Microdetermination of Derivatives of Phenols and Mercaptans by Means of Electron Capture Gas Chromatography

Fred K. Kawahara

U. S. Department of the Interior, Federal Water Pollution Control Administration, Division of Pollution Surveillance, Cincinnati, Ohio 45202

TRACES OF MERCAPTANS and phenols (1, 2) adversely affect the palatability of water. To aid in monitoring waterways, sensitive and rapid methods are needed for measuring these compounds which constitute a small portion of the complex weak acid fraction (3). This fraction is isolated with the aid of the solubility separation procedure (3) from the organic residue left by evaporation of the chloroform extract of the carbon adsorption (4) samples. Activated carbon effectively concentrates the numerous organic pollutants which are carried to the stream by runoff, in domestic sewage, or in industrial wastes. The weak acid fraction should normally contain only the weak acids, such as phenols and mercaptans, which are soluble in 5% sodium hydroxide solution (3). However, a large portion of the weak acid fractions, isolated from the organic materials extracted from river water, is neither phenolic nor mercaptan.

Phenolic compounds in water are usually determined by the nonspecific amino-antipyrene method (2). Modifications in procedure are adopted when impurities or concentration variations are observed. Brand and Keyworth (5) identified and analyzed with an argentometric coulometer the petroleum mercaptans which had been resolved by gas chromatography. The separated mercaptans of the gasoline boiling range were discharged from the column directly into the silver ion titration cell. The quantity of coulombs of electricity necessary to compensate for the depletion of the silver ions is proportional to the concentration of the mercaptan sulfur. This method has a sensitivity of 1 ppm of mercaptan sulfur.

Recently, several interesting approaches have been investigated to develop either faster or selective techniques of analyses. In the gas chromatographic analyses of phenols, Baker (6) employed the direct aqueous injection method. He determined, with use of the flame ionization detector, traces of phenol introduced into distilled water. Flame ionization detector analyses, attempted upon the weak acid fractions from the carbon adsorption extracts (4), revealed that the minimum amount of measurable phenol is a few hundredths of a microgram. We have observed that the presence of large amounts of organic contaminants interferes in the measurement with FID of phenol existing at trace concentration in river water. Thus, the gas chromatographic analyses of phenols with the use of the flame ionization detector appears limited to their measurements in uncontaminated samples at about the tenth of a microgram range.

Because of the numerous contaminants in the weak acid fraction, a highly selective method is required. Thus, the conversion of phenol and mercaptan to a derivative which can

Table 1. Tropernes of Emers and Thoethers						
Pentafluorobenzyl Aryl (or Alkylthio) Ether	mp, ° C	$\mathbf{R.I.}_{n_{\mathrm{D}}^{24^{\circ}}}$	Yield, %	Reten- tion time (min.)	Relative retention (to phenoli ether)	
t-Butylthio		1.4744	99	1.61	0.67	
<i>n</i> -Butylthio		1.4676	98	1.85	0.77	
Phenyl	75–76		96	2.40	1.00	
2-Tolyl	78–79		88	2.72	1.13	
4-Tolyl	7475		85	2.91	1.21	
2,4 Xylyl	50-52		94	3.27	1.36	
2-Chlorophenyl	91–93		99	3.74	1.56	
4-Chlorophenyl	66–67		94	4.11	1.72	
2,4-Dichlorophenyl	73-74		86	5.91	2.46	
n-Decylthio		1.4662	86	7.36	3.06	
n-Undecylthio		1.4665	100	9.68	4.03	
Naphthyl-2	132133		84	10.46	4.35	
n-Dodecylthio		1.4668	96	12.91	5.37	
2-Nitro, 4-chloro-						
phenyl	99–99.5		92	16.26	6.76	

Table I Droportion of Ethern and Thiosthese

exhibit electron capture response seemed desirable for their measurement. The trifluoroacetate (7) of phenol, though sensitive to the electron capture detector, is detectable only at about one microgram. In addition, the trifluoroacetate derivative is limited for use because it hydrolyzes in the presence of water. Hexafluorobenzene (8) has been shown to give a high response to the electron capture detector.

Ethers and thioethers, derived from phenols and mercaptans, respectively, with α -bromo-2,3,4,5,6-pentafluorotoluene, exhibit excellent electron capture response. This property accounts for excellent measurements in the presence of impurities. Only phenols, mercaptans, and acids will react rapidly with the fluoro-organic reagent under the described conditions. Derivatives of phenols and mercaptans are stable in water and are amenable to gas-liquid chromatographic separations.

EXPERIMENTAL

Reagent. Alpha-bromo-2,3,4,5,6-pentafluorotoluene was purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis.; purissium grade was used. This chemical is a lachrymator.

Apparatus. A Perkin-Elmer gas chromatograph, Model 811, with tritium foil electron capture detector of parallel plate design was used. An 8-foot by 0.25-inch aluminum column containing 50-50% mixture of 5% F.S. 1265 and 3% D.C. 200 supported on Chromosorb P of 60-80 mesh size was employed at 200° C. Nitrogen flow was 40 ml per minute. The sensitivity was set at an attenuation of X-50 and X-100, while the power supply was operated on DC 10 volts.

Preparation of Ethers and Thioethers. Phenols and mercaptans were converted to their respective derivatives in the

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Table II.	Analytical Results of Gas-Chromatographic
Sepa	ration of Pentafluorobenzyl Aryl Ethers

(In or	der of	emergence)
afluorobenzyl			

Pentafluorobenzyl aryl ether	% Found	% Added
Phenyl	39.2	37.5
2,4-Xylyl	32.9	30.8
3-Chlorophenyl	31.7	31.7

Table III. Comparative Responses of Phenolic and Thiophenolic Derivatives with Aldrin

Compound	Injection	Response (sq in)
Phenyl pentafluoro- benzylthioether Phenyl trifluoro-	1 nanogram	0.68
acetate Phonyl nontafluoro	1 microgram	0.71
benzyl ether Aldrin	1 nanogram 1 nanogram	0.78 1.09

manner described by Claisen (9). The phenol dissolved in 20 times the weight of acetone is heated with the alkylhalide in the presence of potassium carbonate. Yields varied from 84 to 100%. Table I records the melting points, refractive indices, yields, and retention times of the novel derivatives.

The micro preparation for recovery study of the derivatives was conducted as follows: a mixture of 0.8 mg each of phenol, 2,4-xylenol and 3-chlorophenol was reacted as before, except that 5-fold excess of the fluoro-organic and 20-fold excess of alkaline reagent were used. Solvents were removed carefully and the residue was extracted with 100 ml of ether. This ether extract was washed with 10 ml of water and was dried over sodium sulfate. After the ether was removed, the residue was diluted 1:10,000. From this dilution, $3-\mu l$ injections were introduced for the GLC analyses.

RESULTS AND DISCUSSION

Separation of ethers and thioethers. A mixture of 14 pentafluorobenzyl derivatives as ether and thioether was resolved into 14 components as shown in Figure 1. The concentration for the third through eleventh and the sixteenth compounds was 0.40 nanogram per 5 μ l of injection.

For reasons of convenience, operation at 200° C has received particular attention. However, the operation at 165° C will resolve more completely the derivatives of *o*-cresol and *p*-cresol, but the analysis is time consuming. Gas chromatograms, obtained under either condition, indicate that these compounds exhibit very little tailing.

A synthetic mixture of three phenols was chosen to represent the weak acid fraction of the carbon absorption extract. Its GLC analysis is illustrated in Table II.

These quantitative recovery data are the result of $3-\mu l$ injections, which contained 0.6 nanogram each of phenyl, xylyl, and 3-chlorophenyl ethers. Thus, the procedures for reaction, extraction, concentration, and analyses of the ether derivatives are adaptable on the submicro scale.

To illustrate the high electron capture response of these de-



Figure 1. Separation of various phenols and mercaptans as their pentafluorobenzyl ethers and thioethers, respectively

Equal quantities by weight were used for the 3rd through 11th and the 16th compounds. The 13th through 15th contain twice the quantity while the 12th contains three times the quantity

- 1. Solvent
- 2. Alpha-bromo-2,3,4,5,6-pentafluorotoluene
- 3. 2-Methyl-2-propanethiol
- 4. Butanethiol-1
- 5. Phenol
- 6. o-Cresol
- 7. p-Cresol
- 8. 2,4-Xylenol
- 9. o-Chlorophenol
- *p*-Chlorophenol
 2,4-Dichlorophenol
- 12. *n*-Decanethiol-1
- 13. *n*-Undecanethiol-1
- 14. Beta-naphthol
- 15. *n*-Dodecanethiol-1
- 16. 4-Chloro-2-nitrophenol

rivatives, these responses are compared with those of aldrin and phenyl trifluoroacetate in Table III.

Aldrin was selected as the standard for comparison, because it is analyzed frequently as a pesticide occurring in water, and it responds favorably to the electron capture detector. Because phenyl trifluoroacetate (7) was suggested for use, its effectiveness as an analytical derivative was compared. At the identical trace concentration, phenyl pentafluorobenzyl thioether and phenyl pentafluorobenzyl ether produce 2/3 and 3/4, respectively, of the response produced by aldrin. To obtain the same magnitude of signal, phenyl trifluoroacetate must be present at a concentration 1000 times that of the novel derivatives.

These new derivatives provide the following advantages: excellent stability in aqueous solution, excellent response to electron capture detector and specificity in presence of impurities, suitability to gas chromatographic separations, and analyses at trace concentrations of phenols and mercaptans.

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