Evaluation of Nielsen-Kryger Steam Distillation Technique for Recovery of Phenols from Soil

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The Nielsen-Kryger steam distillation technique has been evaluated for recovery of phenols from soil. Soils are acidified to pH <1 and steam-distilled, and chlorinated phenols are extracted with toluene-methylene chloride (95 + 5). Mean recoveries from 4 samples spiked at 1 μg/50 g clay soil ranged from 67 to 78%. The method has limited utility for the recovery of other substituted phenols on the Environmental Protection Agency priority pollutant list.

Chlorinated phenols are extensively used as herbicides, insecticides, fungicides, antiseptics, and disinfectants. The annual production of pentachlorophenol (PCP) in the United States alone has been reported to exceed 40 000 tons (1). About 90–95% of this amount is used as a wood preservative. 2-Chlorophenol is used mainly for further chlorination to 2,4-dichlorophenol, 2,4,6-trichlorophenol (TCP), and PCP. 2,4,6-TCP is used as a fungicide and bactericide. 2,4-Dichlorophenol and 2,4,5-TCP are used as starting materials for the manufacture of pesticides, including 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), or herbicides, including 2(2,4,5-trichlorophenoxy)propionic acid (silvex).

The extensive use of chlorinated phenols is a potential source of serious environmental contamination. PCP is toxic, not only to wood-destroying organisms, but also to humans and other animals (2,3). 2,4,5-TCP is a precursor of the extremely toxic 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin.

The primary sources of PCP in soil are through its application as a herbicide and leaching from preservative-treated wood. 2,4,5-TCP appears in the soil through the degradation of 2,4,5-T or silvex. Similarly, 2,4-D degrades to 2,4-dichlorophenol. Washout from the atmosphere also contributes to soil contamination by chlorophenols.

Several analytical methods for isolating chlorinated phenols from water, soil, and biological tissues have been reported (4–7). The most common techniques for soil samples have involved 3 steps: extraction with sodium or potassium hydroxide, acidification of the extract, and further extraction from the acidic solution with an organic solvent (4). However, acidification of the basic extract to pH <6 sometimes produces a gel, which makes extraction with an organic solvent very difficult. Treatment of the extract with an ion-exchange resin eliminates some of these difficulties (8), and Soxhlet extraction, shaking with an organic solvent, or sonication (9), gives good recoveries. But these procedures also extract lipids, pigments, waxes, and other high molecular weight organics. Extensive column chromatographic cleanup of the extract is often necessary for trace analysis.

A steam distillation procedure for separation of organics, based on their vapor pressures and water solubilities, could provide a simple, convenient way to isolate chlorinated or other substituted phenols from soil samples (10). Recently, Kan et al. (11) reported the use of a modified Nielsen-Kryger steam distillation apparatus (10) to recover 2,4-dichlorophenol, a degradation product of 2,4-D butoxyethanol ester, from soil. There seems to have been no effort to apply this technique for the recovery of phenols in general from soil.

In our laboratory, the Nielsen-Kryger apparatus has been used extensively since 1978 to recover a large number of organic contaminants from soil. To date, more than 3000 soil samples have been analyzed by this method.

In the present study, we have also evaluated the Nielsen-Kryger steam distillation technique for determination of the Environmental Protection Agency (EPA) priority pollutants in soil. The procedure is obviously not efficient for analysis of compounds with significant water solubility. Such compounds exhibit poor volatility with steam. In addition, the continuous passage of warm water through the extracting solvent tends to scavenge water-soluble compounds back into the aqueous phase and thus back into the boiling flask. In the present work, this effect has been minimized by optimizing the extracting solvent.

Experimental

Apparatus

(a) *Gas chromatograph.*—Varian 3700 gas

Received December 30, 1982. Accepted March 15, 1983.

chromatograph, equipped with linearized ^{63}Ni electron capture and flame ionization detectors, and Varian 8000 Autosampler were used with Spectra Physics SP 4100 data system. Columns were fused silica SE 54, 30 m × 0.25 mm id, film thickness 0.25 μm (J. W. Scientific, Rancho Cardova, CA); and 1% SP 1240DA on 100–200 mesh Supelcoport, packed in a 1.8 m × 2 mm id glass column. Column temperatures: for chlorophenols, 100–200°C, initial hold 12 min, 8°/min to 200°C; for substituted phenols, 50–160°C, initial hold 2 min, 8°/min to 160°C. Injector temperature 200°C; detector temperature 320°C; nitrogen carrier gas. Flow rates: capillary column 2 mL/min; capillary make-up 30 mL/min; packed column 30 mL/min. Chart speed 1 cm/min.

(b) *Steam distillation apparatus.*—The modified design of Veith and Kiwus (10) (Ace Glass, Vineland, NJ) was used.

(c) *Shaker.*—Burrell wrist-action (Burrell Corp., Pittsburgh, PA).

Reagents

(a) *Solvents.*—All solvents were pesticide grade (MC & B, Norwood, OH).

(b) *Chemical standards.*—Analytical standards were purchased from Aldrich Chemical Co., Milwaukee, WI. Stock standards were prepared in acetone and working standards in hexane.

Soil Samples

(a) *Clay soil.*—A number of clay soil samples were collected from the Niagara Falls, NY area. These were homogenized together and stored at 4°C in glass jars. The mixture had a moisture content of about 25%. A blank run showed none of the phenols under investigation.

(b) *Potting soil.*—Potting soil (Hyper-Humus Co., Newton, NJ) was purchased locally.

Procedure

(a) *Spiking of standards.*—A 50 g portion of homogenized clay or potting soil was placed in a 2 L round-bottom flask and cooled in an ice bath. An appropriate phenol mixed standard (1 mL) was then added dropwise with shaking to the soil sample. To distribute the spiked standard uniformly, the flask was stoppered and swirled for another 2–3 min. It was then allowed to stand overnight in a refrigerator.

(b) *Extraction.*—Distilled water (500 mL) was added to the flask, followed by 40 mL sulfuric acid-water (1 + 1). A magnetic stirrer bar was introduced into the flask, and a Nielsen-Kryger distillation column was attached to it. The mixture was stirred at ambient temperature for 30 min, after which 10 mL toluene–methylene chloride (95 + 5) was introduced into the condenser. The flask was refluxed gently for 2 h and cooled, and the small amount of water trapped in the distillation column was drained. The organic layer was then passed through a small amount of washed anhydrous sodium sulfate into a 15 mL centrifuge tube. The walls of the column and the sodium sulfate were rinsed with a small amount of hexane. The combined organic layer was concentrated to ca 5 mL under a gentle stream of dry nitrogen. Most of the toluene was displaced with hexane. To remove the sulfurous material the concentrate was shaken with 2–3 drops of metallic mercury for 30 min.

(c) *Chromatography.*—The extract containing chlorophenols was analyzed on fused silica SE 54 and 1% SP 1240DA columns with an electron capture detector. The extract of other substituted phenols was analyzed on the 1% SP 1240DA column with a flame ionization detector. The peak areas were measured with Spectra Physics SP 4100 data system.

Results and Discussion

Initially, the recovery experiments were carried out by spiking the potting soil, which is rich in organic material, with 2,4,5-TCP. The mean recovery from 1 μg/50 g soil was 62 ± 8% (n = 4). Subsequently, detailed recovery experiments were carried out on a clay soil homogenate. Mean recoveries from soil spiked with various concentrations of chlorinated phenols are shown in Table 1. 3,4,5-TCP was recovered only in trace amounts.

The organic solvent and pH of the slurry were critical factors affecting recovery. Due to the polar nature of chlorophenols and because only a small amount of solvent (about 15 mL) is used, it is essential that the phenols be highly soluble in the extracting solvents. The technique also requires that the solvent mixture be water-immiscible, be lighter than water, and, to prevent solvent loss, have a high boiling point. Toluene–methylene chloride (95 + 5) proved to be the most suitable solvent. Satisfactory results were obtained only when the medium was acidified to pH <1 with sulfuric acid–water (1 + 1). This requirement can be attributed to the fact that phenols are acidic in nature and that at higher pH they are not freed from the soil matrix to be volatile in steam.

Our attempts to isolate phenols on the EPA Priority Pollutant list (Table 2) by this technique

Table 1. Recovery (%) of chlorinated phenols from 50 g soil [a]

Chlorophenol	Added, μg		
	10	1	0.1
	Clay Soil		
PCP	71 ± 3	70 ± 5	58 ± 5
2,3,4-TCP	87 ± 8	78 ± 6	60 ± 4
2,3,5-TCP	87 ± 4	70 ± 5	44 ± 4
2,3,6,TCP	83 ± 2	75 ± 2	77 ± 5
2,4,5-TCP	75 ± 4	67 ± 5	66 ± 5
2,4,6-TCP	88 ± 5	70 ± 6	66 ± 3
3,4,5-TCP	5	ND[b]	ND
	Potting Soil		
2,4,5-TCP	81 ± 2	62 ± 8	51 ± 3

[a] Mean ± SD (n = 4).
[b] ND = not detected.

Table 2. Recovery (%) of substituted phenols from clay soil containing 100 μg/50 g of each phenol [a]

Phenol	Nielsen–Kryger procedure	Exhaustive distillation procedure
Phenol	44 ± 8	56 ± 7
2,4-Dimethylphenol	42 ± 1	99 ± 2
4-Chlorocresol	35 ± 3	96 ± 3
2-Chlorophenol	59 ± 4	97 ± 2
2,4-Dichlorophenol	64 ± 4	92 ± 2
2,4,6-TCP	70 ± 2	98 ± 1
2-Nitrophenol	69 ± 4	91 ± 2
4-Nitrophenol	ND[b]	4 ± 1
2,4-Dinitrophenol	40 ± 5	24 ± 3
4,6-Dinitrophenol	25 ± 7	43 ± 7
PCP	77 ± 4	95 ± 1

[a] Mean ± SD (n = 4).
[b] ND = not detected.

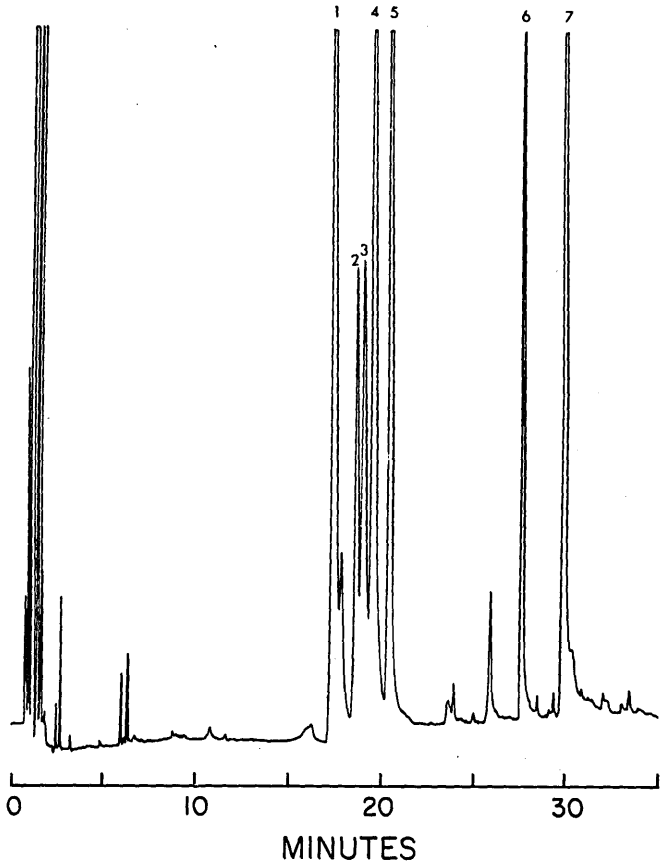

Figure 1. Gas chromatogram of chlorinated phenols on fused silica SE 54 column with electron capture detection. Peak identities: (1) 2,3,5-TCP; (2) 2,4,6-TCP; (3) 2,4,5-TCP; (4) 2,3,4-TCP; (5) 2,3,6-TCP; (6) 3,4,5-TCP; (7) PCP.

had mixed results. 2-Chloro- and 2,4-dichlorophenols, as expected, were isolated in satisfactory yield; but of 4 nitrophenols, only 2-nitrophenol was isolated in moderate yield. Recoveries of 2,4- and 4,6-dinitrophenol were low, and 4-nitrophenol could not be recovered. This is a classic case of intramolecular vs intermolecular hydrogen bonding (12). 2-Nitrophenol, which forms intramolecular hydrogen bonds, has a lower boiling point and is less soluble in water; it is therefore steam-volatile and could be isolated in satisfactory yield. 4-Nitrophenol, with its intermolecular hydrogen bonds, has a very high boiling point and greater solubility in water; these characteristics inhibit its steam distillation. Perhaps the same holds true for 3,4,5-TCP which could not be recovered satisfactorily.

Recoveries of phenol (which is steam-volatile), 2,4-dimethylphenol, and 4-chlorocresol were also very low. As mentioned earlier, this could be due to the inefficiency of the extracting solvent. To assess this, a 50 g sample spiked with substituted phenols was placed in a 3-neck round-bottom flask and, after treatment in a similar manner as described before, was steam-distilled. No organic solvent was placed in the distillation column. The distillate was collected via a short glass tube into a 125 mL filtration flask containing 30 mL methylene chloride and was stirred with a magnetic stirrer. The excess water was allowed to return continuously to the distillation flask via short glass tubing. At the end of 2 h, the organic layer was separated, dried over anhydrous sodium sulfate, and concentrated in a Kuderna–Danish apparatus. The methylene chloride was carefully displaced with hexane, and the extract was analyzed on the 1240DA column with a flame ionization detector. The results are shown in Table 2. The recoveries of these phenols by the exhaustive distillation procedure are much higher than those obtained by the Nielsen-Kryger technique. This clearly

shows that the efficiency of the extracting solvent is a major factor affecting recoveries of these phenols from soil.

The Nielsen-Kryger steam distillation procedure appears to offer a simple, convenient method for isolation of chlorinated phenols from soil. Recoveries compare favorably with those by Soxhlet extraction, shaking with organic solvent, or sonication. The method requires only a small amount of solvent for extraction, thus eliminating losses due to volatilization, which are uncontrollable with a rotary evaporator or a Kuderna-Danish concentrator. It also eliminates the extensive cleanup step to remove numerous undesirable artifacts which other extraction techniques leave in the raw extract. The only impurity that interferes with the analysis is sulfurous material which is co-distilled during steam distillation. This impurity can be conveniently removed by shaking with a few drops of metallic mercury (13).

One advantage of using a fused silica or 1240DA column for analysis is that derivatization of the phenols is unnecessary (Figure 1).

The method has more limited utility for recovery of other substituted phenols which are highly soluble in water. However, in view of recent reports suggesting that similar techniques permit the efficient recovery of a variety of nonphenolic organic compounds, the method described here may find application as a rapid screening technique for a variety of contaminants in soil.

Acknowledgments

The authors are greatly indebted to A. Richards and R. Pause for their valuable advice during the course of this work.

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