



## Project Summary

# Development of Analytical Test Procedures for the Measurement of Organic Priority Pollutants in Sludge

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The tremendous diversity of sludge characteristics presents a considerable challenge to precise and accurate determinations of trace levels of the organic priority pollutants in sludges. The primary objective of this research program was the development of test methods for the analysis of organic priority pollutants in sludges as would be generated from the treatment of municipal and industrial wastewaters. The research program was divided into two stages. In the first stage, a preliminary sludge analysis protocol was developed based on existing wastewater procedures. This was done to satisfy an immediate need of the U.S. Environmental Protection Agency (EPA) for test methods to be used in support of a project initiated to determine the occurrence and fate of the organic priority pollutants in representative publicly owned treatment works (POTW). Based on the experience in this program and as a result of a systematic study of sludge analysis techniques, a refined and revised analytical protocol was developed.

This report details the second phase of the project, which was a systematic study of sludge analysis techniques. For purposes of analysis, a separate procedure was provided for the purgeable and extractable organic priority pollutants in sludges. In each case, the components were identified and quantitated using GC/MS techniques. The development of a procedure for the analysis of the volatile components

involved an investigation of various purging procedures intended to improve recoveries, reproducibilities, and detection limits.

Since sludges contain a wide variety of extractable organics which can interfere with the GC/MS analysis, the development of suitable cleanup procedures was required. Selected techniques of extract cleanup were applied in various combinations, the most successful of which are included in the recommended protocol.

*The project summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 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).*

### Analysis of Purgeables from Sludge -- Method Development

This aspect of the research was directed toward applying and modifying the purge and trap GC/MS procedures developed by the EPA for wastewater analysis.

Preliminary experiments with sludges for various POTW indicated that most but not all sludges could successfully be purged if the sample aliquot was diluted to approximately 0.5% (w/v) total solids. Recoveries for analytes spiked into POTW sludges and analyzed by this procedure showed poor precision during the recovery

determinations and a decrease in the method detection limit as a consequence of the sample dilution. Efforts to overcome these deficiencies form the basis of this study. Table 1 lists the priority pollutants used to develop the methods.

**Table 1.** *Representative Purgeable Organic Priority Pollutants Used for Method Development and Evaluation Experiments*

**Purgeables:**

Benzene  
Carbon Tetrachloride  
Chlorobenzene  
Chloroform  
1,2-Dichloroethane  
1,1-Dichloroethene  
Ethyl Benzene  
Tetrachloroethene  
1,1,1-Trichloroethane  
Trichloroethene  
Vinyl Chloride

**Extractables:**

1,4-Dichlorobenzene  
Hexachloroethane  
bis-(2-Chloroisopropyl)Ether  
bis-(2-Chloroethyl)Ether  
Acenaphthylene  
2,6-Dinitrotoluene  
Fluoranthene  
Benzidine  
3,3'-Dichlorobenzidine  
Benzyl n-Butyl Phthalate  
bis-(2-Ethylhexyl)Phthalate  
Benzof(a)pyrene  
Phenol  
2,4-Dimethylphenol  
2,4-Dichlorophenol  
Pentachlorophenol

The relative influences of dissolved solids and suspended solids on the purging efficiencies of analytes from sludges were investigated by determining analyte recoveries from spiked sludge and spiked sludge supernatant (SS). Aliquots of primary POTW sludge (4.8% solids) were centrifuged, and the supernatants were decanted. The supernatants and replicate aliquots of unfractionated sludge were spiked and analyzed by the preliminary POTW sludge method.

The recoveries for the spiked compounds from the SS were both higher and less variable than from the unfractionated sludge for all compounds. Furthermore, the range of recoveries observed for the supernatant aliquots was similar to those typically observed for spiked clean water. Hence, it is likely that the presence of dissolved solids in the primary sludge does not significantly affect the purging efficiencies of the spiked compounds.

The addition of salt or a high-boiling hydrophilic organic compound (with a very low tendency to purge from water), to sludge aliquots prior to purging was evaluated as a means of enhancing the purging efficiencies of volatile compounds, or at least improving the reproducibility of purging. The recoveries of compounds spiked into sludge and SS indicated that interactions of the purgeable compounds with the SS may have a significant influence on their purging efficiencies. The addition of salt or high-boiling organic was an attempt to alter favorably those interactions to provide a consistent matrix for purging.

The influences of salt or an organic on purging from aqueous media were investigated by analyzing spiked clean water by purge and trap GC/flame ionization detection (FID). Aliquots of volatile-free water were spiked and diluted to 10 mL prior to analysis with one of three diluents: (a) volatile-free water; (b) saturated sodium chloride in volatile-free water; or (c) 10% ethylene glycol in volatile-free water. The detector responses were compared to determine the influence of each diluent. Ethylene glycol was selected as the organic additive because of its low volatility, good aqueous solubility, and general availability.

Recovery experiments were also conducted with primary POTW sludge (2% solids). Spiked and unspiked sludge aliquots were diluted with the salt or ethylene glycol solutions and analyzed by the preliminary purge and trap GC/MS methods. No specific advantages from adding salt or ethylene glycol were apparent. Recoveries for all compounds were good. Recoveries for carbon tetrachloride were significantly higher than typically observed using the preliminary POTW sludge protocol. However, both additives appeared to increase significantly the tendency of the sludge to foam during purging. Hence, the use of salt and ethylene glycol in sludge dilutions did not provide significant overall improvements for the sludge method.

### Alternative Purging Hardware Systems

Alternative purging hardware systems which provide mechanical mixing during purging were evaluated for their potential to enhance desorption of analytes from the sludge solids to the supernatant and to improve transfer to the purge gas stream. All systems evaluated were designed to be used as direct replacements for the conventional purge tube in the purge and trap system employed in the

preliminary POTW sludge method. Four hardware systems were evaluated. Three configurations were fabricated using a small round-bottom flask: stirred purging, stirred impinging, and sonicated impinging. The fourth system evaluated was a stirred-purge configuration using a specially designed bottom frit tube.

The efficiencies of transfer of volatile compounds from aqueous solution to the gas phase afforded by the stirred purging, stirred impinger, and sonicated impinger systems were evaluated by comparing the chromatographic responses for compounds spiked into water and analyzed with these systems. The chromatographic responses for identical solutions were analyzed via the conventional purge tube.

The performance of the bottom frit tube with and without mechanical stirring was compared with that of the conventional purge tube for spiked water analyzed by purge and trap GC/FID. The responses observed for a few compounds analyzed in spiked water with the bottom frit tube without stirring were lower than those from the conventional purge tube. The bottom frit tube with stirring produced responses generally as high or higher than the conventional tube. These results likely reflect poorer contact of the sparging bubbles with the water in the unstirred bottom frit tube relative to the conventional purge tube.

### Recoveries

The performance of the bottom frit tube was further evaluated by determining the recoveries for compounds spiked into aliquots of primary POTW sludge (2% solids) immediately prior to analysis. The sludge aliquots were diluted and analyzed by the purge and trap GC/MS method using the stirred bottom frit tube in place of the conventional purge tube. Good recovery data were obtained for all the compounds except carbon tetrachloride. The carbon tetrachloride response was too low to determine under the specific GC/MS operation conditions utilized. Recovery determinations were very reproducible. No foaming was observed with the bottom frit tube, whereas aliquots of the same sample previously analyzed with the conventional purge tube foamed profusely.

Since good data on accuracy and precision were obtained with the stirred bottom frit tube and there was no appreciable foaming, the system was evaluated for its capability to purge larger aliquots of sludge without troublesome foaming. Aliquots of 2.5, 5.0, and 10.0 mL of primary sludge (2% solids) were spiked with 250 ng of each of the purgeable

spiking compounds just prior to analysis, diluted as required to 10 mL with volatile-free water, and analyzed by the preliminary POTW sludge GC/MS method. The recoveries of the spiked purgeable compounds in different volumes of sludge are shown in Table II. Recoveries for all compounds were good and did not appear to be strongly dependent on the volume of sludge purged. No foaming problems were encountered, even with 10-mL aliquots. Evidently, the force imparted by the magnetic stirring bar swirling the sludge aliquot was an efficient foam dispersion mechanism.

Recoveries did not appear to be dependent on the size of the aliquot purged even though the spike concentrations ranged from 125 µg/L in the 2.0-mL aliquots. Recoveries of compounds in 10.0-mL aliquots of spiked sludge (at 25 µg/L) analyzed with the stirred bottom frit tube were very similar to those in 2.0-mL aliquots of spiked sludge (at 125 µg/L) using the conventional purge tube. In addition, no foaming was observed stirred purging, even while purging 10.0-mL aliquots of undiluted sludge.

### Precision and Accuracy—Purgeables

The precision and accuracy of the purgeables method were evaluated by determining recoveries for spiked compounds from five primary sludges. The subject sludges, three from POTW receiving various fractions of wastewater from residential and industrial sources and two from plants treating industrial wastewaters, were selected to provide a wide variety of sludge characteristics with which to test the performance of the method. The results of these determinations are shown in Table III.

Although the recoveries observed were generally good, many recovery determi-

**Table III.** Accuracy and Precision for Purgeable Organics

| Compound              | Three POTW Sludges |       |                |                    | Two Industrial Sludges |       |                |                    |
|-----------------------|--------------------|-------|----------------|--------------------|------------------------|-------|----------------|--------------------|
|                       | Spike Recovery     |       | Spike Recovery |                    | Spike Recovery         |       | Spike Recovery |                    |
|                       | Spike Level        |       | Mean (%)       | Standard Deviation | Spike Level            |       | Mean (%)       | Standard Deviation |
|                       | Min                | Max   |                |                    | Min                    | Max   |                |                    |
| Benzene               | 1                  | 100   | 160            | 55                 | 1                      | 100   | 98             | 25                 |
| Chloroform            | 2                  | 200   | 100            | 58                 | 2                      | 200   | 76             | 22                 |
| 1,1-Dichloroethene    | 5                  | 170   | 170            | 53                 | 5                      | 500   | 110            | 51                 |
| Tetrachloroethene     | 3                  | 300   | 150            | 33                 | 3                      | 300   | 150            | 70                 |
| Vinyl chloride        | 50                 | 500   | 130            | 38                 | 5                      | 500   | 110            | 47                 |
| 1,2-Dichloroethane    | 5                  | 500   | 140            | 51                 | 5                      | 500   | 100            | 28                 |
| Trichloroethene       | 20                 | 200   | 160            | 69                 | 2                      | 200   | 140            | 44                 |
| 1,1,1-Trichloroethane | 16                 | 1,600 | 130            | 47                 | 16                     | 1,600 | 110            | 40                 |
| Chlorobenzene         | 2                  | 200   | 120            | 36                 | 2                      | 200   | 160            | 62                 |
| Ethyl benzene         | 5                  | 500   | 120            | 26                 | 5                      | 500   | 150            | 55                 |

nations were likely influenced by relatively high concentrations of the spiking compounds in the unspiked sludges. Several compounds were present in some of the sludges at levels greater than the spike level, and in some cases concentrations in the unspiked sludges were more than 10 times the spike level. Recoveries for the latter cases were not representative of the method precision and accuracy and were excluded from the table. Zero or very low recoveries were observed for carbon tetrachloride in all sludges except Industrial No. 2. Carbon tetrachloride and, to some extent, chloroform are frequently troublesome compounds because of poor sensitivity to mass spectrometric detection. Although the detection limits for these compounds were chosen based on previous work, their detection limits in these particular sludges are evidently higher than is typical. Determinations of vinyl chloride, chlorobenzene, and 1,1,1-trichloroethane were frequently obscured by coeluting interferences in the POTW sludges.

Nonetheless, in most cases, the recoveries observed were both good and reproducible. Only 11% of all recovery

determinations were less than 50%. More than 63% fell within the range of 50-150% recovery. An additional 25% of the recovery determinations exceeded 150%. The relative standard deviations (RSD) for triplicate recovery determinations were generally low. More than 90% of the RSD were 30% or less. Of those, 27% were less than 10% RSD. The method reproducibility was surprisingly good considering the difficulty in removing representative aliquots from a heterogeneous sample matrix.

### Analysis of Extractables from Sludge--Method Development

The method development and evaluation experiments described in this section were conducted using a subset of the organic priority pollutants to simplify sample spiking and recovery determinations. These compounds were selected to represent the physical and chemical characteristics of most of the organic priority pollutants. The list of spiking compounds is shown in Table I.

The primary objective in developing the extraction method was to adapt industrial wastewater screening methods for sludge extraction and extract cleanup, so as to provide extracts of sufficient quality for GC/MS analysis. Many of the extractable compounds were expected to associate strongly with the sludge solids. It was anticipated that the wastewater extraction method (simple liquid-liquid partitioning with dichloromethane) would not provide sufficient contact of the extracting solvent with the solids to allow efficient extraction of those compounds from sludges, and would be hindered by formation of emulsions. A procedure using a high speed homogenizer probe to provide vigorous mixing and blending of the sludge aliquot with the extracting solvent was evaluated.

**Table II.** Recovery of Spiked Purgeable Compounds from Spiked Sludge by Stirred Purging with a Bottom Frit Tube; Effect of Different Volumes of Sludge.

| Compound                       | Spike Level (ng) | 10-mL Aliquot Unspiked Sludge (ng) | Spike Recovery (%) |      |       |
|--------------------------------|------------------|------------------------------------|--------------------|------|-------|
|                                |                  |                                    | 2.5 mL             | 5 mL | 10 mL |
| Benzene                        | 250              | 49.2                               | 133                | 142  | 148   |
| Carbon Tetrachloride           | 250              | ND <sup>a</sup>                    | 77                 | 68   | 55    |
| Chloroform                     | 250              | 43.6                               | 101                | 123  | 122   |
| 1,1-Dichloroethene             | 250              | 123                                | 112                | 165  | 194   |
| Tetrachloroethene <sup>b</sup> | 250              |                                    |                    |      |       |
| 1,2-Dichloroethene             | 250              | ND                                 | 102                | 114  | 152   |
| Trichloroethene <sup>b</sup>   | 250              |                                    |                    |      |       |
| 1,1,1-Trichloroethane          | 250              | ND                                 | 102                | 117  | 133   |
| Chlorobenzene                  | 250              | 19.0                               | 135                | 108  | 61    |
| Ethyl Benzene <sup>c</sup>     | 250              | 118                                |                    |      |       |

<sup>a</sup> ND = not detected.

<sup>b</sup> Ion plots for all unspiked and spiked samples exhibited saturated peaks.

<sup>c</sup> Ion plots for all spiked sludge samples exhibited saturated peaks.

Unfortunately, this vigorous homogenization/centrifugation procedure also extracted large quantities of lipids, fatty acids, and other high molecular weight compounds present in POTW sludges. These compounds can cause significant interferences during GC/MS analysis and necessitate extract cleanup.

Three alternative extraction procedures were evaluated for sludges in an attempt to develop a more efficient, selective, and less time consuming extraction method. The procedures evaluated include: continuous liquid-liquid extraction (CLLE), steam distillation, and microextraction. As expected, each of these procedures achieved promising recoveries for concentrating spiked compounds from water.

None of the tested methods resulted in any significant improvements over the preliminary protocol. Hence, the homogenization/centrifugation method was selected for the sludge protocol. This selection necessitated additional evaluation of extract cleanup procedures as alternatives or supplements to the gel permeation chromatography (GPC) method used in the preliminary POTW protocol.

### Extract Cleanup Studies

Successful employment of a rigorous, nonselective extraction procedure for sludges, necessitated the use of a very selective and efficient extract cleanup procedure to produce extracts of sufficient quality for reliable GC/MS determination. Two extract cleanup mechanisms were evaluated to meet these requirements, molecular size discrimination and polarity selection. Various GPC procedures were evaluated to determine the optimum molecular size fractionation procedure. The polarity-based cleanup method evaluated was adsorption chromatography on silica gel and Florisil. The performance of adsorption procedures was evaluated for sludge extracts both with and without GPC precleaning.

Five GPC packings (Bio-Beads SX-2, SX-3, SX-4, SX-8, and Sephadex LH-20) were evaluated with three solvent systems. The solvents tested were dichloromethane, 15% cyclohexane in dichloromethane, and 50% cyclohexane in dichloromethane.

Adsorption chromatography experiments were performed using 1% deactivated Florisil or 3% deactivated silica gel. The elution scheme was:

- fraction I: 20 mL hexane
- fraction II: 50 mL 10% dichloromethane in hexane
- fraction III: 50 mL dichloromethane in hexane

- fraction IV: 150 mL 5% acetone in dichloromethane

The elution volumes and peak profiles data obtained for the various gels and solvent combinations indicate that the best overall separation is obtained with SX-3 gel when dichloromethane is the eluting solvent. Furthermore, the selection of dichloromethane as the elution solvent is directly compatible with the homogenization/centrifugation of sludge extracts.

The Base/Neutral (B/N) and acid extracts of sludges were chromatographed in one or more 5.0-mL injections. The combined cleaned extract fractions were concentrated to 1-5 mL for GC/MS analysis. Extracts that were still highly colored were cleaned by a second pass through the GPC column.

The B/N and acidic extracts were analyzed by GC/MS according to the procedures described in the industrial wastewater protocol.

The recoveries observed for most of the test compounds were fairly good, although several compounds were not recovered from the primary sludge. These compounds were hexachloroethane, benzidine, 3,3'-dichlorobenzidine, and pentachlorophenol. Part of the loss of hexachloroethane can be attributed to volatilization during extract concentrations. Dilution of the primary sludge extracts to reduce the concentration of interfering coextractants also reduced the spike levels to at or near the detection limit.

### GC/MS Procedures

Capillary GC/MS procedures were evaluated as an alternative to the packed column GC/MS methods described above. Four wall-coated-open-tubular (WCOT) capillary columns were evaluated using standard performance test mixtures and solutions of the B/N and acidic test compounds. Of the four columns tested,

the SE-54 fused silica column exhibited the best overall performance.

The suitability of the SE-54 fused silica column for analyses of sludge extracts was evaluated by chromatographing the spiked sludge extracts prepared for the evaluation of adsorption chromatographic cleanup procedures. The better resolution and inertness of the SE-54 capillary column (relative to the packed column) provided GC/MS data for B/N extracts that were easier to interpret.

### Precision and Accuracy—Extractables

The recovery data was shown to vary somewhat from various sludge sample types. Some of this effect is likely due to the high concentration of some of the analytes in the unspiked sludge samples. In general, recoveries were lower for the more polar compounds, such as benzidine. Of all recovery determinations, 49% fell within the range of 50-150%. An additional 19% were lower than 50% recovery, and only 8% of the recoveries were greater than 150%.

The accuracy of the method was somewhat dependent on the particular sludge samples. However, the precisions of the recovery determinations were good. The relative standard deviations for triplicate determinations were 30% or less for 95% of the measurements and 10% or less for 62% of the measurements. In view of the complexity and diversity of municipal and industrial wastewater treatment sludges, the precision and accuracy results presented here demonstrate that the protocol developed can reliably be applied to the analysis of the organic priority pollutants in sludge. The success of this protocol for the variety of extractable compounds for which it was developed and evaluated indicates that the methods included may also be useful for many nonpriority pollutant analytes.

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*The complete report, entitled "Development of Analytical Test Procedures for the Measurement of Organic Priority Pollutants in Sludge," (Order No. PB 84-129 048; Cost: \$26.50, subject to change) will be available only from:*

*National Technical Information Service  
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