

COMPLETION REPORT

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**DEVELOPMENT OF A SIMPLIFIED CHLORINATED
HYDROCARBON SCREENING TECHNIQUE
FOR WATER AND SEDIMENT**

By

PAUL H. TEMPLET

for

**Office of Water Policy
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Project Completion Report

1. Development of a Simplified Chlorinated Hydrocarbon Screening Technique for Water and Sediment.
2. Paul H. Templet, Principal Investigator
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4. Disclaimer: "Contents of this publication do not necessarily reflect the views and policies of the United States Department of the Interior, nor does mention of trade names or commercial products constitute their endorsement by the U.S. Government."
5. Abstract: The development of a simple screening technique for chlorinated hydrocarbons in water and sediment was undertaken. Extraction and concentration techniques were used as an alternative to the present costly and time consuming methods. Water samples spiked with known amounts of six chlorinated hydrocarbons were passed through Sep-Paks, a Waters Assocs. C-18 disposable column, and the adsorbed compounds eluted with methanol. The methanol extract was analyzed directly by furnace evaporation and decomposition into a microcoulometer cell and reported as total organic halide (TOX). Recoveries were variable and were a function of the Sep-Pak loading, concentration and volume of samples and type of chlorinated hydrocarbon. Chlorinated phenols exhibited the best recoveries (100%) and volatile compounds the worst (Ca. 20%). The technique offers promise as a qualitative screening procedure for natural waters.

Dried sediment were spiked with known amounts of the same six chlorinated hydrocarbons, extracted with hexane and analyzed for TOX using furnace microcoulometry. Sediments run directly without the extraction step exhibited interferences from naturally occurring sulfur compounds and inorganic chlorides. The extraction step affords an additionally opportunity for a 100-fold concentration. Recoveries ranged from 100% (PCB and chlorophenols) to 20-30% (Tetrachloroethylene and chloroform) for volatile compounds. The lower recoveries may never be encountered in field samples since volatiles may have already been evaporated from the sediment or soil.

6. Purposes and Objectives:

- a. To develop and test recovery efficiencies of methods for rapidly concentrating dilute chlorinated hydrocarbons contaminants contained in water samples.
- b. To test the recovery and sensitivity of microcoulometry for selected chlorinated hydrocarbons.
- c. To test the recovery efficiency and sensitivity of the technique for chlorinated hydrocarbons in sediment matrices in association with water.
- d. To streamline the procedures to allow large numbers of samples to be screened in a rapid manner.

7. Discussion:

Related Research

Coulometry is a well known method for the determination of inorganic chlorides and sulfurs. When combined with a furnace to convert total organic halides (TOX) to inorganic chloride it assumes an important role in environmental chemistry. In the past the microcoulometer (and furnace) has been used for light halogenated hydrocarbons in drinking water (1-5), surface waters (6-7) and other environmental samples including plant (8) and animal (9-10) extracts.

The usual procedure (EPA Interim Method 450.1) involves adsorption of the chlorinated organic compounds onto activated carbon followed by carbon combustion in a furnace and analysis in a microcoulometer cell for TOX (11-12). Considerable effort has been expended in perfecting the adsorption medium (13-19) but there are still problems with repeatability.

One interesting deviation from the use of carbon involves using Sep-Pak (8), a Waters Assocs. product Sep-Pak is a C-18 disposable cartridge used to adsorb and concentrate organics from water samples.

Although there are numerous studies on the use of TOX on water samples there appears to be a lack of data on the use of TOX for sediment samples either directly or by first extracting the sediment and then concentrating the extract. The Hall detector has been used for TOX determinations of ash, coal samples (20) by Soxhlet extraction, reconcentration and gas chromatography using a short column.

This research uses a Sep-Pak for collecting and concentrating the chlorinated hydrocarbon from water and then eluting the hydrocarbon with methanol. The methanol is directly transferred to the microcoulometer furnace. The sediment sample is dried, extracted, the extract concentrated and injected into the furnace.

Methods and Procedures:

1. Six chlorinated hydrocarbons were selected for screening after a review of the chemical literature. These compounds represented a cross section of commercially available chlorinated hydrocarbons which are found as contaminants in water and sediment. The compounds are 1,2,4 trichlorobenzene, PCB 1248, 2-chlorophenol, chlorobenzene, tetrachloroethylene and chloroform.
2. Stock standard solutions (5000 and 10,000 ug/ml) of the compounds were used as received from EPA and added to water to yield 0.5, 5.0 and 50ppm standard solutions. These water solutions were then extracted by passing a volume through Sep-Pak, a Waters Assocs. C-18 disposable cartridge. The chlorinated hydrocarbon of interest was then eluted from the Sep-Pak with methanol and analyzed directly with the microcoulometer for total organic halide (TOX). Subsequently lower volumes of spiked samples were extracted as the Sep-Pak quickly became saturated.
3. A large soil sample was air dried, crushed and screened to obtain small uniform soil particles. The soil was tested for composition by the hydrometer method and found to contain 8.9% clay, 64.7% silt and 26.4% sand. One hundred gram samples of the soil were then inoculated with each of the six chlorinated hydrocarbons. The chlorinated hydrocarbons were added to the soil as a solution in methanol, shaken and the methanol evaporated. The final concentration of the chlorinated hydrocarbon in the soil was either 1mg/kilo or 0.5 mg/kilo.
4. Each of the inoculated soils (100g) was then extracted with 100 mls hexane, the hexane evaporated to 1ml final volume and analyzed for TOX by microcoulometry. The extraction step was found to be necessary to eliminate interferences, probably sulfur, which occurred when the soil samples were burned directly in the microcoulometer furnace.
5. Water and sediment extracts were analyzed on a Dohrmann Microcoulometer with a furnace and a boat inlet system (Fig.1). Extracts were injected into the boat and the boat pushed into a two-zone furnace. The first zone operated at 250°C and the second at 800°C. After the solvent in the extract was burned off the sample was pushed into the hot zone where all organic chlorides are converted to chloride (Cl^-). The inorganic chlorides are then swept by carrier gases into a microcoulometer cell where they are stoichiometrically precipitated as AgCl . The amount of silver consumed is electronically measured. Standards and reagent blanks were run in every case to calibrate the instrument and to determine background responses.

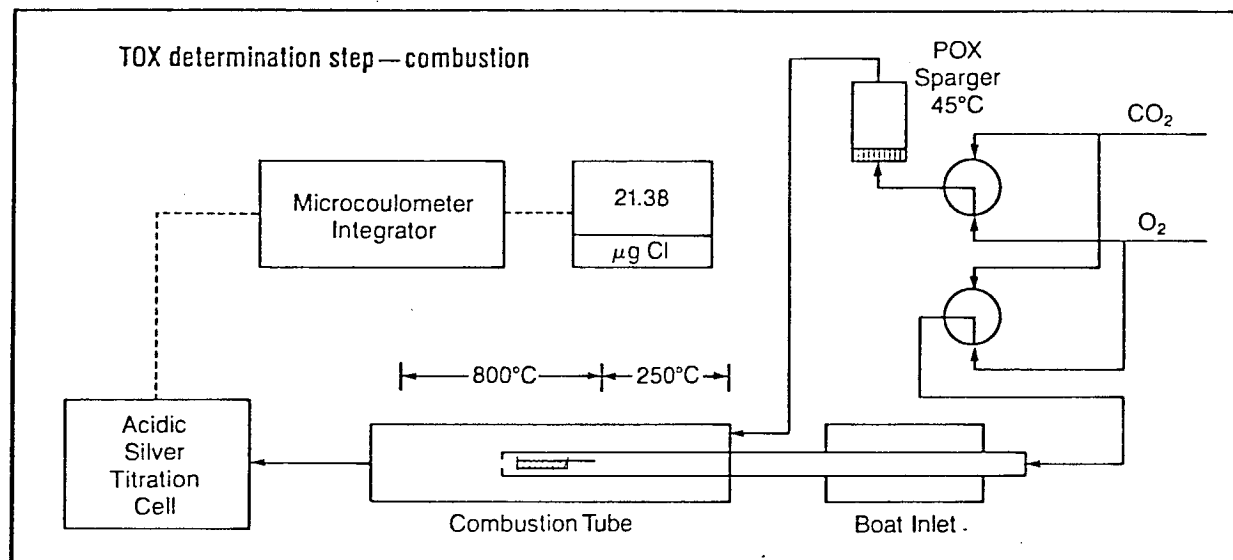
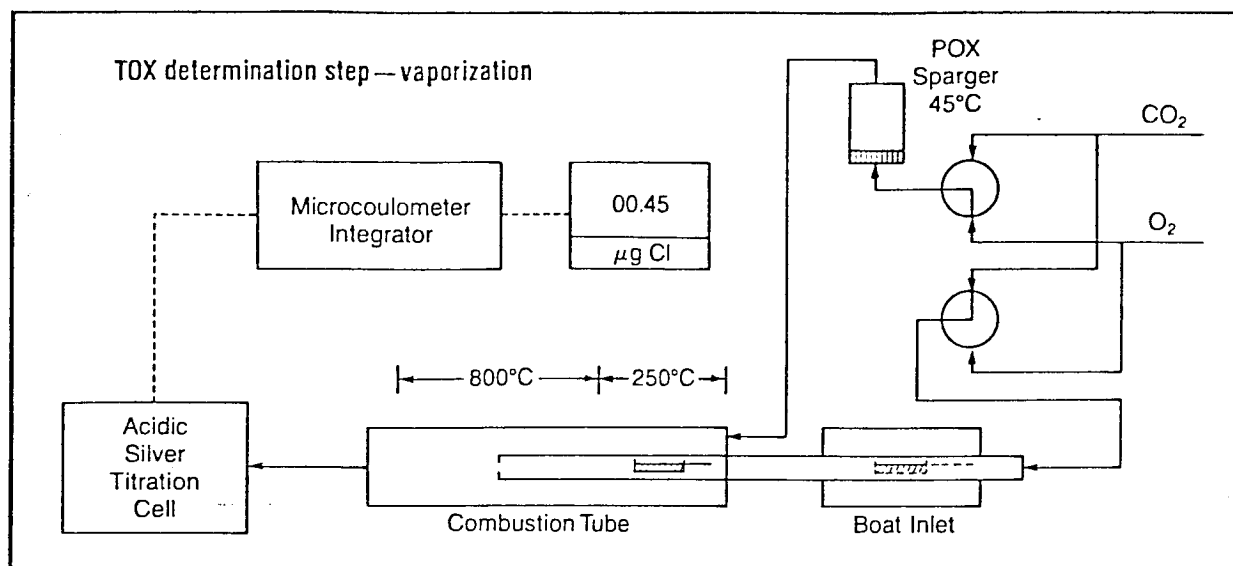


Figure 1. Total organic Halide (TOX) Instrumentation.

Findings and Significance

Water

1. The use of Sep-Pak to concentrate chlorinated hydrocarbons from a water sample appears to have validity, however recoveries appear to be affected by the volume of samples, the type of chlorinated hydrocarbons and surface effects. For example those hydrocarbons extracted from small volumes gave good recoveries. This could be due to surface effects whereby the spiked chlorinated hydrocarbon is adsorbed on the surface of the glass container. Larger volume samples would have a larger surface for adsorption. This hypothesis was confirmed when a solvent wash of the bottle after elution through the Sep-Pak exhibited substantial portions of the compound of interest still to be on the glass surface.

In some cases the chlorinated hydrocarbon was only partially trapped by the Sep-Pak. Extraction of tetrachloroethylene by traditional hexane extraction yielded a recovery of 33% while Sep-Pak trapping and elution had an average recovery of 21% at the 1.0ppm level.

The various extraction efficiencies are shown in Table I.

Table I. Recoveries Using Sep-Pak

	2-chlorophenol				1,24 Trichlorobenzene				PCB-1248		
Conc (ug/ml)	50	5	0.5		50	5	0.5		50	5	0.5
Vol. of Sample (mls)	10	100	1000	100	10	100	1000	100	10	100	1000
wt. of chlorinated hydrocarbon (mg)	500	500	500	50	500	500	500	50	500	500	500
Recovery (%)	100	82	56	58	88	-	68	85	33	28	43

	Chloroform			Chlorobenzene			Tetrachloroethylene		
Conc. (ug/ml)	100	10	1.0	100	10	1.0	100	10	1.0
Vol. of Sample (mls)	10	100	100	10	100	1000	10	100	1000
wt. of chlorinated hydrocarbon (ug)	1000	1000	100	1000	1000	1000	1000	1000	1000
Recovery (%)	92	27	22	78	-	18	70	-	30

The significance of this data is that Sep-Pak does offer the promise of being an effective means of concentrating chlorinated hydrocarbons in water samples in a qualitative screening technique. Quantification would require other analytical techniques. Surface effects are not a problem in the field if waters are pumped through the Sep-Pak and not bottled first. The varying recoveries shown in Table I indicate that the volume of sample to be extracted via Sep-Pak would be a function of the lower limits of detection desired. However, pumping ten liters of water through two Sep-Paks in series, the second

to check for breakthrough, would trap enough sample for detection assuming a 50% recovery and a 5ppb contamination level in the water. Those samples showing evidence of chlorinated hydrocarbon contamination would be submitted for further detailed analysis by Gas Chromatography (GC)/Mass Spectroscopy (MS) or Electron Capture (EC)/GC.

2. Sediments

Interferences from the numerous inorganic chlorides and the sulfur compounds found in soil preclude the use of direct combustion of the soil in the microcoulometer's furnace. An extraction step is necessary to isolate the chlorinated hydrocarbons from the soil and its interferences. However, the extraction of 100g of soil with 100mls of hexane is a simple step and worth the effort since it eliminates the interferences. The 100 fold concentration by evaporation of the hexane to 1ml is a further improvement. The recoveries determined from the spiked soil samples are shown in table 2.

Table 2. Soil Recoveries

<u>Chlorinated hydrocarbon</u>	<u>Concentration (ug/g)</u>	<u>Recovery (%)</u>
2-chlorophenol	0.5	100
1,2,4 Trichlorobenzene	0.5	93
PCB 1248	0.5	150
Chloroform	1.0	30
Chlorobenzene	1.0	71
Tetrachloroethylene	1.0	21

The volatile compounds, chloroform and tetrachloroethylene are undoubtedly being lost to the air during the extraction and solvent steps. Samples taken in the field are not expected to have this problem since volatile components will, in all likelihood, already have been lost. The excessively high recovery of the PCB is due to peak shape problems of the microcoulometer which gives an overly broad peak which tails badly for this compound.

The recoveries appear fairly good for this range of compounds and holds promise as a screening technique for chlorinated hydrocarbons in soil matrices. It may be quantifiable but further work is needed to verify this premise. The significance of this data is that soils can be scanned quickly for contamination at 1/10 of the GC/MS cost and those showing elevated readings can be submitted for further analysis by GC/MS or EC/GC.

D. Conclusions

1. The use of Sep-Pak to concentrate chlorinated hydrocarbons from water followed by microcoulometry analysis offers promise as a screening technique but recovery variability may pose problems. The variability is a function of concentration, total weight of compound trapped on the Sep-Pak, volume of water sample and the type of compound (polar vs. non polar). Even with these uncer-

tainties however, the method presented here is useful as a qualitative screening technique. Quantification would have to occur in a more intensive GC/MS analysis of those samples found to contain chlorinated hydrocarbons above a background threshold.

2. The use of microcoulometry to determine chlorinated hydrocarbons in sediment or soil matrices shows good recoveries for a range of chlorinated compounds. However, due to sulfur and inorganic chloride interferences, the soil cannot be run directly but must be extracted and concentrated. The extraction step, using hexane, allows the sample to be concentrated 100-fold as well as removing interferences. Volatile compounds, e.g. chloroform and tetrachloroethylene, are lost during soil drying and extraction volume reduction and recoveries are reduced. However, volatile chlorinated hydrocarbons are not normally encountered in soil samples since they are quickly lost to the air.

In summary both techniques appear to offer useful screening alternatives to the presently used techniques for water and sediment analysis which are cumbersome, time consuming and costly. Those screened samples exhibiting TOX above a background threshold could be submitted to more detailed analysis.

9. Literature Citations

1. Bellar, T.A., Lichtenberg, J.J., "Determining Volatile Organics at the ug/L level in Water by Gas Chromatography," J. Am. Water Works Assoc. 66(12):739 (1974).
2. Mieure, J.P., "A Rapid and Sensitive Method for Determining Volatile Organohalides in Water," J. Am. Water Works Assoc. 69(1):60 (1977).
3. Kajino, K., Yagi, M., "Formation of Trihalomethanes During Chlorination and Determination of Halogenated Hydrocarbons in Drinking Water" in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment B.K. Afghan, D. Mackay, Ed. (New York: Plenum Press, 1980) P. 491.
4. Nicholson, A.A., Meresz, O., "Analysis of Volatile, Halogenated Organics in Water by Direct Aqueous Injection - Gas Chromatography" Bull. Environ. Contam. Toxicol, 14(4): 435 (1975).
5. Glaze, W.H., Peyton, R.P., Rawley, R., "Total Organic Halogen as Water Quality Parameter: Adsorption/Microcoulometric Method," Environ. Sci. Tech. 11(7): 685 (1977).
6. Wegman, R.C.C., Greve, P.A., "The Microcoulometric Determination of Extractable Organic Halogen in Surface Water, Application to Surface Waters of the Netherlands," Sci. of the Total Environ. 7:235 (1977).
7. Takahashi, Y., Morre R.T., and Joyce R.J., "Measurement of Total Organic Halides (TOX) and Purgeable Organic Halides (POX) in water using Carbon Absorption and Microcoulometric Determination," Conference Proceedings, ACS Div. of Envir. Chem. Presented March 23-28, 1980-Houston, TX.
8. Eskins. K., Dutton H.J., Analytical Chem 51(11) 1885-6 (1979).
9. Alles, G., Bauer U., Selenka F., Zentsalbl Bakteriolo, Mikrobial Hyg Abtl, Org.B (1981) 174(3) 238-48.
10. Donkin, P., Mann, S.V., and Hamilton, E.I., Microcoulometric Determination of Total Organochlorine Pesticide and Polychlorinated Biphenyl Residues in Ovey Seal Blubber, Amalytica Chimica Acta 88 289-301 (1977).
11. Jekel, M.R., Roberts, P.V. Environ. Sci. Technol. 1980, 14, 970-975.
12. "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, Revision B", U.S. Environmental Protection Agency: Washington
13. Sylvia, A.E., Bancroft, D.A., Miller, J.D., "Analytical Note-A Method for Evaluating Granular Activated Carbon Adsorption Efficiency," J. Am. Water Works Assoc. 69(2): 99 (1977).

14. Mullins Jr., R.L., Zogorski, J.S., Hubbs, S.A., Allegeier, G.D., "Activated Carbon Adsorption of Organics from the Aqueous Phase, Volume 1" (Ann Arbor Science Publishers, Inc., 1980) 273.
15. Suidan, M.T., Kim, B.R., Snoeyink, V.L., "Reduction of Free and Combined Chlorine with Granular Activated Carbon" in Activated Carbon Adsorption of Organics from the Aqueous Phase, Volume 1 (Ann Arbor Science Publishers, Inc., 1980) p. 397.
16. Jain, J.S., Snoeyink, V.L., "Adsorption From Bisolute Systems on Activated Carbon," J. Water Poll. Control Fed. 45: 2463 (1973).
17. Weber Jr. W.J., Pirbazari, M., Long, J.B., Barton, D.A., "Activated Carbon Adsorption of Organics from the Aqueous Phase, Volume 1" (Ann Arbor Science Publishers, Inc., 1980) 317.
18. McGuire, M.J., Suffet, I.H. "Adsorption of Organics From Domestic Water Supplies," J. Am. Water Works Assoc. 70(11): 621 (1978).
19. Singer, P.C., Yen, C-Y., "Activated Carbon Adsorption of Organics from the Aqueous Phase, Volume 1" (Ann Arbor Science Publishers, Inc., 1980) 167.
20. Nutton, C.P., Haile, C.L., Redford, D.P., Determination of Total Organic Halogen in Environmental Extracts by Gas Chromatography with Hall Detection, Anal. Chem. 50 598-599 (1984).