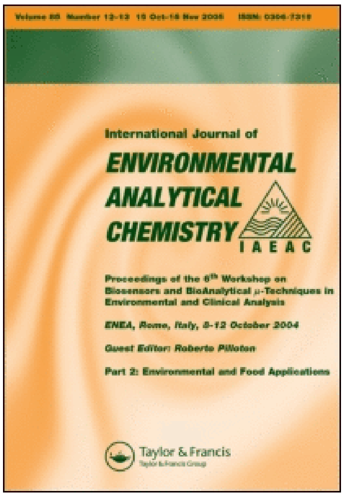

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H. Kanai[a]; R. Goo[b]; V. Inouye[c]; L. Yazawa[a]; C. Chun[d]
[a] Hawaii State Dept. of Agriculture, Measurement Standards Division, Honolulu, Hawaii [b] Dept. of Public Works, Toxics Laboratory, Honolulu, Hawaii [c] Environmental Chemistry Laboratory, Hawaiian Electric Co, Honolulu, Hawaii [d] Crime Laboratory, Honolulu Police Dept., Honolulu, Hawaii

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RECOVERY STUDIES ON DICHLOROMETHANE/AQUEOUS PARTITIONING OF PHENOL AND SOME OF ITS ALKYL DERIVATIVES

H. KANAI[1], R. GOO[2], V. INOUYE[3], L. YAZAWA[1] and C. CHUN[4]

[1]*Measurement Standards Division, Hawaii State Dept. of Agriculture, Honolulu, Hawaii 96813.* [2]*Toxics Laboratory, Dept. of Public Works, City and County of Honolulu, Honolulu, Hawaii 96913.* [3]*Environmental Chemistry Laboratory, Hawaiian Electric Co, Honolulu, Hawaii 96913.* [4]*Crime Laboratory, Honolulu Police Dept., City and County of Honolulu, Honolulu, Hawaii 96817*

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The recoveries of phenol and some of its alkyl derivatives in the preconcentration/cleanup of environmental samples using the dichloromethane/aqueous partitioning technique is known to be poor. Studying the recovery data of phenols which were spiked at different steps of partitioning/solvent evaporation procedure, it was found that the poor recoveries are mainly due to inefficient extraction of phenols into dichloromethane rather than to loss by evaporation or irreversible sorption.

KEY WORDS: Phenols, solvent extraction, water.

INTRODUCTION

There are many applications of phenols in industry. One example is the use of both hindered and unhindered alkylphenols as gasoline additives[1,2] and the analyses of these compounds as an aid in gasoline identification have been described[3,4]. The solid-phase preconcentration methods[5] employing the Octadecyl (C_{18}), Octyl (C_8), or Amberlite XAD extraction columns yield greater than 90 % recoveries of phenols in relatively clean aqueous samples. However, when concentrating phenols using dichloromethane/aqueous partitioning method, recovery is rather poor. According to Standard Methods[6], the percent recoveries of phenol and 2,4-dimethylphenol are 43 % and 62 %, respectively. Yet, the dichloromethane extraction[6,7] is also used because among its advantages phenols and other pollutants in complex aqueous matrix can be preconcentrated in single extraction.

The poor recoveries of phenol and some of its alkyl derivatives in this procedure may

Table 1 Boiling points, melting points, solubilities, pKa.

compound	*bp (°C)*	*mp (°C)*	*pKa (25°C)*	*sol (g/100g, 25°C)*
1) phenol	182	79	9.99	9.3
2) 2-methylphenol	203	79	10.28	2.5
3) 4-ethylphenol	195-197	78	10.00	sl
4) 2,6-dimethylphenol	203	73	10.50	sl
5) 2,5-dimethylphenol	212	—	10.21	sl
6) 3,4-dimethylphenol	227	—	10.32	sl
7) 4-propylphenol	231-232	106	—	sl
8) 2,3,6-trimethylphenol	230-231	—	—	sl
9) 2-nitrophenol	217	—	7.23	.2
10) 4-nitrophenol	279	—	7.15	1.7
11) cyclohexanol	161	67	18	3.6
12) dichloromethane	39.8-40	—	—	—

bp=boiling point, mp=melting point, sol=solubility in water, and sl=slightly. The solubilities of compounds 1,2,9,10, and 11 were from references (12, 13), respectively, and the remaining ones were from reference (16). The bp and mp values were from reference(160. The pKa values were from reference (17). Previous studies in this laboratory show that the solubility of phenols listed in this study is much greater in dichloromethane than in water.

be due to either inefficient partitioning of the analytes into this organic solvent, loss occuring during solvent evaporation, or irreversible sorption on drying agent or active sites in the glassware. To our knowledge there has not been a detailed study on this subject.

The partitioning efficiency of phenols between dichloromethane and water is determined by the relative strengths of their respective solute-solvent intermolecular forces, such as hydrogen bonding and van der Waals forces. The formation of hydrogen bond between phenol and water is widely known[8,9]. While the hydrogen bonding nature of chloroform was well documented by Pimental and McClennan[10], evidence for this type of bonding has not been found for dichloromethane according to Kagarise[11] who had studied the the C-H stretching bands of this solvent. As listed in Table 1, the boiling points of phenols and dichloromethane are around 200° C and 40° C, respectively. However, according to the kinetic theory of gases certain fraction of phenolic molecules may acquire enough energy to escape into the atmosphere below their boiling points. This agrees with our observation that whenever bottle of phenols are opened at approximately standard temperature and pressure their odor are noticeable. The possibility of phenols adsorbing on the anhydrous sodium sulfate drying agent or onto active sites in the glassware during sample preparation should also be studied.

To learn more about the dichloromethane/aqueous partitioning of phenols and losses during solvent evaporation, the recovery data of phenol and some of its alkyl derivatives which were spiked at different steps of this extraction/solvent evaporation procedure were studied. The recoveries of ortho-and para-nitrophenols were also studied to find out the effect of intra- and inter-molecular hydrogen bonding on the partitioning efficiency. The loss due to sorption was studied by comparing the recoveries of phenols passed through the drying agent and the glasswool. Study on irreversible adsorption of the analytes onto the glassware was not attempted.

EXPERIMENTAL

Apparatus and reagents

A Hewlett-Packard (HP), model 5890 gas chromatograph (GC), equipped with flame ionization detector was controlled by HP model 300/9133 data station. A HP-1 (30 m × 0.53 mm × 2.5 um) megabore column coated with crossed linked methyl-silicone was used. 500 mL Kuderna-Danish (K-D) concentrator flasks, 3-ball macro and micro Synder columns, and 10 mL K-D tubes (Kontes) were used. Volume calibration on 10 mL K-D tubes was checked with distilled water. Reagent grade chemicals were used. Standard chemicals were purchased from Aldrich.

Dichloromethane extraction of phenols from water[6,7]

One milliter of standard spiking solution consisting of 23.0, 21.4, 21.8, 23.6, 23.8, 22.6, 23.3, 22.8, 21.4, 22.9 ppm standard solution of phenol, 2-methylphenol, 4-ethylphenol, 2-nitrophenol, 2,6-dimethylphenol, 4-propylphenol, 2,5-dimethylphenol, 3,4-dimethylphenol 3,4-dimenthylphenol, 2,3,6-trimethylphenol and 4-nitrophenol in methanol was added into a 2-L separatory funnel containing 1 L of pH 1 distilled water whose acidity had been adjusted with concentrated phosphoric acid. 60 mL of dichloromethane was added and shaken for 30 sec. The extract was collected in a 250 mL Erlenmeyer flask. This was repeated three times. The combined solution was passed through 22 mm × 250 mm chromatographic column containing 10 g anhydrous sodium sulfate and was collected in K-D apparatus consisting of 10 mL tube and 500 mL concentrator flask. After adding boiling chips, a 3-ball macro Synder column was attached and the solvent was evaporated on a 65° C water bath. When apparent volume of the liquid had reached about 3 mL, the K-D apparatus was removed from the water bath and cooled for about 15 min. A 3-ball macro Synder column was replaced by a 2-ball micro Synder column after rinsing the concentrator flask with about 2 mL of dichloromethane and the solvent was evaporated approximagely to .5 mL. After cooling, the sample was diluted to 1 mL with methanol before GC analysis.

Spiking at 3-ball and 2-ball macro and micro Synder column

One mL standard solution was spiked into K-D apparatus containing 180 mL of dichoromethane and evaporated as stated above. Another 1 mL of the same standard solution was spiked into a 10 mL K-D tube which contained 3 mL of dichloromethane. After attaching 2-ball micro Synder column, the solvent was similarly evaporated as before.

Spiking at 10 mL K-D tubes

One mL of standard solution was transferred into two sets of 10 mL K-D tubes each containing 3 mL dichloromethane. A stream of nitrogen was passed over one set of K-D tubes at room temperature and another set of K-D tubes in 35° C bath.

Sorption loss on sodium sulfate

180 mL dichloromethane extract containing standard phenols identical to the partitioning procedure was passed through drying column with glasswool, minus the 10 grams of anhydrous sodium sulfate and was evaporated in K-D apparatus.

GC analysis

Inlet and detector temperatures were set at 250° C and 270° C respectively. The oven was initially set at 35° C for 2 min. and temperature programmed at the rate of 15° C/min to the final temperature of 240° C. The flow rate of nitrogen carrier gas was about 1.6 mL/min. One uL of each sample was injected into the GC.

RESULTS AND DISCUSSION

Table 2 Percent recoveries of phenols spiked at different steps of sample preparation.

		evaporation (%)			*solvent extraction (%)*	
compound	3B	2B	Rm	35	S	U
1) phenol	90	100	100	90	48	47
2) 2-methylphenol	92	100	100	91	76	77
3) 4-ethylphenol	90	100	100	93	77	76
4) 2,6-dimethylphenol	92	100	100	94	77	76
5) 2,5-dimethylphenol	93	100	100	94	77	78
6) 3,4-dimethylphenol	92	100	100	96	78	78
7) 4-propylphenol	92	100	100	96	79	80
8) 2,3,6-trimethyl-l phenol	89	100	100	90	74	72
9) 2-nitrophenol	92	100	100	91	98	99
10) 4-nitrophenol	92	100	100	90	43	40

Percent recoveries of phenols (1) through (10) for "S" and "U" are averages of four and two determinations, respectively. "S" and "U" refer to drying column with sodium sulfate and without (glasswool only), respectively. 3B and 2B and 2-ball micro Synder column apparatus, respectively for solvent evaporation. Rm and 35 refer to recoveries of phenols which were spiked into 10 mL K-D tubes of which one set was at room temperature and another set was immersed in 35° C water bath and solvent was evaporated by passing a stream of nitrogen.

Recovery

According to column 3B in Table 2, the volatilization loss was about 10 % for the ten phenols studied because there was no loss in the final evaporative step using the 2-ball micro Synder column. The solvent extraction data should equal the net recovery for this method and this value plus about 10 % of the evaporative loss should equal the amount of phenols which were partitioned into dichloromethane from water because there was no loss through irreversible sorption of the analytes on the sodium sulfate drying column as recovery data on the columns "S" and "U" on Table 2 show. The solubility of phenols in dichloromethane is much greater than in water (Table 1). Yet, if loss due to evaporation is corrected for the solvent extraction data, then only 58 % and 53 % of phenol and para-nitrophenol, respectively were partitioned into dichloromethane from the aqueous phase. Except for ortho-nitrophenol which is 98 %, the rest of alkylphenols were partitioned into dichloromethane at about 85 % to 90 % efficiency when evaporative loss is taken into account.

Role of hydrogen bonding

Compared to cyclohexanol the hydroxyl group of phenol is highly polarized which results in stronger hydrogen bonding with water, and also higher boiling and melting points than similar alcohols (Table 1).[12,13] According to Dearden and Forbes[14] and Ito[15], a solute-solute intermolecular hydrogen bonding occurs only at solute concentration greater than 0.01 mole/Liter, and below this only solute-solvent intermolecular hydrogen bonding seems to be formed for phenols. Among the phenols studied, para-nitrophenol has the highest acidity in aqueous media and along with phenol should form a strong hydrogen bond with water. However, solubility in water is not determined by pKa values alone as indicated by the greater solubility of phenol and even cyclohexanol over para-nitrophenol (Table 1). Since phenol molecules have polar and non-polar parts, the water solubility depends on the balance between these portions. As the non-hydroxyl portion of phenolic molecule increases in size, the van der Waals forces between molecules also increase in magnitude and thus the effectiveness of hydrogen bonding decreases[18]. When either phenol or para-nitrophenol is partitioned between dichloromethane and water, the attraction between these two solutes and dichloromethane is probably through van der Waals forces. However, besides the van der Waals forces, both solutes form strong intermolecular hydrogen bond with water. This may explain the incomplete partitioning of many phenols into dichloromethane because according to Reichardt[19], the bond dissociation enthalpies for normal hydrogen bonds and covalent bonds are about 3 to 10 kcal/mol and about 50 to 100 kcal/mol, respectively. Thus hydrogen bonds are approximately ten times weaker than covalent bonds, but about ten times stronger than the van der Waals forces. The near complete partitioning of ortho-nitrophenol into dichoromethane from aqueous phase can be attributed to the formation of intramolecular hydrogen bond between the hydroxyl and the nitro groups so that no intermolecular hydrogen bonding occurs with water. The molecules with intramolecular hydrogen bonding have properties that are about equal to those of non-bonded molecules similar in size.[18]

Compared to phenol and para-nitrophenol, the improved partitioning of alkylphenols into dichloromethane may be due to electronic and steric factors which hinders the formation of strong intermolecular hydrogen bonds with water. The electron releasing effect of alkyl groups lowers the acidity of these compounds relative to phenol which should decrease the strength of the hydrogen bond (Table 1). The substitution at the ortho position of phenol is known to sterically hinder formation of strong hydrogen bonds.[20] These ortho alkylphenols are only slightly soluble in water and very soluble in dichloromethane. However, when partitioned between these solvents, about 10 % to 15 % of these solutes remain in water which shows the powerful role of hydrogen bonding in dichloromethane/aqueous partitioning. It should be pointed that this study considered only one level of analyte (20 ppb) and one pH level (pH 1). Also it did not address the possibility of losses of phenol from irreversible adsorption onto the glassware.

Evaporative loss

The net evaporative loss during this procedure for phenols is about 10 %. As listed in Table 2, phenols were not lost in the final evaporative step of this procedure either through the 2-ball micro Synder column apparatus of the method of blowing down the solvent with a stream of nitrogen at room temperature. However, when the bath temperature had been changed to 35° C, about 5 % to 10 % of phenols in 10 mL K-D tubes were lost during solvent evaporation.

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