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Concentration of Organic Pollutants in Water by Evaporation at Reduced Pressure

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Synopsis. The relative volatilities α of various organic compounds were obtained as a parameter to determine the recovery for the concentration at reduced pressure and room temperature. The evaporation technique is an efficient method for concentrating large molecular weight compounds and ionizing compounds, if ionization is promoted by adjusting the pH of water.

While the research on water pollution and water treatment was conducting, it was sometimes necessary to determine organic pollutants of sub-ppm levels. The authors[1-4] studied various chromatographic methods such as steam carrier gas chromatography (SCGC), gel chromatography (Gel C), and high performance liquid chromatography (HPLC) for direct analyses of organic pollutants in water. However, development of a feasible concentration method is neccesary for these analytical techniques, since direct injection into SCGC, Gel C, or HPLC and analyses by other methods provide only a limited success at ppm levels. In the analysis of drinking water, Cathorne *et al.*[5] used the evaporation technique with a rotary evaporator and the extraction by methanol. These methods are applicable to only small sample sizes and no experiments has been done to ascertain the recovery efficiency. Loy[6] and Kuo *et al.*[7] used the distillation technique to concentrate volatile organics in the distillate. These methods required elevated temperatures, and are considered to be unsuitable for organic compounds that hydrolyse or decompose at elevated temperatures. Cathorne *et al.*[5] obtained large sample sizes by using a freeze-dryer. However, there has been no report on its efficiency for various organic compounds. The purpose of this study is to investigate the recovery efficiency of concentration method at room temperature using the freeze-dryer as a simple and efficient apparatus for concentrating organic pollutants in water for subsequent analytical techniques.

Experimental

The aqueous solutions ranging from 2 to 20 mg/L of organic compounds shown in Table 1 were used in this study. The sample number for each compound as shown in the table is used in Figs. 2 and 3.

The apparatus used in this study consisted of a Yamato freeze-dryer model D-35. It was connected to a vacuum pump, with evacuation rate of 300 L/min, as shown in Fig. 1. The inner container of the freeze-dryer was cooled by a Neslob Cooler to a temperature of −35 to −45 °C. Kjeldahl flasks were filled with 50 mL (V_0) of the sample solutions whose initial concentrations were C_0, cooled in another freezer to form a layer of ice, and then attached to the trap by means of flask joints. The cooling of the samples before evaporation prevented a loss of liquid due to scattering at a sudden decrease in pressure. If the temperature was not controlled during the evaporation, the liquid would freeze, and the concentration process would become time-consuming. Therefore, during the evaporation process, the flasks were partially immersed in a water bath maintained at a temperature of 35 °C so that the solutions in the flasks were kept at a temperature of about

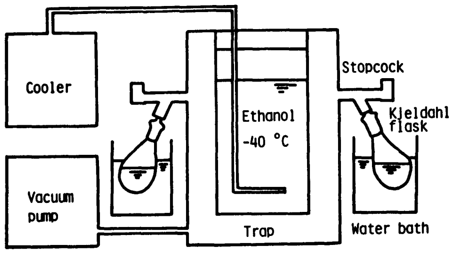

Fig. 1. Apparatus for concentrating organic pollutants by evaporation.

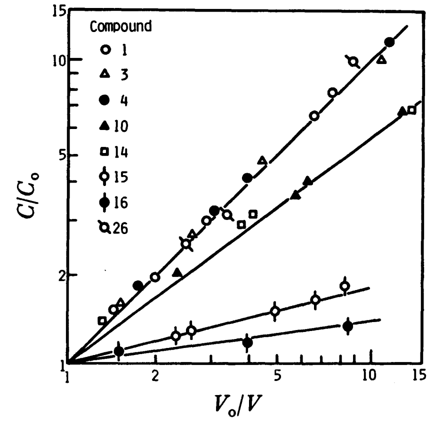

Fig. 2. Relationship between log V_0/V and log C/C_0 of solutions of organic compounds.

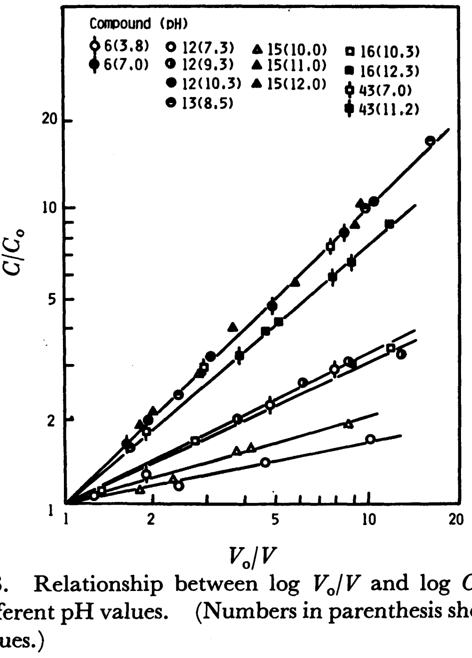

Fig. 3. Relationship between log V_0/V and log C/C_0 at different pH values. (Numbers in parenthesis show pH values.)

TABLE 1. EXPERIMENTAL VALUES OF RELATIVE VOLATILITY α OF ORGANIC COMPOUNDS TESTED

Compound No.	Name	α	$\frac{P_{org}}{P_{H_2O}}$	Compound No.	Name	α	$\frac{P_{org}}{P_{H_2O}}$
1	Sodium benzenesulfonate	0.0	0.0	27	Methyl acetate	5.0	9.1
2	Sodium			28	Ethyl propionate	1.4	1.6
	p-methylbenzenesulfonate	0.0	0.0	29	Ethyl butyrate	0.9	0.7
3	Sodium 1-butanesulfonate	0.0	0.0	30	Butyl acetate	2.1	—
4	1-Nonanesulfonic acid	0.0	0.0	31	Acetaldehyde	3.1	42.8
5	Sodium			32	Propionaldehyde	0.5	14.7
	p-ethylbenzenesulfonate	0.0	0.0	33	Isobutyraldehyde	1.0	—
6	*m*-Chlorobenzoic acid	0.2	—	34	Butyraldehyde	0.6	5.1
7	Benzoic acid	0.2	0.0	35	Hexanal	0.8	—
8	*p*-Hydroxybenzoic acid	0.0	—	36	Benzaldehyde	1.6	0.0
9	*m*-Hydroxybenzoic acid	0.0	0.0	37	Isobutyl methyl ketone	1.2	—
10	*m*-Toluic acid	0.3	—	38	Diethyl ketone	1.7	1.5
11	*m*-Nitrobenzoic acid	0.1	—	39	Acetone	1.4	10.8
12	*o*-Nitrophenol	1.3	0.0	40	Methylamine	1.0	127.7
13	*o*-Chlorophenol	1.6	0.1	41	Ethylamine	0.5	49.8
14	Resorcinol	0.3	0.0	42	Propylamine	0.6	13.7
15	Phenol	0.8	0.0	43	Butylamine	0.3	—
16	*o*-Cresol	0.9	0.0	44	Aniline	1.3	0.0
17	Formic acid	0.7	1.9	45	*p*-Nitroaniline	1.6	0.0
18	Acetic acid	0.7	0.7	46	1,6-Hexanediamine	0.0	—
19	Butyric acid	0.7	0.0	47	*o*-Aminobenzoic acid	0.1	—
20	Hexanoic acid	0.6	0.0	48	Isobutyl alcohol	1.6	—
21	Heptanoic acid	0.6	0.0	49	Pentyl alcohol	2.1	—
22	Lacic acid	0.0	—	50	Isopentyl alcohol	1.4	—
23	Malic acid	0.0	—	51	Octyl alcohol	1.4	0.0
24	Malonic acid	0.0	—	52	Benzyl alcohol	0.7	0.0
25	Sodium oxalate	0.0	—	53	Polyethylene glycol	0.0	0.0
26	Adipic acid	0.0	—	54	Humic acid	0.0	0.0

20 °C. At fixed intervals of time, each flask was removed in turn and the weight of the residual solution was measured to obtain the solution volume V. The solution volume V was found to decrease linearly with time at a rate of about 1 mL/min in this method. The concentration C of the residual solution was measured using TOC analyser, TOD analyser, or UV spectrometer. In this way, the volume ratio V_0/V and concentration factor C/C_0 were obtained.

Results and Discussion

If the relative volatility α, which is defined as the ratio of concentration ratio of two components in vapor phase to that in the liquid phase, equals 1.0, no separation takes place. If α is less than 1.0, concentration is possible by the evaporation method. If α is greater than 1.0, concentration is impossible by the evaporation method, but the concentration will be possible by trapping the vapor. The following equations were obtained by considering mass balance; $(C-\mathrm{d}C)\times(V-\mathrm{d}V)=CV-\alpha C\mathrm{d}V$ or $(\alpha-1)C\mathrm{d}V=V\mathrm{d}C-\mathrm{d}C\mathrm{d}V\simeq V\mathrm{d}C$, where $\mathrm{d}V$ is the change in volume of solution and $\mathrm{d}C$ is the change in concentration of solution within a short time. Integrating the above equation between C_0 and C, and V_0 and V, we obtain $(1-\alpha)\log V_0/V=\log C/C_0$. Thus, a plot of $\log C/C_0$ against $\log V_0/V$ will give a straight line with slope $(1-\alpha)$. Therefore, if the value of α for the organic compound in aqueous solution is known, the recovery for the concentration method by evaporation can be predicted from the values of $(1-\alpha)$.

When the sample solution is assumed to be ideal and to obey Raoult's Law, the equilibrium partial pressure p equals the product of its vapor pressure P for pure compound and its mole fraction x in the liquid, and the total pressure P_T is obtained as $P_T=p_{org}+p_{H_2O}=P_{org}x+P_{H_2O}(1-x)$. Thus, the mole fraction of the organic compound in the vapor phase is $y=p_{org}/P_T=P_{org}x/P_T$, and that of water is $1-y=p_{H_2O}/P_T=P_{H_2O}(1-x)/P_T$. Consequently, the value of α can be given as $\alpha=y(1-x)/x(1-y)=P_{org}/P_{H_2O}$ for the ideal solution. However, actual water samples containing organic compounds which require concentration are not necessarily ideal, and the values of α for various organic compounds have not been reported so far.

Examples of the plot of $\log C/C_0$ against $\log V_0/V$ are shown in Fig. 2. For almost all the compounds, the plots could be represented approximately by straight lines, although some volatile compounds in the initial unsteady period deviated from the lines. The values of α for the various organic compounds were computed, and the results are shown in Table 1 together with the values of P_{org}/P_{H_2O} at 20 °C. It was found that the values of α for large molecular weight compounds such as humic acid and polyethylene glycol, sulfonic acids, and dicarboxylic acids were approximately 0, and these compounds could be concentrated with 100% recovery, while the values of α for benzaldehyde and aliphatic esters, alcohols, and ketones were larger than 1, and no concentration was expected. There are many compounds whose values of α were not equal to the calculated values of P_{org}/P_{H_2O}. Furthermore, the values of α for ionizing compounds like acids and amines increased with increasing concentrations, while those of non-ionizing compounds such as propionaldehyde and benzyl alcohol did not show any distinctive change. The experiments were repeated by adjusting the pH of solutions to 7 and 10—12 for acids and amines, and phenolic compounds, respectively. The representative results are shown in Fig. 3. All the tested compounds, except *o*-nitrophenol, can be concentrated with approximately 100% recovery at the pH values where 99% to 99.9% ionization of the compounds were secured, For *o*-nitrophenol, which has a large α value in the unionized form, approximately 100% recovery was obtained at 99.99% ionization.

This concentration method was applied to preconcentrate anionic surfactants in river water and biologically treated sewage before analyses with HPLC. The recovery of nearly 70% by means of TOC was obtained after $V_0/V=10$ was attained. Since anionic surfactants are mainly sulfonates or sulfates, it can be assumed that the recovery of the surfactants was 100%. In the analyses of phenolic compounds and sulfonates in treated wastewater from an oil refinery, preconcentration was necessary, and the recovery of approximately 90% was obtained by means of TOC after V_0/V reached 10.

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