



Project Summary

Evaluation of Methods for the Determination of Total Organic Halide in Water and Waste

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Various methods were evaluated for determining the total organic halides (TOX) in groundwater and in waste oil samples. From three inorganic halide species generation approaches and three inorganic halide determinative techniques evaluated for groundwater analyses, one combined approach, which used Schoeniger flask oxidation with colorimetric chloride determination, was chosen for laboratory validation and method detection limit (MDL) studies. Groundwater samples were also analyzed for TOX using EPA Method 9022, "TOX by Neutron Activation Analysis."

The Schoeniger flask/colorimetric chloride and neutron activation analysis methods gave TOX results for spiked groundwaters comparable to those obtained using Interim Method 450.1 at halide levels above 0.2 mg/L.

Oil sample analysis using the sodium biphenyl reagent and a colorimetric chloride method was found to be unsatisfactory for the analysis of various oils spiked with PCBs due to interferences in the colorimetric determinative step which resulted in recoveries greater than 100 percent.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This program is a continuation of EPA Contract No. 68-03-2984, "Surrogate

Methods for Priority Pollutants in Wastewater." The objective of the work conducted under this research program was to evaluate additional direct and indirect methods for TOX analysis.

Indirect methods evaluated included Parr bomb oxidation, Schoeniger flask oxidation, and sodium biphenyl dehydrohalogenation as species-generation approaches for conversion of organic halide to inorganic halide. The determinative techniques evaluated for the inorganic halide produced included ion chromatography, chloride ion selective electrode, and a colorimetric halide procedure. In all cases, the sample preparation procedure used was the charcoal adsorption technique from Interim Method 450.1. The primary thrust of this portion of the program was to select the best species generation approach and best determinative technique, and to combine these approaches into a TOX method for use as a less costly alternative to the microcolorimetric determinative technique of Interim Method 450.1.

Neutron activation analysis using the sample preparation procedure from Interim Method 450.1 was the only direct approach evaluated. This method was chosen for its ability to distinguish between the various halogen species at parts-per-million levels.

In addition to these methods for the determination of TOX in aqueous samples, the sodium biphenyl reagent approach was evaluated for the analysis of TOX in transformer oil samples. The determinative technique for these evaluations was the colorimetric chloride method used for the aqueous sample analyses.

Analytical Methods Evaluation

Evaluation of Oxidation Approach

Three oxidation approaches were evaluated for the conversion of organic chlorine to chloride ion: Schoeniger flask combustion, Parr bomb combustion, and sodium biphenyl dehydrohalogenation. The reference determinative technique for the first two comparisons was ion chromatography (IC). For the sodium biphenyl approach, ion chromatography was not suitable because of interferences caused by high nitrate concentrations, and the ASTM D-512 colorimetric chloride procedure was used.

Schoeniger Flask Procedure

The Schoeniger flask procedure was evaluated for halide blank levels due to glassware, absorbing solution, sample wrapping papers, and glassware cleaning methods

Recovery of halide spiked onto granulated activated charcoal (GAC) and adsorbed from aqueous solutions onto GAC was also evaluated. In all spiking experiments a three component spiking solution containing tetrachloroethylene, 2,4,6-trichlorophenol and bromoform was used.

The Schoeniger flask procedure was found to be superior to both the Parr bomb and the sodium biphenyl reagent procedures (described below) in terms of halide recovery and halide blank levels, and was used in conjunction with the ASTM D-512 colorimetric method for chloride ion for method validation.

Parr Bomb Oxidation Procedure

The Parr bomb oxidation procedure was evaluated for halide blank levels from apparatus and reagents, recovery of halide spiked onto GAC, and effect of absorption time after sample ignition. The Parr bomb procedure was unsuitable for halide analysis because of incomplete combustion of the GAC and associated poor halide recovery.

Sodium Biphenyl Reagent Procedure

The sodium biphenyl reagent procedure was evaluated for halide recovery for standards in methanol and for standards spiked onto GAC and in reagent water. Blank halide levels associated with the reagents and glassware were also investigated.

The sodium biphenyl procedure was found to be unsuitable because of high halide blank levels associated with the reagent; also, the extraction procedure was found to be too difficult for routine use due to the presence of the GAC at the interface between the organic and aqueous phases in the separatory funnel.

Evaluation of Determinative Technique

Three determinative techniques were evaluated: ion chromatography, chloride ion specific electrode (ISE), and the ASTM D-512 colorimetric chloride procedure.

Ion Chromatography

IC was evaluated using a Dionex S₂ column over two chloride concentration ranges: 0.1 to 0.35 $\mu\text{g}/\text{mL}$ and 2.0 to 10.0 $\mu\text{g}/\text{mL}$. In addition, the linearity of response for chloride and bromide over the range of 2 to 10 $\mu\text{g}/\text{mL}$ and the separation of six common anions was evaluated with an S₁ column.

The chloride response on both columns and the bromide response on the S₁ column were linear over the ranges tested. Due to peak broadening, the detection limit for bromide, estimated at 0.5 $\mu\text{g}/\text{mL}$, was much higher than that for chloride (approximately 0.05 $\mu\text{g}/\text{L}$). In the evaluation of anion separation, bromide and nitrate ions were only partially resolved. The high nitrate level associated with the GAC was found to obscure small amounts of bromide and to render IC ineffective for halide speciation in GAC digests from the Schoeniger flask oxidation procedure.

Ion Specific Electrode

The ISE determinative technique was initially evaluated for linearity of response over a range of 1 to 100 $\mu\text{g}/\text{mL}$, and the detection limit for both chloride and bromide was found to be approximately 1 $\mu\text{g}/\text{mL}$. ISE evaluations were stopped when it was determined that extremely high recoveries (>240 percent), presumably due to some interference in the GAC digest, were observed in spiked GAC samples prepared using the Schoeniger flask oxidation procedure.

ASTM D-512 Colorimetric Chloride Procedure

The ASTM colorimetric procedure was evaluated for reagent blank levels, chloride and bromide response, and the effect of nitrate interference. The response for

both chloride and bromide was linear from 1 to 4 $\mu\text{g}/\text{mL}$. The estimated detection limit for both halides was found to be approximately 0.5 $\mu\text{g}/\text{mL}$, and nitrate appeared to have no effect on response

Blank and spiked charcoal samples were prepared by the Schoeniger flask oxidation technique and analyzed by the colorimetric procedure. Comparison of the results of these samples with similar results obtained with ISE and IC showed that ISE was least effective for halide determination, while IC and the colorimetric method were essentially similar. The colorimetric procedure was chosen for the determinative technique for validation since the IC method was not capable of halide speciation with the GAC matrix and also due to the less sophisticated and less costly nature of the colorimetric method.

Method Validation

The MDL of the Schoeniger flask/colorimetric halide procedure was determined by the analyses of spiked and unspiked replicates of reagent water according to the standard EPA protocol. A detection limit of 0.15 mg/L was calculated with an average recovery of 57 percent.

For method validation, three identical sets of samples were prepared and analyzed by the Schoeniger flask/colorimetric procedure, EPA Method 9022 (neutron activation analysis), and Interim Method 450.1. A summary of recovery results obtained in these analyses is provided in Table 1. Agreement between the methods was good for samples which contain halide concentrations above approximately 0.2 mg/L. Below this value, the halide blank of the Schoeniger flask/colorimetric halide procedure prevents the determination of TOX in the samples

Evaluation of EPA Method 9022

A series of spiked charcoal samples were prepared and analyzed to evaluate the neutron activation analysis procedure (EPA Method 9022) as a direct method for TOX determination. Chloride recoveries obtained ranged from 91 percent for low-level spiked samples to 87 percent for high-level spiked samples. Bromide recoveries ranged from 90 percent for low-level spiked samples to 88 percent for high-level spiked samples.

Evaluation of Waste Oil Methodology

Ten PCB-spiked oil samples obtained from the Quality Assurance Branch of the Environmental Monitoring and Support

Table 1 Summary of Recovery Results for Validation Samples Obtained Using the Schoeniger Flask TOX Method, Interim Method 450.1, and Neutron Activation Analysis Method 9022

Sample Identification	Spike Level, mg/L	Average Halide Amount Found for Given Method, mg/L			Average Percent Recovery for Given Method		
		Schoeniger Flask TOX	Interim Method 450.1	Neutron Activation Analysis	Schoeniger Flask TOX	Interim Method 450.1	Neutron Activation Analysis
Reagent water	Unspiked	0.19	0.020	0.087	-- ^a	--	--
Reagent water	0.51	0.48	0.43	0.049	56	81	78
Groundwater #1	Unspiked	0.23	0.044	0.12	--	--	--
Groundwater #1	0.51	0.59	0.56	0.59	70	94	92
Groundwater #1	1.0	1.3	1.3	1.5	105	120	135
Groundwater #2	Unspiked	1.3	1.7	2.7	--	--	--
Groundwater #2	5.1	4.2	4.0	7.2	58	45	88
Groundwater #2	10.2	7.9	8.2	10.1	65	64	72

^aNot applicable.

Laboratory at Cincinnati, Ohio, were analyzed for organic chloride content using the sodium biphenyl reagent species generation method and the ASTM colorimetric chloride determinative. High recoveries ranging from 145 percent to 268 percent were obtained for these oil samples. To evaluate these high recoveries, an analytical curve study was performed by spiking a PCB-free transformer oil with Arochlor 1254. Results showed a high positive bias for all samples, although this bias was reduced considerably with increased sample dilution.

Conclusions and Recommendations

Based on the results of spiked reagent water and groundwater samples analyzed, the Schoeniger flask oxidation and colorimetric halide TOX procedure is recommended as an alternative to Interim Method 450.1 for use as a TOX screening method for aqueous matrices, with the caveat that this procedure is applicable only to levels of TOX at or above 0.2 mg/L in aqueous matrices. This method provides a significantly less costly alternative for the analysis of samples which contain low parts-per-million levels of organic halogen and gives results comparable to those obtained with Interim Method 450.1.

The results of the evaluation of EPA Method 9022, Total Organic Halides by Neutron Activation Analysis, indicate that this direct method also is an appropriate technique for TOX analysis and offers the additional advantage of pro-

viding individual chlorine and bromine values for the sample at levels equal to TOX detection limits achievable with the microcoulometric determinative technique of Interim Method 450.1.

The sodium biphenyl reagent and colorimetric halide determinative technique for analysis of total organic chloride from oil matrices is not suitable as a screening procedure in its present form. Further evaluation of the sodium biphenyl reagent with some alternative determinative technique, such as microcoulometric titration, is recommended. Perhaps an additional cleanup step for the extract prior to the colorimetric determinative step would establish the usefulness of this technique at those halide levels in the range of from 20 to 350 µg/g.

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The complete report, entitled "Evaluation of Methods for the Determination of Total Organic Halide in Water and Waste," (Order No. PB 85-166 304/AS; Cost: \$13.00, subject to change) will be available only from:

National Technical Information Service

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