



Project Summary

Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater

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Various methods for determining total purgeable and nonpurgeable organic halides in wastewater have been reviewed. Two approaches, digestion with sodium biphenyl (SBP) followed by colorimetric detection, and combustion followed by microcoulometric titration, were selected for laboratory evaluation. The latter approach involved the use of a commercial instrument (Dohrmann Model DX-20) which had been designed specifically for the separate analysis of purgeable organic halide (POX) and total organic halide (TOX) using carbon adsorption.

The microcoulometric titration approach was found to be simpler to conduct and more precise than the SBP digestion approach. Surrogate methods for POX and TOX in water and extractable organic halide (EOX) in water and solids were evaluated for a number of wastewater and solid samples. The results obtained using the POX surrogate method generally agreed within a factor of two with the results obtained by EPA Method 624 (GC/MS using the purge and trap technique). TOX results were generally much higher than results obtained by solvent extraction--GC methods (EPA Method 625 and/or 612).

The EOX approach, using the Dohrmann DX-20, involved significant modification of the sample inlet system of the instrument to allow the injection of 5-25 μL volumes of solvent directly into the combustion furnace. Precise and accurate determination of the

priority pollutant organic halides was obtained using this approach.

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).

Evaluation of a Method for Determining TOX in Wastewater

In this phase of the study, the microcoulometric titration approach (EPA Method 450.1) was found to be simpler to conduct and more precise than the SBP digestion approach in aqueous and solid waste samples, and the decision was made to discontinue efforts on the SBP approach in favor of the pyrolytic combustion microcoulometric titration approach. It was concluded, however, that the SBP approach does appear to be viable and may be advantageous in certain situations (e.g., in laboratories where a microcoulometric system is not available and the sample load does not justify purchasing the device). The Dohrmann DX-20 system was found to be easily assembled and relatively simple to operate. The slightly modified Method 450.1 was applied to a variety of wastewater samples, both spiked and non-spiked as listed below:

- Reagent water
- Industrial effluent from an aniline manufacturing facility

- Two industrial effluents from separate chlorinated hydrocarbon manufacturing facilities
- An aqueous leachate from a ferrous chloride spent catalyst waste sample
- POTW sewage from the Columbus, Ohio plant

For comparative purposes, the values obtained for POX as well as by solvent extraction/GC approaches (either EPA Method 625 or 612) were presented.

In virtually all cases, good recovery (90% or better) was obtained for the 1,2,4-trichlorobenzene (TCB) spike and analytical precision was generally 5-10% relative standard deviation (RSD). Further inspection of the data revealed that the TOX values were considerably greater than the combined POX and "extractable OX" values, and indicated that polar, non-extractable materials such as chlorinated humic acids were contributing to the TOX values.

A limited study was conducted to assess the feasibility of using the Dohrmann DX-20 system to determine the EOX content of water samples. The Dohrmann DX-20 system was modified by replacing the boat entry system with a Teflon-lined silicone septum held in place with a ball and socket glass fitting (supplied).

The method involved extraction of a one-liter sample aliquot with three 60-mL aliquots of cyclohexane, concentration of the extract by Kuderna Danish (K-D) concentration to 1 mL and injection of a 25 μ L aliquot of the extract. Recoveries were acceptable (>70%) in all cases, indicating that this approach can be used successfully to determine EOX content of water samples. The surrogate TOX method for wastewaters was presented in the appendix of the report.

Determination of EOX Content of Solids

The development of a method for determining EOX in solids was considered to be necessary because of the need to isolate and analyze separately the suspended solids in wastewater samples being analyzed by EPA Method 450.1. The approach selected was to extract the solid residue with a polar organic solvent (ethyl acetate) and to analyze the extract using the Dohrmann DX-20 microcoulometric system, modified for solvent injection. The EOX procedure was evaluated using the solid samples described below:

- A garden soil which had been air-dried and passed through a 30-mesh sieve

- Wet solids (47% solids) isolated from the aniline wastewater
- Wet solid waste (64% solids) obtained from a solid waste landfill
- Ferrous chloride spent catalyst waste (85% solids) from a chloroethylene manufacturing plant
- Drying and solid waste (50% solids) from a chloroethylene manufacturing plant

The solids were spiked with methanol stock solutions of TCB, trichloroaniline (TCA) or trichlorophenol (TCP) at various levels. TCB was recovered from all solids samples at the 25 μ g/g spike level better than 80%. TCA and TCP showed only about 50% recovery at the 25 μ g/g spike level.

Removal of potential interferences by inorganic chloride was also investigated. Washing the ethyl acetate extract with one mL of 1 M Ag NO₃ solution was effective in removing virtually all of the inorganic chloride.

In order to assess the detection limit of the method, seven replicates of a process blank and a 15 μ g/g (TCB as CL) process spike were analyzed on the Dohrmann DX-20. The data obtained indicated that the method can detect approximately 10 μ g/g of EOX.

Based on these data, the EOX/solids surrogate method appears to work quite well. However, because of the larger diversity of solid-sample type, this method should not be assumed to be accurate for uncharacterized samples without further validation. The surrogate method for EOX in solids was presented in the report's appendix.

Determination of POX in Water Samples

This phase of the study involved the use of the Dohrmann DX-20 system equipment with a special purging device. The sample preparation and workshop steps were essentially identical to those specified in EPA Method 624. For POX analysis, a 10-mL or smaller aliquot of water sample is placed in the purge device and a stream of CO₂ is passed through the purge tube. The purged components enter the combustion tube (held at 800°C) and are converted to the corresponding hydrogen halides.

Initial experiments to evaluate the recovery of the organohalide priority pollutants from reagent water revealed recoveries of 75% or greater for olefinic and aliphatic chlorine-containing

compounds and recoveries of approximately 50% for the chloroaromatics and bromine-containing compounds. Relative standard deviations were 10% or less in all cases indicating that the system was operating at good precision in spite of the low recoveries obtained.

Wastewater samples on which the method was evaluated are listed below:

- Columbus tap water
- Columbus POTW final effluent
- A final effluent from a plant producing aniline and related compounds
- Two final effluent samples from separate plants producing chlorinated hydrocarbon solvents (treated by steam stripping prior to discharge)
- An aqueous leachate from a spent FeCl₂ catalyst solid waste (chloroethylene manufacturing)
- A wastewater from a chemical manufacturing plant in which methylene chloride is used as a solvent

Results and Conclusions

Results of the analysis for the various water samples using the surrogate POX method were compared with results from analyses by EPA Method 624. The results obtained agreed quite well (within a factor of two) in most cases. Based on the results obtained in this study, it appears that the surrogate POX method can be used as an indicator of organic halide pollution in a variety of water types. However, several limitations of the method should be recognized. First, the recovery of purgeable organic halides is seldom greater than 85-90% and can be as low as 40-50%. Secondly, the recovery of brominated species is not quantitation and, at least in the case of bromoform, levels of less than 100 μ g/L cannot be quantified. The POX value obtained in an uncharacterized water sample will vary considerably depending on the properties of compounds present (e.g., bromine vs chlorine, percent halogen, purging efficiency, etc.). In view of these uncontrollable factors, the agreement between GC/MS and the surrogate POX was considered to be satisfactory.

In order to assess the low limit of detection of the surrogate POX method, several compounds were run according to the EPA/EMSL protocol for determining method detection limits (MDL). MDL's of 2-5 μ g/L were obtained in all cases except bromoform, which was not recovered at the 30 μ g/L level.

The surrogate POX method for wastewaters was presented in the report's appendix.

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Stephen Billels is the EPA Project Officer (see below).

The complete report, entitled "Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater," (Order No. PB 84-134 337; Cost: \$14.50, subject to change) will be available only from:

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