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Simple, Quick, and Sensitive Method for Determination of Total Chlorinated Organic Compounds in Wastes and Related Materials

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Chemicals which resist degradation in the environment due to their high biological and chemical stability are termed persistent organic pollutants (POPs). Some POPs, moreover, possess potent chronic and long-term toxicity, such as carcinogenicity, and tend to accumulate in biota fat tissues in the ecosystem. Typical POPs are polychlorinated biphenyls (PCBs) from electrical transformers, chlordane (a termite control agent) impregnated into waste woods, waste chlorinated pesticides, and chlorinated organic solvents in sludge from chemical plants. Twelve chemicals designated as POPs by the United Nations Environmental Program (2001) are chlorinated organic compounds: PCBs, dioxins, chlorinated pesticides (chlordane, Aldrin, and Dieldrin), and chlorinated hydrocarbons (trichloroethylene). The United Nations Environment Program (UNEP) has been monitoring these chemicals worldwide (Wania and Mackay 1996). It is possible to analyze ultra trace chlorines from POPs using highly expensive modern instruments, such as gas chromatography/mass spectrometry (GC/MS), and HPLC/mass spectrometry (LS/MS). However, these methods require complex and tedious sample preparation steps. Moreover, it is almost impossible to use these instruments at the site of waste materials. Therefore, a simple, quick, and sensitive method to detect and to estimate the amount of total POPs in a large quantity of waste materials is necessary for establishing their adequate management in the environment.

MATERIALS AND METHODS

In order to develop a simple, quick, and sensitive method for determination of total chlorinated organic compounds in waste, a sample containing persistent organic pollutants (POPs), such as PCBs and chlordane, was reacted with sodium metal and the chloride ions formed were subsequently detected with silver nitrate.

Tetrahydrofuran (THF), silver nitrate, trichloroacetic acid, trichloroethylene, tricloroacetaldehyde, sodium metal (purity, 98%), 2,4,6-trychloroaniline, 2,4,5-trychloronitrobenzene, and hexanonyl chloride were bought from Wakao Pure Chemical Industries, Ltd. (Osaka, Japan).

Soil was collected from sediment in the basin of a river where process-effluent from a chemical plant (manufacturing regenerated papers from pressure sensitive papers containing PCBs) had been dumped. Collected soil samples were air dried and then were screened with a 0.5 mm × 0.5 mm sieve (total PCBs content, 566 mg/kg dry soil; total chloride content in PCBs, 246 mg/kg dry soil).

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Soil was also collected from the under-floor, where chlordane had been applied as an antitermite agent. Collected soil samples were air dried and then were screened with a 0.5 mm × 0.5 mm sieve (chlordane content in soil, 2.3 mg/g dry soil, *cis*-chlordane; 1.30 mg/g dry soil, *trans*-nonachlor; 0.35 mg/g dry soil, *cis*-nonachlor).

Waste wood treated with chlordane was collected from a site where a house had been torn down. After dirt and stains were removed from the surface of the collected wood, the wood surface was cut off (approximately 2–3 mm thickness) and then cut into small pieces (Waste wood sample #1).

Waste wood was also collected from a site where waste building materials had been unlawfully dumped in Chiba Prefecture. After dirt and stains were removed from the surface of the collected wood, the wood surface was cut off (approximately 2–3 mm thickness) and then cut into small pieces (Waste wood samples 2–11).

Waste oils were collected randomly from 31 waste drum cans from a site where waste materials had been unlawfully dumped (Can samples 1–31).

Water samples were collected from leachate (Water samples 1 and 2) and from wastewater with possible organochlorine contamination (Water samples 3 and 4).

Screened soil samples were ground (20 g) and then mixed with 50 mL of ethyl acetate. The sample solution was extracted under ultrasonic irradiation. The filtrate was dried over 10 g of anhydrous sodium sulfate. The sample solution was concentrated to 0.5 mL with a rotary evaporator, followed by purging with purified nitrogen gas. An ethanol/THF (2/1) solution (20 mL) was added to a sample solution and mixed well. Sodium metal (0.2 g) was added to the solution and then allowed to stand for 30 min. After unreacted sodium metal was filtered off, concentrated nitrous acid solution (1 mL) was added while stirring. After the solution became acidic, the precipitates were filtered off. A saturated ethanol solution of silver nitrate (3%) was added to the 1 mL filtrate drop by drop. The presence of a white suspension produced by silver chloride was visually examined.

Ethyl acetate (50 mL) was added to 5 g of waste wood sample and then the solution was treated as described above.

Ethyl acetate (50 mL) was added to 1 g of waste oil sample while stirring. Water and contaminants were removed by passing the solution through 10 g of anhydrous sodium sulfate; a 30 mL of ethanol/THF (2/1) solution was added to the filtrate while stirring and then the solution was treated as described above.

An aqueous silver nitrate solution (5%) was added to a water sample drop by drop (< 1 mL). The samples with albescence were further treated by Procedure I and the samples without albescence were further treated by Procedure II.

Procedure I. A water sample (5 mL) was passed through an IC-Ag solid phase extraction cartridge (Alltech Japan, Tokyo, Japan) using a water pump at 0.5 mL/min. After the first 1 mL of eluate was discarded, the last 4 mL eluate was saved for further examination. The cartridge was conditioned with 5 mL of purified water prior to use.

Procedure II. Ethanol (9 mL) was added to 1 mL of the water sample or 1 mL of the above eluate sample. Sodium metal (0.2 g) was added to the sample solution and allowed to stand for 30 min. After the unreacted sodium metal was removed, 1 mL of concentrated nitrous acid solution was added to the reaction solution while stirring. The solution was confirmed to be acidic with a Litmus paper. After the precipitates were filtered off, 1 mL of saturated ethanol solution of silver nitrate (3%) was added to the 1 mL filtrate drop by drop. The presence of white suspension produced by silver chloride was visually examined.

RESULTS AND DISCUSSION

Table 1 shows detection capability at 1 m*M* and 0.5 m*M* of selected organic chlorine compounds (four different types of structure) obtained by the silver nitrate solution (SNS) method in the present study.

Table 1. Detection capability at 1 m*M* and 0.5 m*M* of selected organochlorine compounds.

Organochlorine	1 m*M*	Cl^- Conc.	0.5 m*M*	Cl^- Conc
Trichloroacetic acid	positive	163 μg/mL	semi positive	81.5 μg/mL
Trichloroethylene	positive	132 μg/mL	semi positive	66 μg/mL
2,4,6-Trichloroaniline	positive	196 μg/mL	semi positive	98 μg/mL
Hexanoyl chloride	positive	135 μg/mL	semi positive	67.5 μg/mL

The detection capability for four tested samples was 1 m*M*. The lowest detection limit of trichloroacetic acid obtained by the Beilstein test was 11.9 m*M*, which was approximately 10-fold higher than that of the SNS method. Therefore, the SNS method was chosen and modified to develop our new method, which satisfies the objective of this study. In order to apply the SNS method to organochlorine compounds, chlorine atoms must be released from a compound as chloride ions. This can be achieved by reduction of the organochlorine compound with sodium metal in an ethanol solution (Bruck 1962).

Solid and oily samples may contain inorganic chlorides. Therefore, it is necessary to use a solvent which does not dissolve inorganic chlorides for extraction and/or dilution. Ethanol used for the reaction with sodium metal was not applicable because it dissolved a small amount of the inorganic chlorides. Among the solvents tested, ethyl acetate gave the most satisfactory result for extraction. However, ethyl acetate reacted with sodium metal to yield orange polymer, which inhibited the reaction of sodium metal. Therefore, solvent exchange with ethanol was conducted prior to reacting a sample with sodium metal. However, if ethyl acetate was removed completely (dryness) before addition of ethanol, volatile organic chlorides such as trichloroethylene evaporated off from the sample. Consequently, a small amount of ethyl acetate needed to remain in a sample, and it was found that if the amount of ethyl acetate was less than 1/9 of the ethanol in a sample solution, it did not inhibit the reaction of sodium metal. Therefore, ethyl acetate concentration in an ethanol solution for the reaction of organic chlorides and sodium metal was maintained at below 10%.

Samples which did not dissolve well in ethanol (e.g., waste oil) yielded a solute after being reacted with sodium metal followed by concentrated nitrous acid treatment. Consequently, application of the SNS method was difficult. However, use of THF as a co-solvent resolved this problem. The optimum ratio of ethanol:THF was 2:1. Further experiments were conducted using 10 mL of ethanol:THF (2:1) solution for the reaction with metal sodium. An ethyl acetate extract was concentrated to 0.5 mL and then ethanol/THF solution was added.

Water samples, such as waste water and leachate, tend to contain inorganic chlorides. Some organochlorine, such as trichloroacetic acid and trichloroacetaldehyde, were not recovered by a liquid-liquid extraction with ethyl acetate because of their high water solubility. Therefore, various solid phase extractions were conducted to remove chloride ions from the sample. Among solid phases tested, IC-Ag solid phase gave the most satisfactory result. Capacity of this solid phase was 5 mL for a sample containing high levels of chloride ion (e, g., seawater). Because the reaction between water and sodium metal was too vigorous, ethanol was added to water samples prior to their reaction with sodium metal. The optimum ratio of water/ethanol was 1:9.

In order to validate IC-Ag solid phase extraction (SPE), an aqueous solution containing water soluble trichloroacetaldehyde and sodium chloride (50 m*M* each) was eluted through this solid phase. Albescence occurred in the original solution with silver nitrate treatment, whereas it did not occur in the eluate from the IC-Ag SPE cartridge, indicating that inorganic chloride was removed with this cartridge. After 1 mL of eluate was reacted with sodium metal in 10 mL of ethanol solution, addition of SNS yielded albescence in the solution, indicating that tricloroacetaldehyde was present in the eluate. These results indicate that the validation of IC-Ag SPE was successful.

The SNS method is a qualitative method for chloride ion. However, it is possible to estimate a rough concentration value of samples. If SNS was added to serial dilutions of a sample, it is possible to determine the dilutions between the samples with albescence and without albescence. For example, if the sample with 50-fold dilution exhibited albescence but the sample with 60-fold dilution did not, estimated chloride ion concentration in the sample was 50–60 m*M* and the limit of detection is 1 m*M*.

Table 2 shows the results of chloride ion analysis on the samples collected from various places by the newly developed method (SNS method).

Samples from river sediment and under-floor soil samples clearly exhibited the presence of organic chlorides. Chloride ion concentrations in these samples estimated by the method described above were 5.5 mmol/kg for sediment and 27.5 mmol/kg for under-floor soil. According to the precision analysis on PCBs in the same sediment sample, chloride ion concentration was 6.9 mmol/kg (Yasuhara 2003). If the recovery efficiency of chloride ions was estimated as 70–90% in the present method, the results from the present study are roughly consistent with that of precision analysis. Two out of 11 samples of waste woods showed the presence of organic chlorides. Among 31 oil samples from waste drum cans, 25 were viscous or grease-like oils. Four can samples contained a water layer and 6 were aqueous with suspension. Thirteen oily samples exhibited the presence of organic chlorides, whereas 6 aqueous and water layers from 4 oily samples did not show albescence. Water samples 2 and 3 showed the presence of organic chlorides, and the estimated concentrations of chloride ion were 5 mol/L and 10 mmol/L, respectively.

It is known that samples from river sediments, under-floor soils, and waste woods may contain organochlorines, suggesting that the method developed in the present study is applicable to actual samples from waste materials (Yasuhara 2003).

Table 2. Results of qualitative analysis of chloride ions in samples collected from environmental wastes obtained by a newly developed method.

Sample	Result	Sample	Result	Sample	Result	Sample	Result
River		Waste		Can #		Can #	
sediment	+	wood #		10	+	25	–
		9	+	11	–	26	–
Beneath		10	–	12	–	27	–
floor	+	11	–	13	–	28	–
				14	+	29	+
Waste		Can #		15	–	30	+
wood #		1	–	16	–	31	+
1	+	2	–	17	–		
2	–	3	+	18	–	Water #	
3	–	4	–	19	+	1	–
4	+	5	+	20	–	2	+
5	–	6	+	21	–	3	+
6	–	7	+	22	–	4	–
7	–	8	+	23	+		
8	–	9	+	24	–		

+: positive (chloride is present)
–: negative (chloride is absent)

Therefore, the newly developed, simple, quick, and sensitive method can be used to detect and to roughly estimate the quantity of POPs in waste materials. As mentioned above, it is almost impossible to use expensive advanced instruments to analyze POPs at the site of waste materials, which have been dumped continuously and consistently in large quantities. It is possible to prepare a portable field kit with the SNS method for determination of presence and estimation of quantities for POPs at the dumping sites. A portable field kid should have standard solutions of various Cl^- concentration for comparison with a field sample. Once the presence of POPs is determined by the SNS method, further precision analysis of POPs by using advanced instruments, such as GC/MS and LS/MS, can be performed if it is necessary to assess pollution caused by POPs in that area.

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