utilizes a reaction detector whereby cerium(IV) sulfate is allowed to react with phenols in the column effluent, and the cerium(III) thus produced is detected by fluorescence spectroscopy. The detector shows good linearity in the region 10–230 ppb of phenol, and combined with suitable concentration techniques, the lower limit of detection of phenols in environmental samples was shown to be about 0.4 ppb.

INTRODUCTION

One of the major drawbacks to the wider use of high-speed liquid chromatography (HSLC) for the analysis of environmental pollutants is the relatively low sensitivity of detectors commercially available. In this paper a highly sensitive technique for the analysis of some of these contaminants is presented, with emphasis placed on separation and detection of phenols in water samples. The importance of a sensitive method for the analysis of phenols is illustrated by the following statement[1]. "Roughly 25% of the pesticides on the world market today are compounds possessing a substituted phenol moiety which may be more or less easily cleaved from the molecule. Such compounds are found among certain herbicides, a few fungicides, numerous carbamates, and several organophosphorus insecticides. Thus, a reliable and sensitive general phenol analysis could be a useful tool for the determination of a relatively large number of pesticides."

A wide variety[2–4] of phenols may be introduced into the aquatic environment. Waste effluents of coking plants, brown coal distillery plants and the pulp and paper industry are among the primary inputs of phenols into the environment. Phenols are components of plastics and raw materials for dyes and drugs. In addition, as described above, certain pesticides hydrolyze in natural waters to give phenols.

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Phenols are toxic to most organisms. Guaiacol (2-methoxyphenol), a component of pulp mill waste, is known to cause gastrointestinal irritation. Other effects of phenols on man have been well documented[3]. Toxicity to aquatic biota, high oxygen demand and the imparting of objectionable taste to fish and drinking water are further problems associated with phenols in the environment. For example, it has been shown[5] that 2-chlorophenol, when present in concentrations as low as 2 ppb (2 μg/l), will impart a disagreeable taste and odour to drinking water.

While numerous analytical procedures[2,6–8] exist for "total phenols" in water, it is obviously apparent that there exists a great need for a method for the analysis of individual phenols in water at very low concentrations. Several methods for the analysis of phenols by gas chromatography have been reported[2]. Direct aqueous injection of water samples leads to problems of stability of the flame ionization detector and tailing on the column. It should be noted, however, that this latter problem seems to have been overcome as reported by Di Corcia[9]. In addition, less volatile phenols are difficult to determine by gas chromatography. Kawahara[10,11] has developed a method whereby the pentafluorobenzyl ethers of the phenols are prepared and subsequently detected using an electron capture detector at levels of about 0.36 ng of phenol.

Since certain difficulties are encountered in the above methods, HSLC would seem to be an ideal tool for the analysis of phenols. As indicated by Bhatia[12], if aqueous solvents are used, direct injection of a water sample is possible and problems of low volatility do not arise. However, the resolution and sensitivity (about 700 ppb for phenol) reported[12,13] are not suitable for the wide range of phenols encountered in the environment.

The technique described herein employs a reaction detector somewhat similar, but apparently more sensitive, to that described by Katz and co-workers[14–16]. Column effluent was mixed with cerium(IV) sulfate and sulfuric acid by means of a proportionating pump. Phenols in the effluent were oxidized and the cerium(III) ion thus produced was detected by fluorescence spectroscopy[17,18]. Concentrations of about 10 ppb could be detected without prior concentration of the sample.

EXPERIMENTAL

Materials

Phenols and other compounds tested were used as obtained from the suppliers without further purification. Pesticide grade acetonitrile (Fisher Scientific, Pittsburgh, Pa., U.S.A.) was used in the chromatographic separations.

Cerium(IV) sulfate (2.5×10^{-5} *N*) was prepared as follows. To a storage bottle that had previously been allowed to stand in contact with a 10^{-4} *N* solution of cerium(IV) sulfate[19] were added 1 ml of 0.1 *N* cerium(IV) sulfate stock solution (Fisher Scientific), 3920 ml distilled water, 80 ml concentrated sulfuric acid and 9.6 g sodium bismuthate. The solution was boiled for approximately 30 min and allowed to cool and settle before using. A filter tube was used on the feed line to the proportionating pump to prevent any sodium bismuthate from entering the system. Solutions thus prepared showed only slight background fluorescence and were found to be stable for at least two weeks.

Preparation of environmental samples

Water obtained from Hamilton Harbour was filtered, spiked with a mixture

of phenols and then concentrated by the method of Afghan *et al.*[6]. Five hundred milliliters of this water were acidified to pH 2 and extracted with three 20-ml portions of *n*-butyl acetate. The combined organic portions were then extracted with 8 ml of 1.6 *N* sodium hydroxide solution. The aqueous phase was made neutral (pH 7) and diluted to 10 ml. Thus a fifty-fold concentration was achieved. Afghan *et al.*[6] report that any sulfides or mercaptans which are present in the sample may be removed by prior treatment of the sample with 10^{-3} *M* bismuth nitrate in hydrochloric acid.

Liquid chromatography

A Waters Associates Model ALC 202 liquid chromatograph equipped with a modified Milton Roy pump capable of pressures of 3000 p.s.i.g. was employed. This chromatograph is equipped with a UV detector operating at 254 nm. Injections were accomplished by means of a sampling valve (Waters Associates) with sample loops of nominal volumes of 85, 200 and 1000 μl. Two columns were used in this study, *viz.* (a) 0.61 m $\times$ 4.83 mm I.D. $\times$ 6.35 mm O.D. packed with Bondapak C18/Corasil (Waters Associates) using the tap and fill method of Kirkland[20]; (b) 1 m $\times$ 2.1 mm I.D. $\times$ 6.35 mm O.D. packed with Permaphase ODS (DuPont Instruments).

Gradient system

The gradient was generated by the method of Scott[21]. In this method, a Milton Roy pump (pump 1, Fig. 1) delivered acetonitrile at a flow-rate of 0.36 ml/min to a graduated cylinder initially containing 100 ml distilled water. This flask was stirred magnetically and served as the solvent reservoir for pump 2, which delivered solvent to the column at a flow-rate of 1.05 ml/min. Using the equations of Scott, these parameters should give a slightly concave gradient. The shape actually generated was determined using acetone in place of acetonitrile (keeping flow-rates constant) and using the UV detector to monitor the gradient. The gradient agreed well with that calculated. The per cent acetonitrile in the mobile phase is shown on the chromatograms in Figs. 5 and 6.

Detection system

Fig. 1 shows the complete liquid chromatographic system. After passing through the UV detector, the column effluent was segmented into small portions by means of a Technicon proportionating pump. To these portions was added a mixture of cerium(IV) sulfate and 23 *N* sulfuric acid with the aid of the same pump. The combined flows were passed through a short coil maintained at 25° and into the cell compartment of a Model MFP-2A Hitachi Perkin-Elmer fluorescence spectrophotometer. To minimize diffusion effects, the debubbler was located in the cell compartment as close to the flow cell as possible. The flow cell consisted of a short piece of normal-wall 2-mm-bore Spectrosil tubing (Thermal American Fused Quartz Company). Fluorescence measurements were made using an excitation wavelength of 260 nm and emission wavelength of 350 nm with excitation and emission slit widths of 6 and 16 nm, respectively. Sample sensitivity was set at a position of four. Signals from the fluorescence spectrophotometer were fed to a Hewlett-Packard Model 3370A integrator and thence to a Honeywell Electronik 194 dual-pen recorder. The above integrator is not suitable for the integration of small wide peaks due to its inability to reject noise spikes. However, the integrator did allow the output to the recorder

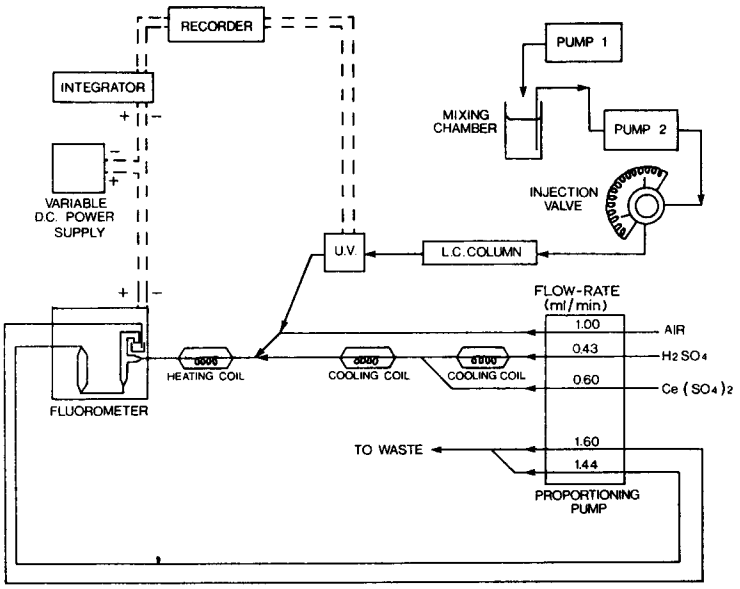


Fig. 1. Liquid chromatographic system used in this study. Solid lines indicate solvent flow and dotted lines indicate electrical connections. See text for further details.

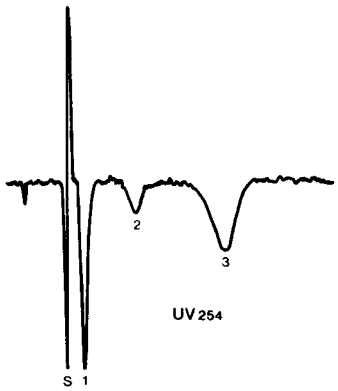
to be varied from 1 mV to 1000 mV. A variable d.c. power supply was employed to subtract background fluorescence from the output of spectrophotometer amplifier.

RESULTS AND DISCUSSION

The reaction of cerium(IV) ion with organic compounds has been well documented[22–24]. One of the major problems encountered in trace analysis is the inherent instability of cerium(IV) when in contact with fresh glass surfaces or heat[19,25]. Cerium(III) ion is thus present in most solutions of cerium(IV). Sodium bismuthate was used to oxidize most of the cerium(III) but traces remaining and/or produced on standing caused a background fluorescence signal which had to be subtracted out electrically to attain a reasonable baseline.

A more serious problem was also due to the presence of cerium(III) ion. In our initial experiments, a severe baseline drift was observed when gradient elution was used. This was probably due to precipitation of cerium(III) sulfate in the flow cell as the organic content in the solvent increased. This problem was overcome by mixing the cerium(IV) sulfate with fairly concentrated (23 *N*) sulfuric acid, in which cerium(III) is presumably more soluble.

As described in Experimental, the column effluent was segmented with air bubbles by means of the proportionating pump. It was then allowed to react with the reagents in the reaction coil for about 4 min at 25° before passing through the flow cell. Due to this segmentation, the flow system did not lead to significant peak broadening or loss in resolution. Figs. 2 and 3 show the separation of three phenols under isocratic conditions. Each of these chromatograms compares the signals from the UV and fluorescence detectors. As can be seen, peak broadening is minimal and it is felt



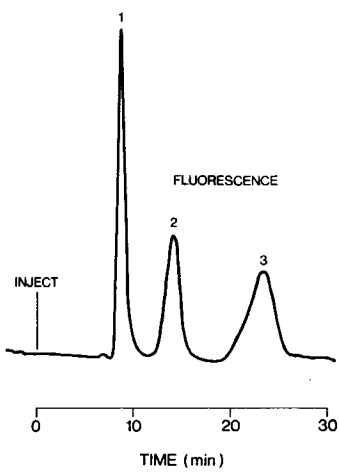
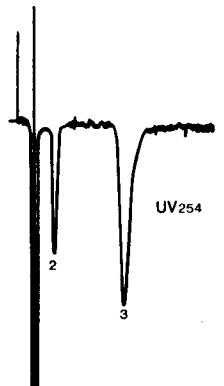


Fig. 2. Separation of phenols on the C18/Corasil column (0.61 m × 4.83 mm I.D.). Mobile phase: acetonitrile–water (25:75) at 1.05 ml/min. Sample size: 85 μl. Detectors: UV (0.08 absorbance units full scale) and fluorescence (200 mV full scale). 1 = Phenol (18.5 ppm); 2 = *p*-chlorophenol (20.2 ppm); 3 = 1-naphthol (23.4 ppm); S = solvent.



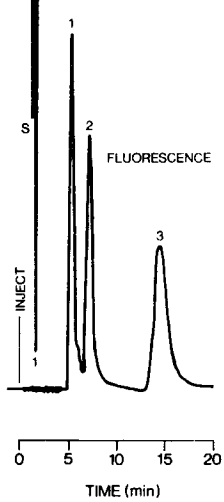


Fig. 3. Separation of phenols on the ODS column (1 m × 2.1 mm I.D.). Mobile phase: acetonitrile–water (5:95) at 1.05 ml/min. Sample size: 85 μl. Detectors: UV (0.08 absorbance units full scale) and fluorescence (200 mV full scale). 1 = Phenol (18.5 ppm); 2 = *p*-chlorophenol (20.2 ppm); 3 = 1-naphthol (23.4 ppm); S = solvent.

that some sacrifice in resolution can be made when compared to the gain in sensitivity of the fluorescence detector. Note that the cerium(IV) sulfate concentrations used for these two particular separations were increased to 2×10^{-3} *N*. This was necessary so that phenol concentrations could be adjusted for simultaneous UV and fluorescence detection, since the concentration of cerium(IV) sulfate will determine an upper limit of detection (see below). Indeed, the use of high concentrations is to be avoided since

it leads to lower sensitivity due to self-quenching effects[18]. The concentrations of cerium(IV) sulfate for other separations shown were 2.5×10^{-5} *N*.

All phenols tested gave a response with this fluorescence detection system, although in some cases, the response was fairly low. The response factors relative to phenol both on a weight (response per gram of compound/response per gram of phenol) and a mole (response per mole of compound/response per mole of phenol) basis are given in Table I. These values are averages of at least two determinations and were obtained with 200-μl injections of the phenols using acetonitrile–water (4:6) as the

TABLE I

RELATIVE RESPONSE OF PHENOLS WITH CERIUM(IV) SULFATE-FLUOROMETRIC DETECTION

Mobile phase: acetonitrile–water (4:6).

Compound	*Weight basis*	*Mole basis*
Phenol	1.000	1.000
o-Chlorophenol	0.50	0.68
p-Chlorophenol	0.50	0.69
2,4-Dichlorophenol	0.24	0.42
2,4,6-Trichlorophenol	0.10	0.22
Pentachlorophenol	0.04	0.12
o-Cresol	0.64	0.74
m-Cresol	0.78	0.90
p-Cresol	0.50	0.57
2,4-Dimethylphenol	0.44	0.57
2,6-Dimethylphenol	0.43	0.55
Catechol	0.47	0.55
Resorcinol	0.88	1.03
Hydroquinone	0.47	0.55
Pyrogallol	0.41	0.55
Orcinol	0.52	0.79
2,4-Dihydroxybenzaldehyde	0.40	0.58
4-Hydroxybenzoic acid	0.42	0.62
2-Methoxyphenol (guaiacol)	0.69	0.89
3-Methoxyphenol	0.59	0.78
4-Methoxyphenol	0.42	0.55
o-Vanillin	0.85	1.37
Eugenol	0.47	0.81
Isoeugenol	0.52	0.92
Syringic acid	0.20	0.41
1-Naphthol	0.56	0.86
2-Naphthol	0.53	0.80
2-Nitrophenol	0.25	0.37
3-Nitrophenol	0.25	0.37
4-Nitrophenol	0.13	0.19
2,4-Dinitrophenol	0.002	0.004
2,4-Dinitro-*o*-cresol	0.004	0.01
Picric acid	0.01	0.02
4-Aminophenol	0.51	0.59
3-Chloro-7-hydroxy-4-methylcoumarin	0.23	0.51

mobile phase, with the chromatographic column bypassed. It appears from the values in Table I that a lower response is generally obtained as substitution increases. These results would seem to be consistent with an oxidative coupling mechanism that has been proposed[24] for phenols. In addition, the nitro-substituted phenols seem to react to a lesser extent.

By injecting a solution of ferrous ethylenediammonium sulfate[26] (see Table IV), it was determined that approximately five moles of phenol react with one mole of cerium(IV) ion. Since there is a possibility that the ferrous ethylenediammonium sulfate did not react completely under the experimental conditions, five moles would represent a minimum value.

It is interesting to note that some phenols which are not detected by the standard 4-aminoantipyrine (4-AAP) method for "total phenols" could be detected quite easily by the fluorescence detection system described in this report. For example, it is claimed[1] that the 4-AAP method will not detect *p*-cresol, *p*-aminophenol, *p*-nitrophenol and 2,4-dinitrophenol. The method is also reported[6,27,28] to be fairly insensitive to 4-alkoxy-substituted phenols (*e.g.*, 4-methoxyphenol and *o*-vanillin) and chlorinated phenols (*e.g.*, *p*-chlorophenol and 2,4,6-trichlorophenol), although it should be mentioned that a similar method using 3-methyl-2-benzothiazolinone does react with some of the above phenols[1].

Fig. 4 is a graph showing the variation of detector response with concentration of phenol. These results were obtained for 1-ml injections of solutions containing different concentrations of phenol. The graph is fairly linear in the region 9 to 229 ppb (correlation coefficient = 0.9987). On going to higher concentrations, the curve starts to level off. This is not due to a failure of the instrumentation, but is instead a result of the cerium(IV) concentration. Theoretically, all of the cerium(IV) ion would be reacted when phenol is present at concentrations greater than about 270 ppb if a 2.5×10^{-5} *N* solution of cerium(IV) sulfate is used. This calculation is based on one mole of phenol reacting with five moles of cerium(IV) ion and taking into consideration the relative flow-rates of column effluent and cerium(IV) sulfate. This latter reagent could be used in higher concentrations (see, for example, Figs. 2 and 3) to attain a greater linear dynamic range, but at these concentrations, the detector exhibits more noise, and less sensitivity. In addition, at these higher concentrations, more baseline drift is observed when gradient elution is employed. In any case, most environmental samples hopefully should not contain phenols in concentrations greater than 75 ppb[29]. We believe the failure of the line to pass exactly through the origin is due to noise sensed by the integrator.

Fig. 5 shows a separation of a synthetic mixture of phenols which may be found[3] in pulp mill effluent. Gradient elution was used and the percent acetonitrile in the mobile phase is given. As can be seen, the phenols present were not detected to any appreciable extent by the UV detector but could easily be detected by the cerium(IV) sulfate-fluorescence detector at concentrations as low as 20 ppb without any prior concentration of the sample. The reader will note that the sample volume was about 1000 μl. This volume would seem to be quite large for HSLC but Eisenbeiss and Sieper[30] have shown that fairly linear detector responses could be obtained with injections of 750–1000 μl. The results in Fig. 4 confirm these findings. In addition, these authors point out that if the compounds to be chromatographed are dissolved in the mobile phase, then these compounds will be strongly retained at the head of

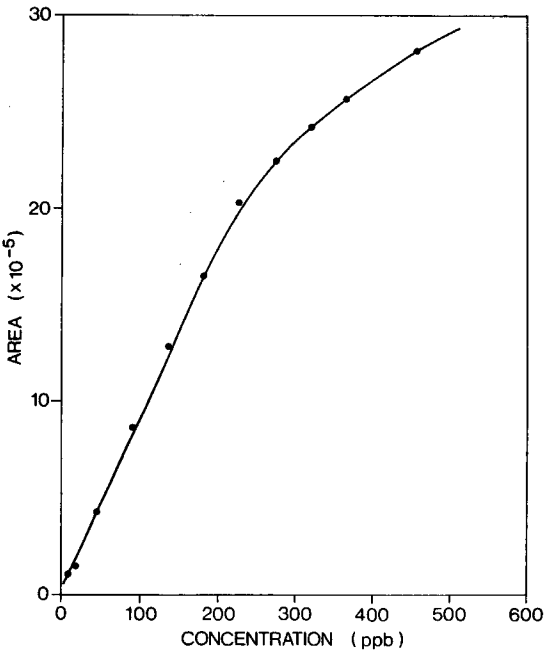


Fig. 4. Graph illustrating response of the cerium(IV) sulfate-fluorescence detection system to phenol. Column: C18/Corasil (0.61 m × 4.83 mm I.D.). Mobile phase: acetonitrile–water (2:8) at 1.05 ml/min. Sample size: 1000 μl.

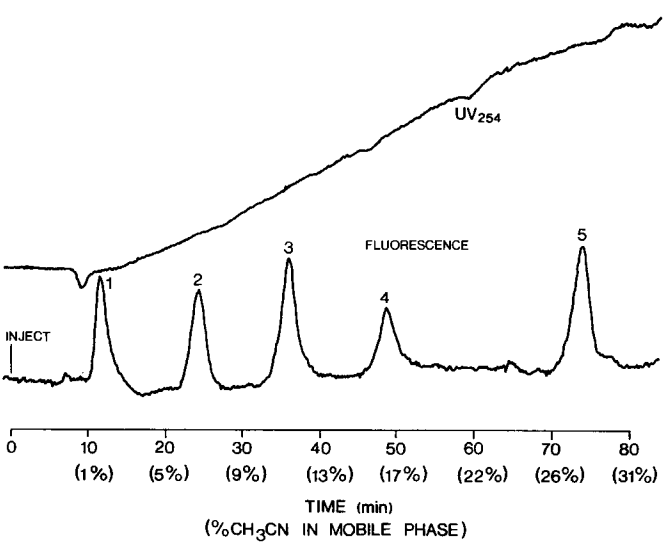


Fig. 5. Separation of a synthetic mixture of phenols reported to have been found in pulp mill effluent on the C18/Corasil column (0.61 m × 4.83 mm I.D.). Gradient elution from water to approximately 36% acetonitrile–64% water (% acetonitrile shown in bracketed numbers). Sample size: 1000 μl. Detectors: UV (0.08 absorbance units full scale) and fluorescence (2 mV full scale). 1 = Syringic acid (64 ppb); 2 = phenol (23 ppb); 3 = guaiacol (43 ppb); 4 = *o*-vanillin (27 ppb); 5 = eugenol + isoeugenol (146 ppb).

the column where, in effect, they are concentrated. Referring again to Fig. 5, injection was made at the same time the gradient was started. Since it took about 6 min for the gradient to reach the column due to the associated tubing, it is felt that the phenols would probably remain at the head of the column and not start to move down the column until the mobile phase contained a significant fraction of acetonitrile.

Fig. 6 is a chromatogram showing the separation of some chlorinated phenols using gradient elution. The detection and identification of these particular phenols is important since it has been shown[5] that they impart disagreeable tastes and odours to drinking water when present in very low concentrations (see Table II).

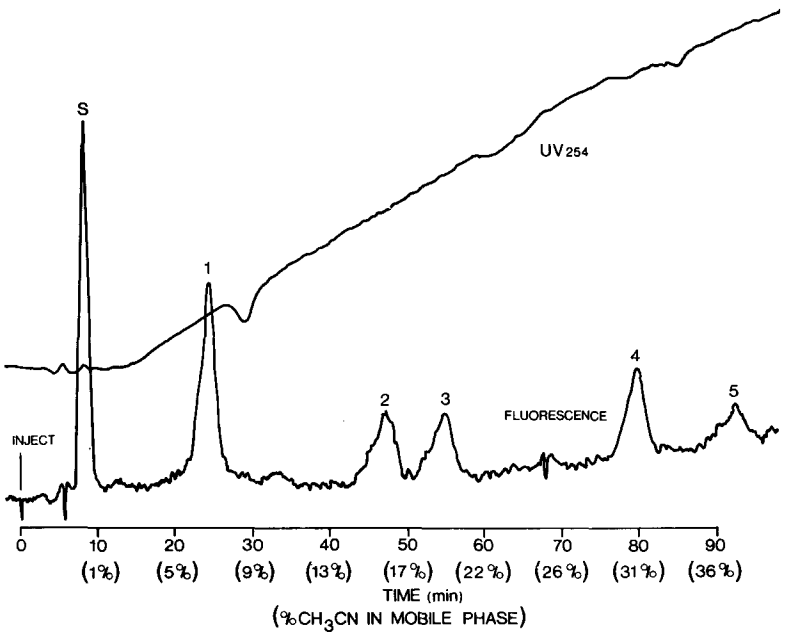


Fig. 6. Separation of chlorinated phenols on the C18/Corasil column (0.61 m × 4.83 mm I.D.). Conditions, see the legend to Fig. 5. 1 = Phenol (18.4 ppb); 2 = *o*-chlorophenol (22.5 ppb); 3 = *p*-chlorophenol (20.2 ppb); 4 = 2,4-dichlorophenol (52.2 ppb); 5 = 2,4,6-trichlorophenol (42.6 ppb); S = solvent.

A sample of water taken from Hamilton Harbour was filtered and then spiked with the same mixture of chlorophenols used in Fig. 6. The solution was concentrated fifty-fold using published procedures[6] and chromatographed giving the results shown in Fig. 7. A "blank" (unspiked sample) was concentrated in the same manner and its chromatogram is also shown in Fig. 7. In addition to concentrating the sample, this procedure removes many components which would interfere with the analysis and therefore should be an integral part of the determination of phenols. All of the chlorinated phenols except 2,4,6-trichlorophenol can be seen quite easily in the spiked sample. The latter phenol is either hidden by the noise or is lost in the concentration procedure. As can be seen, the technique allows the liquid chromatographic analysis of phenols at concentrations as low as 0.4 ppb.

TABLE II

TASTE AND ODOUR THRESHOLD CONCENTRATIONS[5] (pp[6])

Component	*Geometric mean threshold (ppb)*	
	Taste	*Odour*
Phenol	>1000	>1000
o-Chlorophenol	4	2
p-Chlorophenol	>1000	250
2,4-Dichlorophenol	8	2
2,6-Dichlorophenol	2	3
2,4,6-Trichlorophenol	>1000	>1000

The success achieved with phenols encouraged us to determine if other types of compounds would be detected by this system. A variety of compounds were tested, including carbamates (carbaryl, IPC), organophosphorus pesticides (malathion, parathion, coumaphos), and some chlorinated pesticides such as DDT, toxaphene and 2,4-D. The results given in Tables III and IV show that, for the most part, the responses are less by a factor of about 1000 compared to phenol. Therefore, the response for most of these would be comparable to that obtained by a UV detector. However, two

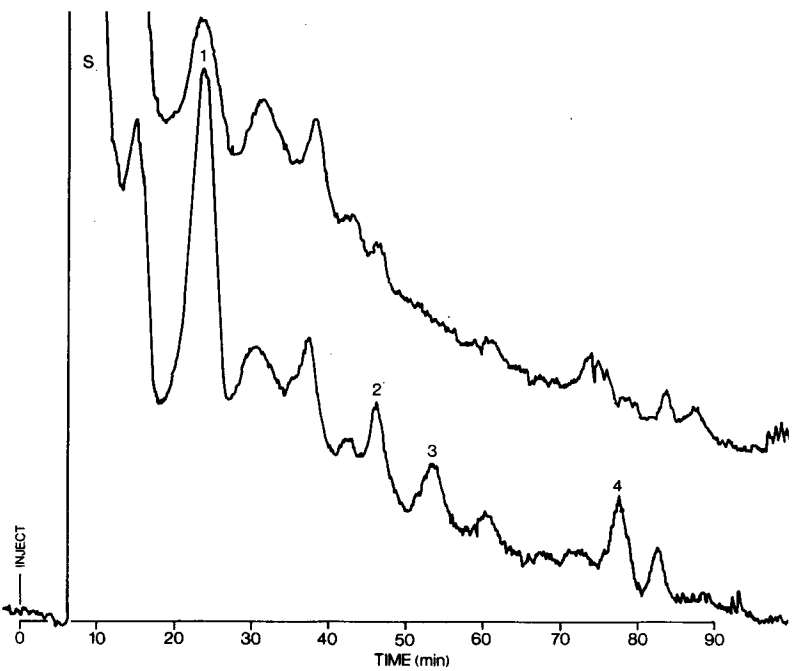


Fig. 7. Analyses of phenols in a water sample from Hamilton Harbour. Conditions: see the legend to Fig. 5. Upper chromatogram shows "blank" sample after concentration procedure. Lower chromatogram shows water sample "spiked" with 0.37 ppb phenol (1), 0.45 ppb *o*-chlorophenol (2), 0.40 ppb *p*-chlorophenol (3), 1.0 ppb 2,4-dichlorophenol (4), and 0.85 ppb 2,4,6-trichlorophenol (not seen) and then concentrated.

TABLE III

RELATIVE RESPONSE OF VARIOUS COMPOUNDS WITH CERIUM(IV) SULFATE-FLUOROMETRIC DETECTION

Mobile phase: acetonitrile–water (4:6).

Compound	*Relative response*	
	Weight basis	*Mole basis*
Phenol	1.000	1.000
Dimethyl phthalate	0.001	0.003
Malathion	0.0001	0.0004
Parathion	0.001	0.004
p-Nitrophenol	0.13	0.19
Aroclor 1260	0.001	0.002
IPC (Propham)	0.001	0.003
Carbaryl	0.18	0.38
1-Naphthol	0.56	0.86
Coumaphos	0.011	0.041
3-Chloro-7-hydroxy-4-methylcouramin	0.23	0.51
2,4-D	0.001	0.003
Lindane	0.0002	0.0005
DDT	0.0009	0.004
Toxaphene	0.0002	0.0009

points should be noted. First and foremost, the reaction conditions described were optimized for phenols and not for other types of compounds. Owing to the flexibility of the system, many of the variables such as reaction time, temperature and concentrations of the reagents could be altered. For example, Sharma and Mehrotra reported[31] that phthalic acid is completely oxidized by cerium(IV) to carbon dioxide in refluxing 50% sulfuric acid for 180 min, consuming about 30 moles of cerium(IV) per mole of acid in the process. From the results in Tables III and IV it can be calculated that only 0.015–0.025 mole of cerium(IV) was consumed in reaction with dimethyl phthalate under the conditions used in this report. Thus the yield could probably be increased, even without going to the drastic conditions described by

TABLE IV

RELATIVE RESPONSE OF VARIOUS COMPOUNDS WITH CERIUM(IV) SULFATE-FLUOROMETRIC DETECTION

Mobile phase: water.

Compound	*Relative response*	
	Weight basis	*Mole basis*
Phenol	1.000	1.000
p-Chlorophenol	0.52	0.71
Resorcinol	0.95	1.11
Sodium sulfide	0.05	0.04
Sodium tetrathionate	0.0004	0.001
Dimethyl phthalate	0.002	0.005
Ferrous ethylenediammonium sulfate	0.051	0.21

Sharma and Mehrotra. Indeed, there are a great many reports[23,24] in the literature of organic compounds which can be oxidized by cerium(IV). In addition, as noted earlier, a great many pesticides consist of a substituted phenol moiety and some are in fact cleaved *in vivo* to yield phenols[4,32,33]. Thus, it should be possible to analyze for some of these pesticides by hydrolysis to the parent phenol either before or after chromatography. For example, *p*-nitrophenol gives about 100 times the response of parathion (Table III), the parent organophosphorus pesticide. Similarly, carbaryl could be hydrolyzed to 1-naphthol and coumaphos to 3-chloro-7-hydroxy-4-methylcoumarin, where in both cases the phenols give a greater response than the parent pesticide.

CONCLUSIONS

The present work has demonstrated a highly sensitive technique for the liquid chromatographic analysis of phenols using a cerium(IV) sulfate-fluorescence detection system. The system was able to detect all phenols tested, some at concentrations as low as 0.4 ppb. We believe this to be one of the lowest detection limits yet reported in the literature for HSLC.

Work is currently proceeding on techniques for the analysis of other environmental pollutants using this detection system.

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