

ADA-OKLAHOMA 74820
**Solvent Minimization in the Continuous Liquid/Liquid Extraction
of Aqueous Samples for Semivolatile Organics**

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Introduction

Continuous extraction (CE) of aqueous samples is quickly replacing separatory funnel extraction for semivolatile organics. The advantages of continuous liquid/liquid extraction over separatory funnel extractions include the following:

- 1) improved extraction efficiencies and accuracy due to the increased number of theoretical plates associated with the re-distilled solvent being continuously exposed to the sample;
- 2) savings in manpower due to the reduction of both time and physical labor;
- 3) the effectiveness of the CE technique in highly contaminated matrices containing suspended solids (a problem with Solid Phase Extractions);
- 4) the effective elimination of emulsions common with separatory funnel extractions of environmental samples; and the
- 5) improved precision using CE.

One disadvantage of the traditional CE procedure is the considerable volumes of solvent that is required to perform the analysis versus the separatory funnel method. A commonly used "macro-sized" extractor is illustrated in Figure 1. The continuous extraction technique frequently requires 600 to 1000 mLs of methylene chloride solvent to perform a single extraction. Compare this to the 180 to 360 mLs to perform a routine separatory funnel extraction. Given the overall expense of using methylene chloride, both the initial purchase cost and the extremely costly disposal fee (\$200+ per 55 gallon drum), it would be desirable to miniaturize the procedure in order to minimize the volume of solvent. Miniaturization was considered more desirable than Solid Phase Extraction (SPE) or other technologies, which involve different chemistries than liquid/liquid extraction, since the use of these techniques for EPA's programs would require obtaining analytical "variances". Such variances may take many years to obtain.

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A design for a miniaturized continuous extractor (Figure 2) was developed so as to maintain the sensitivity of the procedure, yet minimize the solvent necessary to perform the analysis. A full liter of sample was extracted, as per the current Agency protocols (SW-846, EPA NPDES Methods 625 and 608, SDWA Method 508, Superfund CLP Statement of Work) to assure sensitivity and to help assure a sample aliquot of sufficient size to be accurately representative. This sample volume also avoids the necessity for concentration of the extract obtained to a smaller final volume to maintain sensitivity, e.g., less than 0.5 mL. It was decided to avoid attempts to reduce the final extract volume to less than 1 mL, since the extract could easily go to dryness. Going to dryness would result in the loss of the more volatile compounds.

A series of extraction recovery experiments were performed using the prototype extractor design to determine the:

- * Necessity for design modifications and/or extraction protocols necessary to maximize target compound recoveries with the goal being to obtain the performance specifications (% recovery and standard deviation), required by current Agency protocols (EPA Methods 625 and 608).

- * Effect upon the analytical results (accuracy and precision). Recovery of semivolatile organics, pesticides and PCBs listed as target compounds under the Superfund Contract Laboratory Program, EPA methods 608 and 625 (NPDES) and 508 (SDWA) were determined. This work followed the "initial demonstration of capability" procedures specified per the 600 series methods. These procedures test the performance of the method (all steps of the method) against specified accuracy and precision criteria specified for each target compound. In addition, the performance of the miniature extractors (employing 200 mLs of solvent--Figure 2) were compared to "macro" size extractors (employing 700-1000 mLs of solvent--Figure 1). These larger "macro" CEs have been routinely used by our laboratory for the analysis of semivolatile organic compounds since 1986.

- * Ease and practicality of use.

- * Consistency with the Agency's mandatory analytical procedures. As part of this work, it was determined whether special variances by the Agency are necessary for use of these protocols in the NPDES, SDWA, Superfund and RCRA programs.

- * Effectiveness of the extractor in recovering compounds from wastewater samples.

Disclaimer

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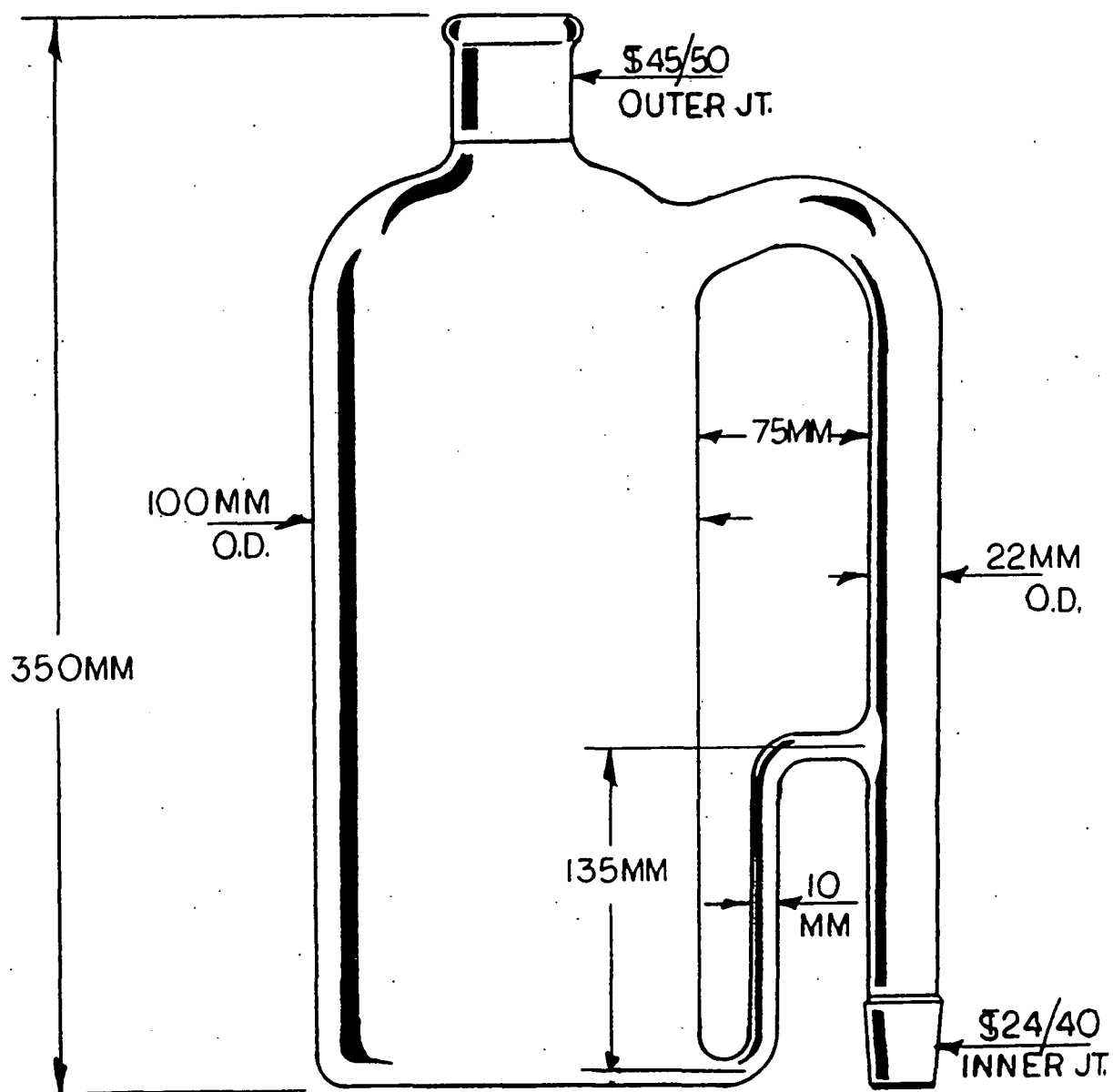
I. Experimental

A. Reagents & Equipment

Note: Brand names and catalog numbers are included for illustrational purposes only.

1. Methylene chloride, B&J high purity solvent, product #300, contains cyclohexene preservative to inhibit HCl formation.
2. Sulfuric acid, Baker, Instra-Analyzed, #9673-03, 6N H₂SO₄ prepared by slowly adding 167 mLs of concentrated H₂SO₄ to 833 mLs of reagent water.
3. Multi-range pH paper strips, EM-Reagents ColorpHast, pH indicator strips, pH 0-14.
4. Boiling Stones, Hengar Co., carborundum #12 granules, #133-B. Conditioned by muffling at 450°C for 3-4 hrs.
5. Sodium sulfate, anhydrous, granular, Mallinckrodt, product #8024. Muffled for 3-4 hours at 450°C. Stored in glass.
6. Glass wool, Pyrex brand, fiber glass, sliver 8 micron, Corning Glass Works. Muffled for 3-4 hours at 450°C.
7. Muffle furnace, Blue M Power-O-Matic 80.
8. Muffle furnace, Blue M Touch Master, Model #CFD-20F-6.
9. Heating mantle, Glas-Col Apparatus Co., Terre Haute, In 47802 Cat. No. TM98, (80 Watt, 115 V).
10. Variable transformer, Staco Energy Products Co., type 3PN1010.
11. 125 mL boiling flask.
12. 1000 mL graduated cylinder.
13. Allihn condenser, 45/50 joint, 4 ball, with special drip ring to catch condensation from room humidity.
14. 3-ball Snyder columns, (macro- and micro-).
15. 500 mL Kuderna-Danish evaporative flask.
16. 10 mL graduated Kuderna-Danish concentrator tube.
17. Continuous extractor, one piece, glass, obtained from LAB Glass, Inc., Vineland, Pa. (Figure #2--"Micro-" and Figure #1--"Macro-"). The "macro-" size extractors are routinely employed in environmental laboratories. The miniature ("micro-") extractors cost about \$100/each.
18. Drummond pipet, 100 uL dispensing pipettor, Model #375, used for pipetting spikes.
19. Volumetric pipet, 1 mL.
20. Volumetric flasks, 1 mL, 2 mL and 10 mL.
21. Milli-RO15 Millipore (10 megaohm-cm, deionized water) System.
22. Carbon filter system (made internally, 5 lbs. activated charcoal) for final polishing of lab pure water.
23. Screw cap vials with teflon-faced silicone septa, 1.8 mL, Cat. Nos. 3-3286 (vials) and 3-3210 (caps and septa), Supelco, Bellefonte, Pa.
24. Pyrex funnels (for sample addition), 60°, 145 mm stem length.
25. Pyrex stirring rods (for sample pH adjustment), 370 mm length, and 15 mm diameter.
26. Finnigan MAT 4500 GC/MS. The system equipped with: a

Figure 1



CATALOGUE

DESCRIPTION

DATE 6-28-93

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SCALE

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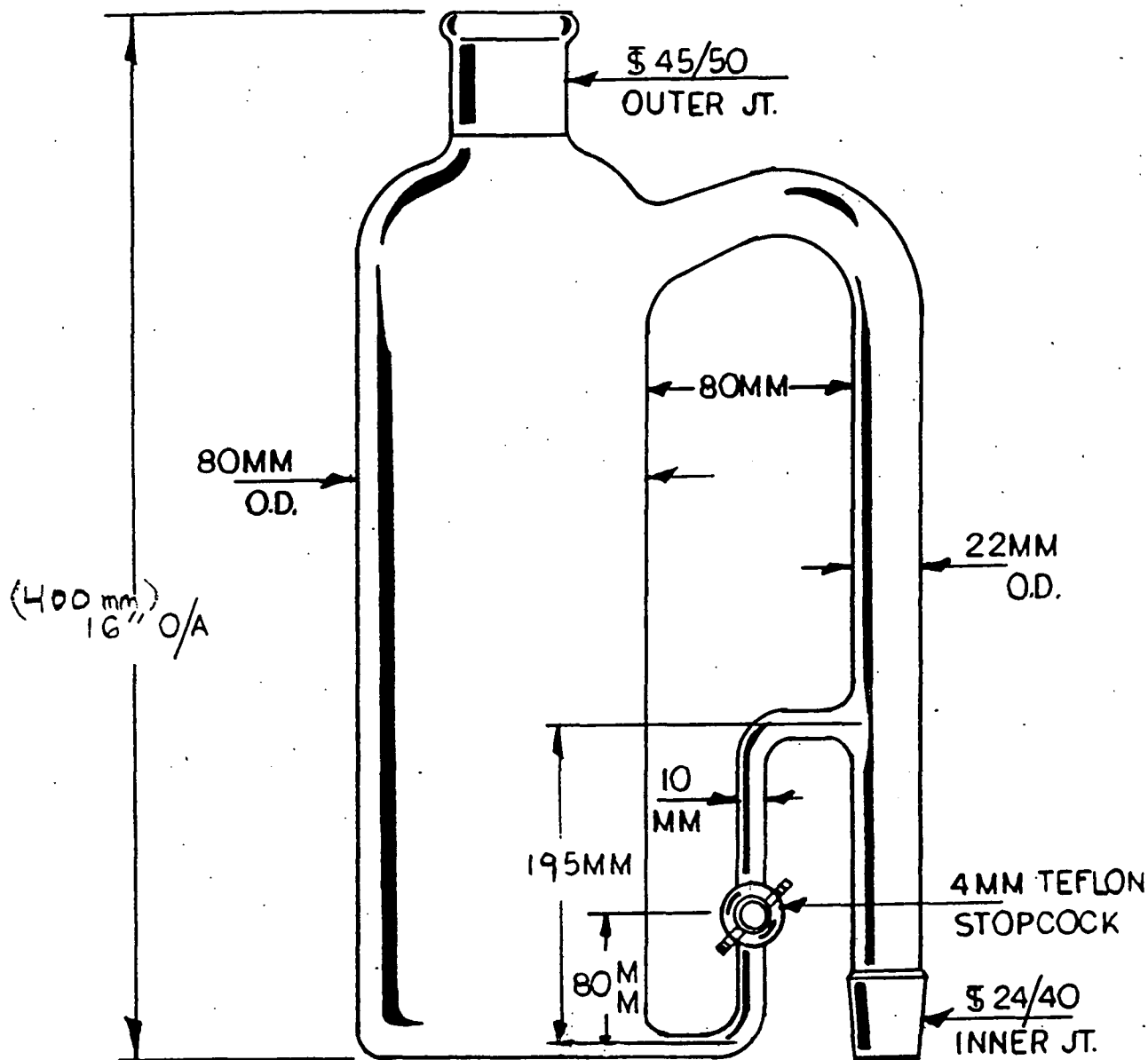
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RAW MATERIAL COMPONENTS

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Figure 2



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- quadrupole analyzer and EI source; an HP 7673 automatic sampler and an Incos data system. The Fused Silica Capillary Column (FSCC) was a DB-5, J&W Scientific, 30M x 0.32mm ID with a film thickness of 1 um. The GC temperature program was: 30°C for 2 minutes, ramped to 300°C at 10°C/minute.
27. HP 5890 Series II Gas Chromatograph/ECD/FID system, with an HP 7673 automatic sampler and HP 3365 Chemstation data system. The ECD was equipped with a Supelco SPB-608, FSCC, 30M x 0.53 mm ID, with a film thickness of 0.50 um. The GC program for the pesticides, (ECD) was from 150°C to 280°C at 10°C/minute, with a final hold of 10 minutes. The FID was equipped with a Supelco #2-4050, SPB-5 FSCC, 60M, 0.32 mm ID, with a 0.25 um film thickness. For FID analyses, the GC was programmed from 50°C to a 280°C at 5°C/minute, with a final hold of 10-25 minutes (compound dependent).
 28. S-EVAP, solvent recovery system (during K-D process), Organomation, Inc., South Berlin, MA.
 29. Re-circulating water bath (condenser cooling), FTS Inc., model RC-25.
 30. Methanol, B&J, purity suitable for Purge & Trap analysis.

B. Calibration standards and Spiking Solutions/Procedures

The calibration and spiking solutions used were all from EPA's QA Materials Bank in RTP, NC or from certified CRADA vendors. A detailed listing of the sources and preparation procedures for the following solutions is included in the Appendix: spiking solutions (general); calibration standards and multiple point curve preparation; internal standards; Superfund CLP "Matrix Spikes" (MS); Superfund CLP "Surrogate Compound" spikes; BNA spiking QC solutions (CRADA); benzidine/s and aniline/s spiking solutions; Pesticide spikes (single component analytes, toxaphene, chlordane, and PCBs).

C. General Procedures:

GC Screening:

The initial phases of this work involved numerous re-designs of the dimensions of the miniaturized CE. As a consequence, a simple spiking mixture was used (matrix spike and/or surrogate spike delineated above). This reduced the expense of using more costly spiking cocktails and provided relatively simple mixtures which could be analyzed via GC/FID. Once the design was optimized, the more complex mixtures were tested using a GC/MS system. This tiered approach saved much expense (reference materials and costly GC/MS use), and helped speed the progress.

Loading the Continuous Extractors:

Miniature or "Micro-" CE Extractors:

In a fume hood the stopcock on the CE solvent return line was

closed (see figure 2), a 125 mL flat bottom boiling flask was attached (containing several boiling stones). 200 mLs of methylene chloride were placed into the continuous extractor. A 500 mL volume of the 1 liter sample was added using a glass funnel with 145 mm glass stem. This procedure helped assure that the aqueous sample would not displace the solvent (avoid water break-through of the solvent layer). The remaining volume of sample was then poured into the extractor. The dense solvent was thus layered below one liter of aqueous sample and therefore exposure of the analyst to solvent vapor was minimized. The extractors were secured in a ringstand with the solvent flask placed in a heating mantle. Each one liter aliquot was adjusted to a pH <2 using 6N H₂SO₄ (5mL auto-dispenser), except for spikes of anilines and benzdines, which were extracted at pH >11 (6N NaOH pH adjustment). Also the pesticides/PCB extractions were performed at pH 5.5-6.5 (no pH adjustment necessary). The samples were stirred using a 370 mm glass rod and a drop of the solution was tested with pH test strips. The samples were then spiked with 100 uL-1 mL aliquots of the appropriate stock solutions.

An Allihn condenser was attached. An FTS refrigerated water recirculator was used to cool the condensers. The temperature of each condenser was 5°C. The stopcock was opened and approximately 50 mL of methylene chloride siphoned over into the boiling flask.

The heating mantles were turned on after the condensers were cold to the touch and extraction continued for 24± 2 hours. All extractions were generally carried out in the dark (no sunlight and a minimum of exposure to fluorescent lighting) to avoid photo-decomposition of light-sensitive compounds.

The extracts obtained were concentrated via the Kuderna-Danish procedure specified by EPA NPDES method 625² (macro followed by micro K-D/Snyder columns). However, a condenser device was employed during the macro K-D step to assure prevention of emissions (S-EVAP from Organomation Assoc., Inc., South Berlin, MA).³ Also, less Na₂SO₄ was employed for extract drying (20-30 grams was used).

"Macro-" CE Extractors (figure #1):

The operation of the these larger extractors was very similar. However, 600-1000 mL of solvent was used and loading of the methylene chloride was without the benefit of a stopcock in the solvent return-line. The flow rate through the extractors was approximately 6 mLs/minute (rheostat set at 60% full scale).

Instrumental Analysis:

A tiered approach of analysis was employed when working with the design configuration of the CE. To help resolve and correct CE design problems, simple spiking solutions were used to verify performance and analyses were performed on the GC/FID. Once the design was finalized all analyses were performed by GC/MS,

except for toxaphene and PCBs, which were via GC/ECD.

GC/MS analysis was performed (GC/MS via 70 eV electron impact as per EPA method 625² for the reported recoveries of the target compounds, except for Toxaphene and PCBs, for which GC/ECD was employed.

Calculations: (The details of calibration solution preparation are included in the Appendix).

A reference solution (same volume of material that was added as the spike), was prepared in a volumetric flask (same volume as the final volume for the K-D process).

The reference solution was analyzed and concentration was verified versus a 100, 50, 20 and 10 ng calibration standard curve prepared from AccuStandard stock solutions. The quantitation was based on internal standard (response factor) calculations as per method 625.

The percent recovery of spiked material was determined as follows:

$$\% \text{ Recovery} = \frac{\text{ng measured in extract} \times 100}{\text{ng measured in reference}}$$

This technique took advantage of the improved precision associated with the internal standard technique.

The exception to this reference solution approach was the analyses of the "BNA Spiking Solution," (48 priority pollutants). Quantitation was performed as based on the AccuStandard "Calibration Standards (GC/MS)". This quantitation procedure for the BNAs was the same for the "macro-" and "micro-" continuous extractors. As resultant extracts were ideally 100 ng/uL, % recovery was the same as the ng/uL measured from the calibration curve.

D. General Quality Control:

- a. All glassware including CEs were solvent rinsed, soap and tap water cleaned, deionized water rinsed and heated in a high temperature oven (400-450°C) for 6-8 hours prior to use.
- b. All surrogate, matrix spike and priority pollutant standards, and spiking materials were certified materials (CRADA) or were obtained directly from the USEPA Quality Assurance Materials Bank in RTP, NC.
- c. The GC/MS mass assignments were calibrated with FC43 prior to analyses.
- d. The GC/MS relative mass abundances were tuned by obtaining the spectrum of DFTPP. This was stressed for the identification of non-target compounds in the analyses of

wastewater.

- e. Immediately before GC/MS analysis, each sample was spiked with an internal standard mixture. GC/FID/ECD used the external standard quantitation technique. Each batch of samples analyzed by GC/MS and GC/FID/ECD included calibration check standards, analyzed throughout each analytical run.
- f. The sensitivity of the GC/MS instrument to 40 ng of d10-phenanthrene was at least 50,000 area counts. The sensitivity of the GC/FID/ECD was confirmed by GC/MS analyses.
- g. All surrogate and matrix spike recovery limits referenced in this study were from the Superfund Contract Laboratory Program (CLP) protocols. The recovery limits for the BNAs and pesticides were as per EPA Methods 625 and 608.
- h. Compound spike recoveries were computed against a the response to a reference standard prepared the same day the samples were extracted. Reference standards and samples were analyzed on the same day and on the same GC/MS or GC/ECD. The exception to this procedure was for the analyses of BNA spikes (48 compounds), in which a freshly prepared multiple point calibration curve was employed to determine the concentration of the analytes and % recovery was calculated vs. the certified values for the spiked QC materials.
- i. Data quantitation was performed by automated procedures using Incos software (GC/MS Finnigan MAT, San Jose, California) and HP Chemstation software (GC/FID, GC/ECD Hewlett Packard, Palo Alto, California).
- j. All compound identifications via GC/MS were made by comparing known reference spectra to those of the unknowns. GC/FID identifications were based on retention time matches to reference material, with GC/MS confirmation. GC/ECD identifications were based on retention time matches to reference materials.
- k. All spikes into aqueous matrices were prepared in a hydrophilic solvent.
- l. Precision and accuracy were routinely based on four (or more) replicate spikes carried through the entire analytical process.

II. Results and Discussion

A major initial challenge of this work was to eliminate the carry-over of water into the solvent reservoir (boiling flask). A

combination of design changes and procedural changes (loading technique) has eliminated this problem and the associated poor recoveries of hydrophilic compounds (erratic and low recoveries).

Miniature Continuous Extractor Design (Height of the S-shaped Solvent Return Line):

Initial trials were performed on continuous extractors (prototype that used approximately 100 mLs of methylene chloride) by analyzing laboratory pure water fortified with the CLP matrix spike and surrogate compounds. This afforded a relatively inexpensive mixture which resulted in simple chromatographic runs which could employ GC/FID analyses. A number of difficulties with these preliminary designs were encountered. One critical parameter was the height of the "S" shaped solvent return-line. The distance from the base of the extractor to the top of the return-line directly determined the depth of the solvent below the aqueous sample. At the initial height of 175 mm, water routinely "broke through" the solvent reservoir during the extraction. In addition, this design included a return glass tubing line with an inside diameter of 4 mm and a 2 mm Teflon stopcock. It was found that any water droplets in the solvent return-line stopped the flow of solvent (surface tension). The height of the "S" tube was adjusted to 185 mm and the inside diameter of the tubing was adjusted to 10 mm. A 4 mm Teflon stopcock was bored out to interface with the 10 mm tubing. These adjustments largely avoided water carryover. Matrix spike and surrogate results were much improved, but water (aqueous sample) would periodically break through the solvent reservoir (base of the continuous extractor). As indicated in Table #1, the recovery of surrogates were acceptable but were more erratic and lower when water was observed in the extract. The greatest reduction in recovery was associated with the phenolic compounds (2-fluorophenol and d5-phenol), which have great affinity for water and could be easily lost during the drying step with sodium sulfate (significant quantities of water causes the Na_2SO_4 to form lumps that could entrap the associated hydrophilic compounds). Matrix spike recoveries were similarly acceptable. Only trace amounts (a few drops) of water were observable in the extracts associated with Table 2. With a height of 185 mm for the "S" line, 150 mL of solvent was necessary for continuous extraction.

In previous work with the "macro" CEs (used routinely by our laboratory since 1986), little concern had been given to losses of methylene chloride during the extraction period. However, recirculating chillers were routinely employed (Neslab-Coolflow 75). During the work with miniature or "micro" CEs, slight but repetitive losses of solvent were visually apparent. For this reason, volumes of methylene chloride were measured before and after the extraction period (24 hours \pm 2 hours). An FTS model RC-25 recirculation chiller was employed and set at 5°C. The chiller was charged with laboratory pure water mixed with 1:1 (v/v) ethylene glycol. Two hundred mLs of methylene chloride and 1 L of water were loaded and the routine extraction procedures were

followed. After the extractions the distribution of solvent was measured:

LOSSES OF METHYLENE CHLORIDE DURING CE EXTRACTION
("MICRO" CE, WITH CHILLER AT 5°C, 24 HOUR EXTRACTION)

CEs were initially charged with 200 mL of CH₂CL₂

DISTRIBUTION OF METHYLENE CHLORIDE (mL) FOLLOWING EXTRACTION

EXTRACTOR **	CE RESERVOIR	SIDE FLASK	TOTAL	LOSS vs 200 mL	% LOSS
1	135	43	178	21	10.5
2	105	75	180	20	10
3	135	48	183	17	8.5
4	140	41	181	19	9.5
AVE.	128	52	181	19	9.6

** Four separate extractor units were tested.

Essentially 10% of the solvent was lost during the extraction. Since methylene chloride is about 2% soluble in water and the extractors were charged with 1000 mL of water, 20 mL of methylene chloride could be dissolved in the aqueous sample and could account for the loss in solvent.

It was determined that a number of variables associated with the miniature extractors could affect water breakthrough. These included: how vertical the extractors were placed in the ring-stand; the height of the "S" return line; and the possible losses of solvent during the extraction (10% on average). To allow for such variables and to reliably avoid water breakthrough, it was decided to extend the height of the "S" line to 195mm. The miniature CEs with the 195 mm return line required 200 mL of methylene chloride.

Continuous Extractor Design (Overall Length):

An additional variable that proved important was the length of the CE extractor above the aqueous sample. During the extraction, solvent collected at the drip tip of the Allihn condenser and dropped to the aqueous sample surface. In the "Macro" extractors, this "drop distance" was sufficient to have the solvent droplets easily break the water surface tension and pass through the sample as small droplets. Such solvent droplets with large surface to volume ratios were thought to provide the best extracting exposure as they "fall" through the sample. However, the miniature or "micro" extractor droplets were accumulating on the sample surface until large pooled droplets of solvent would "fall" through the sample. The micro extractor design was altered by extending the length of the CE extractor 30 mm to 400 mm (figure 2).

Final Miniature ("micro") CE design:

The final dimensions of the one piece, all glass extractor (with Teflon stopcock in the solvent return line) were as follows [Figure 2]: overall height 400 mm; height of solvent return line 195 mm; overall diameter 80 mm; inside diameter of the return line tubing 10 mm; and 4 mm Teflon stopcock bored to interface with the 10 mm tubing. The simple one piece units were easy to charge with both solvent and sample and to mount in the ring stands. Since they were all glass (except for the stopcock), they were easy to clean and the entire extractor could be placed in a high temperature oven (425-450°C) as the final step in the cleaning procedure.

Loading the Extractor:

A combination of closing the stopcock, followed by adding all 200 mLs of the extracting solvent to the CE unit, plus the slow addition of the aqueous sample (a funnel used for about the first half of the sample volume) has minimized water carryover into the boiling flask (described in detail in Section C (General Procedures). This loading technique also minimized the exposure of the analyst to the organic solvent.

Determination of solvent flow rate:

The flow rate of solvent was set at 7.5 mLs per minute. This was adjusted by varying the rheostat settings (80% of full scale). The flow rate was measured by marking the level of the solvent in the reservoir at equilibrium (at a given rheostat setting) and then closing the stopcock for a measured time interval and marking the level of the solvent. The volume of solvent distilled over during the measured interval was determined by filling the emptied extractor with solvent (between the two marked levels). Without a stopcock it would be difficult to determine the solvent flow rate.

Sodium Sulfate and possible alternatives:

The final design of the miniature continuous extractors had minimized solvent use (about a five fold reduction). However, once the extraction was completed, the extract was dried (water removed) by passing it through sodium sulfate. The drying columns specified by EPA Method 625 are 19 mm ID and long enough to allow 100 mm of sodium sulfate. The method specifies that 20-30 mL of methylene chloride be used for rinsing the flask and the drying column after passing the extract through the column. Large volumes of rinse solvent (greater than 20-30 mLs) will negate the effort at minimizing the solvent used during the extraction. Very preliminary results are listed in the Appendix for one possible alternative to the use of sodium sulfate drying columns, namely hydrophobic filters. A sample of prototype filters was provided by Varian Corporation (Sample Preparation Division). 100 ng of the BNA target compounds were placed in 60 mLs of methylene chloride (about the volume of the extract resulting for miniature CE extractions). The filters were rinsed with 5 mLs of solvent and

the extracts were KD concentrated to 1 mL. The recoveries for the target compounds are listed in the Appendix. The use of these type of filters for drying extracts with small amounts of water (2-4 %) would avoid the necessity for sodium sulfate columns and should require far less solvent volume for rinsing. Similarly, syringe "micro- sodium sulfate columns" are now available, which may prove effective.

"Demonstration of Capability" (miniature CEs):

Since the final CE design (figure #2), an extensive series of spiking experiments were performed into laboratory pure water. The experimental design (four replicates, at specified concentrations, and performing all aspects of the analytical method) is that listed in EPA's organic protocols, e.g., 625, 608, 508. This is referred to in these methods as the "initial demonstration of capability". The corresponding analytical methods list specifications for the accuracy (% recovery) and precision (standard deviation), which are to be obtained.

The spiking solutions and procedures for CE as well as quantitation have been described previously.

CLP Surrogate Compounds

The results for the replicate spikes of the CLP surrogates (n=5), were excellent (Table #3). All six compounds were well within the specified recovery criteria.

Priority Pollutant ("BNA Spiking Solution")

Forty-eight BNA compounds (included in the Supelco CRADA mixes) were spiked into laboratory pure water in four separate miniature and macro CEs. Figure #3 is a chromatogram (Reconstructed Ion Current Profile) resulting from the GC/MS analysis of a "BNA" spike extract. The resulting recoveries for both the miniature and macro extractors were all within the acceptance limits as specified by EPA method 625 (Table 4 and 5). All but ten compounds were recovered by the miniature extractor in excess of 90% (average recovery). The troublesome compounds included:

Compound	Average Recovery (Std. Dev.) with n=4	
	"Miniature"	"Macro"
	CE	CE
Phenol	89.4 (1.3)	90.2 (4.9)
1,3-dichlorobenzene	79.3 (1.6)	71.4 (6.5)
1,2-dichlorobenzene	82.9 (2.2)	75.7 (6.4)
1,4-dichlorobenzene	83.8 (2.6)	71.6 (3.1)
N-Nitroso-di-n-propylamine	85.3 (0.5)	86.9 (6.1)
hexachloroethane	75.7 (1.6)	67.5 (2.7)
1,2,4-trichlorobenzene	85.7 (1.6)	78.7 (3.3)
1,1,2,3,4,4-hexachloro-1,3-butadiene	74.2 (1.8)	67.2 (2.6)

Average Recovery (Std. Dev.)
with n=4

Compound	"Miniature" CE	"Macro" CE
2,4-dinitrophenol	73.6 (2.0)	66.1 (4.5)
2-methyl-4,6-dinitrophenol	80.3 (2.3)	80.8 (3.2)

The recoveries obtained for these difficult compounds were in close agreement between the macro and micro extractors, indicating that the recoveries of these compounds were not related to the volume of solvent used for extraction.

Figure #4 depicts the BNA spike recoveries (Tables #4 and #5). As indicated, the agreement in recoveries was good with the most notable exceptions occurring when the "macro-" CE recoveries exceeded 100%. In these cases, the miniature extractors gave recoveries closer to 100%. The five fold reduction in solvent had no adverse affect on the recoveries of these target compounds.

NOTE: These extractions were performed at pH<2. It was found that extraction under acidic conditions greatly improved recovery of short-chain phthalate esters⁴. Also, floc and emulsion formation were minimized, even for the continuous extractor method, which is far less prone to these difficulties than separatory funnel methods. All compounds, except the most basic ones such as aniline or benzidine, were effectively extracted at a pH <2.

Spikes of Benzidines and Anilines

Basic semivolatile compounds (substituted benzidines and anilines) extracted effectively under basic conditions (pH >11), giving spike recoveries near 100% using the miniature extractors (Table 6). One problem encountered involved the recovery of aniline. Though this compound is not a Priority Pollutant (not an NPDES analyte) and has been dropped from the Superfund CLP target list, it was in the spiking mixture and the difficulties encountered were of interest. The recoveries obtained for aniline were routinely in excess of 150% and were thought related to a adverse "solvent effect" (presence of methanol in the reference material suppressing the response of this polar compound. This topic is discussed in more detail in a later section on recoveries of phenolic compounds in the CLP "Matrix Spikes".

Single Component (Priority Pollutant) Pesticides

Single component pesticides (EPA Method 625, 608 and 508) gave average spike recoveries over 90%, with the exception of endrin (80%). As indicated in Table 7, all of the accuracy and precision requirements specified for EPA Method 608 were met (these criteria were used since they are more demanding), though GC/MS was used as the detector for these analyses).

Chlordane

The analyses of 50 ug/L spikes (50 ng/uL in the extracts) proved challenging, but not beyond the quantitation range of the GC/MS. The chromatographic peaks selected for analysis are presented in Figure 5 and the mass spectra associated with the heptachlor component of technical chlordane is presented in Figure 6. The recoveries averaged 108% with a standard deviation of 2.7 (Table 8). The range of recoveries specified by EPA Method 608 were 55.2-109% (limits more restrictive than those in 625).

Toxaphene

The analyses of 50 ug/L spikes (50 ng/uL in the extracts) was performed by GC/ECD. The recovery data ranged from 100-112% for the replicate spikes (n=5) and are presented in Table 9. The accuracy and precision requirements specified for EPA 608 were met.

PCB-1242 and 1260

The average recoveries for spikes of Aroclor 1242 and 1260 (Tables 10 and 11) were 100 and 97.6 % respectively. The accuracy (average % recovery) specified for these PCBs in EPA 608 are (24.8-69.6%) and (18.7-54.9%), respectively.

Figure #7 is the chromatogram associated with one of the spiked extracts (PCB-1260).

WasteWater Sample

Four liters of waste from a secondary effluent at a local wastewater treatment plant was extracted in replicate employing both the "mini-" and "macro" extractors. These analyses included Superfund Surrogate Spikes (Table 12). All the recoveries for the surrogates were within CLP specified limits. The compounds recovered from this sample are presented in Table 13. The sample was selected because it contained significant suspended solids. The resultant CE extracts ("mini-" and "macro") were orange/brown. The results indicate that the environmental matrix was successfully extracted using the miniature extractors, as no apparent bias is indicated.

S-EVAP

This work was conducted without solvent emissions. A device (the S-EVAP) was used during the K-D concentration procedure to assure that methylene chloride was not emitted. The S-EVAP employed special Hopkins condensers during the KD (macro) solvent concentration step prior to GC/MS or GC/FID analyses. The use of this condensing instrumentation for the recovery of methylene chloride and hexane had been reported as effective and of no significant effect upon the recovery of semi-volatile compounds⁵. This current work, "validation" of the miniature continuous extractors, has provided additional data supporting the use of this

pollution prevention device.

Methanol Solvent Effect:

The "solvent effect" of methanol upon acidic semi-volatile compounds became an inadvertent area of study when spikes of acidic compounds (prepared in methanol) into deionized water were compared to spikes made directly into methylene chloride. The spiking solution contained methanol. The adverse affects were compound specific with the greatest effect associated with compounds with an affinity for methanol. The methanol apparently suppressed the response of H-bonding compounds (acidic compounds such as pentachlorophenol) in the analysis of the reference standard. Since methanol does not extract from water using the CE procedures, the test CE extracts were free of methanol and the associated suppression. This effect was related to several different capillary columns and chromatographic conditions (Appendix). The higher the initial GC temperature, the less pronounced the solvent effect. Similarly the thinner the stationary phase, the less "effect" was measured. A tight narrow band of methanol condensed after injection would be associated with the lower initial temperatures (30C) and the thicker column phase. As the initial temperature increased, the methanol would be expected to occupy a wider band, and the "effect" would be reduced.

III. Conclusions

The miniature continuous extractors:

- * Effectively extracted the target semivolatile organics (EPA Method 625, Superfund Contract Laboratory SOW) with recoveries (accuracy) and precision within the performance specifications specified in EPA Methods 625 and 608 (in laboratory pure water and the tested wastewater).

- * Required less methylene chloride per sample extracted, which should result in significant savings in solvent costs. A 3- to 5-fold reduction of methylene chloride required for continuous liquid/liquid extraction was obtained. The use of this device represents a laboratory pollution prevention measure.

- * Required significantly less time to K-D concentrate the resulting extracts, since less volume of extract was involved (50-75 mLs for the miniature extractors versus 200-300 mLs for the macro CE extractors).

- * Significantly reduced the volume of waste solvent to be recycled. This will save on the expense of recycling this halogenated solvent (externally) and/or reduce the number of distillation runs to recover the solvent for direct reuse by the laboratory.

* The extractors were relatively inexpensive (\$100 from Lab Glass, Vineland, New Jersey). The manufacturer has indicated that they are less expensive to produce than the "macro" extractors because of the smaller diameter of the CE extractor (smaller stock tubing is needed for construction).

* Were applicable to most of the Agency's methods for the analyses of semivolatile compounds. The use of "miniaturized techniques" (reduction in scale, which preserve the basic chemistries) do not require the application for a "variance" for use under SDWA and NPDES. This is an extensive confirmation that the analytical results are consistent with the mandated EPA methods. The semivolatile techniques for the RCRA and Superfund programs have few specifications for the extractors. Therefore the use of this device should be applicable to most environmental laboratories for use in the determination of semivolatile organics for the Agency's programs. One notable exception is EPA's Method 608. This pesticide method for wastewater does not include the use of a continuous extractor. However, EPA Method 625 (which uses a different detector, namely MS) includes the extraction of some of the method 608 pesticides using CE. The reality is that the 608 analytes extract well by CE and this extraction technique has been used for years by the Superfund and RCRA programs. However, the analysis via 608 must be followed for compliance under the NPDES program (an issue of program compliance as opposed to an analytical problem).

With this exception, employing this apparatus for the NPDES, Superfund and RCRA programs would require only a demonstration by the laboratory of analytical capability ("initial demonstration of capability" procedure as specified in EPA Methods SDWA, NPDES and RCRA). Though this "demonstration" is not mandated under the Superfund program, such a procedure should be part of the laboratory's routine QC procedure.

In addition, as many of these programs are now operated by State Authorities, prior to use of this device, the State Authority should be consulted (since under delegated programs, States are able to be more restrictive than the Agency).

* Were easy to setup (ring stands, etc.) and load with sample and solvent.

* Retained the necessary analytical sensitivity, since the initial 1 L sample volume was retained as specified by the Agency's organic protocols and the final extract volumes were as mandated. The miniature extractors resulted in no loss of analytical sensitivity. If the sample volume had been reduced, the final extract volume would have to be correspondingly reduced. This is generally undesirable for environmental samples, since these extracts generally have significant suspended/dissolved solids and/or foam.

* Were safer to load, because they use less solvent and because the stopcock allowed the solvent to be loaded and the sample placed

on top. The sample served as a barrier to escaping solvent fumes.

* Unlike extracting devices which employ hydrophobic membranes to help reduce the volume of solvent for extraction (as low as 100 mLs), the miniature extractors do not suffer reduced recoveries for hydrophilic compounds, e.g., phenolics.

Additional Observations:

Several of the BNAs (1,4-, 1,3-, 1-2-dichlorobenzenes and 1,2,4-trichlorobenzene), which are poorly recovered by CE actually should be dropped from the Agency's semivolatile protocols. These compounds are too volatile and too hydrophobic to be sampled in 1 L amber containers (too easily lost to the headspace of these containers). These compounds are already redundantly listed in the Agency's volatile organics methods and their measurement should be restricted to these protocols (required zero head-space septa vial sample containers are mandatory for these methods).

Though the time for extraction in this study was routinely 24 hours, because of the reduction in the solvent reservoir volume with this design, the time required to complete extraction should be reduced (less time for the extracted compounds to be washed from the solvent reservoir below the sample).

"Drip Lips" placed on the condensers used during CE extraction have helped avoid contamination at the condenser/CE joint (45/50) when room humidity condenses. Also this has helped avoid water (condensation) near electrical equipment (mantles, rheostats), which would be an obvious hazard for the analyst.

The use of condensers during the K-D concentration step (S-EVAP) allowed the recovery of solvent, which would otherwise be vented up the fume hood.

IV. References

1. U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-media, Multi-Concentration", OLM01.0, 12/1990.
2. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; 40 CFR Part 136, Federal Register, October 8, 1991.
3. Slayton, J., Molnar, J. and Alvero, M., "Recovery of Solvents Utilized in EPA Methods for Extractable Organics", Pittsburgh Conference, March 1992.
4. Slayton, J. and Trovato, R., "Acid-Neutral Continuous Liquid-Liquid Extraction of EPA Priority Pollutants and Hazardous Substances List Compounds", 28th Rocky Mountain Conf., Aug., 1986.
5. Slayton, J., "EPA Case Study", International Conference and Exhibition on Pollution Prevention in the Laboratory, June 1993.

**Data Tables and Additional
Figures:**

TABLE 1

 MINIATURE CONTINUOUS EXTRACTORS
 185mm RETURN LINE

SURROGATE AQC % RECOVERY MICRO

SAMPLE	2-FLUORO- PHENOL	D5- PHENOL	D5-NITRO- BENZENE	2-FLUORO- 1,1'-BI- PHENYL	2,4,6-TRI- BROMO- PHENOL	D14-TER- PHENYL

CLP TARGET LIMITS						
	(21-100)	(10-94)	(35-114)	(43-116)	(10-123)	(33-141)
NO WATER IN EXTRACT:						
T2062403	67.80	71.06	77.13	84.36	87.54	91.80
T2062404	70.60	72.80	79.86	88.70	89.27	90.30
T2062405	79.60	80.26	85.34	85.50	96.07	90.70
T2062406	83.75	84.70	90.36	81.05	99.00	89.54
T629-01	66.45	71.19	78.36	72.72	86.40	93.07
T629-03	75.55	79.65	85.50	78.70	91.00	99.86
T629-04	65.00	69.64	77.36	74.00	82.15	92.68
T629-05	70.17	74.30	79.79	74.39	84.28	91.79
T629-06	74.75	79.50	85.80	81.01	89.46	97.70

AVERAGE	72.63	75.90	82.17	80.05	89.46	93.05
STD.DEV.	6.28	5.25	4.68	5.58	5.37	3.48

WATER OBSERVED IN EXTRACT:

T2062401	56.46	57.46	67.30	85.40	71.18	90.40
T2062402	41.80	40.90	48.47	51.06	57.37	89.50
T629-02	49.70	53.15	57.77	50.50	62.30	69.32

AVERAGE	49.32	50.50	57.85	62.32	63.62	83.07
STD.DEV.	7.34	8.59	9.42	19.99	7.00	11.92

TABLE 2

MINIATURE CONTINUOUS EXTRACTORS
185mm RETURN LINE
GC\FID

EXPERIMENT: MATRIX SPIKE RECOVERY

GC RUN DATE: 19 Aug 92

REFERENCE: T2081701

REF. FILE #: A081992\001F0101.D

COMPOUND NAME	SAMPLE NUMBER				AVE	
	T2081702	T2081703	T2081704	T2081705	% REC	STD.DEV
Phenol	83.954	85.569	82.658	74.619	81.700	4.024
2-Chlorophenol	85.746	85.447	82.834	71.044	81.268	5.464
1,4-Dichlorobenzene	80.058	61.947	72.310	62.896	69.303	4.338
N-Nitroso-Di-n-Propylamine	78.046	72.118	80.156	70.276	75.149	3.738
1,2,4-Trichlorobenzene	79.523	62.032	72.652	63.317	69.381	4.352
4-Chloro-3-Methylphenol	87.769	87.201	88.104	78.788	85.466	3.648
Acenaphthene	84.490	76.035	83.893	73.806	79.556	3.814
4-Nitrophenol	92.677	92.966	95.578	85.881	91.776	3.550
2,4-Dinitrotoluene	88.453	81.652	91.285	78.054	84.861	4.865
Pentachlorophenol	94.340	93.709	93.473	87.736	92.315	2.410
Di-N-Butylphthalate	86.253	77.747	87.073	76.754	81.957	4.073
Pyrene	88.283	82.337	90.322	78.493	84.859	4.295

RIC
11/12/92 14:14:00

DATA: A1
CALI: CAL01 #3

SCANS 600 TO 3400

SAMPLE: FC43

CONDS.: UPGRADE 30C 2 MIN TO 300 AT 10C/MIN

RANGE: G 1.3675 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

225536.

Figure 3

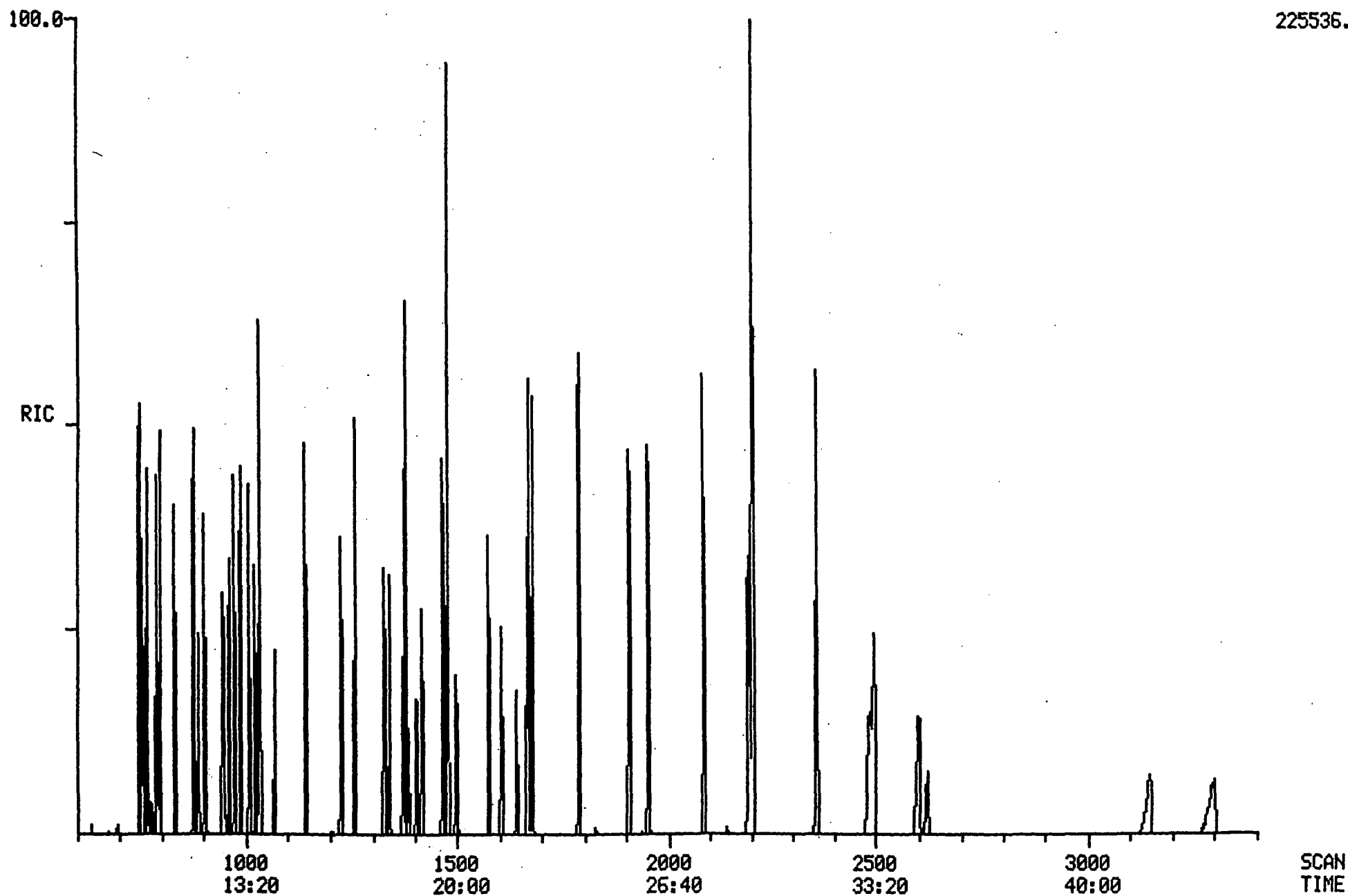


TABLE 3

Surrogate Recovery (Miniature Continuous Liquid/Liquid Extraction)
195mm RETURN LINE

CESUR.WK1

50 ug/L Spike into Lab Pure Water (100 uL of 500 ug/mL of USEPA RTP Repository Standard).

Compound	% Recovery					Average Recovery	Std. Dev. (n-1)	CLP Limits
	Run 1	Run 2	Run 3	Run 4	Run 5			
2-Fluorophenol	87	84.7	91	86.3	88.5	87.5	2.39	21-100
D5-Phenol	92.7	90.6	94.3	90.7	93.9	92.4	1.74	10-94
D5-Nitrobenzene	95.6	93	94.4	93.6	96.4	94.6	1.40	35-114
2-Fluoro-1,1'-biphenyl	95.8	93.7	99.7	97	99.5	97.1	2.54	43-116
2,4,6-Tribromophenol	101.6	96.6	96.7	92.2	97	96.8	3.33	10-123
D14-p-Terphenyl	96	95	93.2	89.6	93.6	93.5	2.44	33-141

TABLE 4

Validation of Miniature Continuous Extractors BNA TARGETS(195 mm S-tube)
 Calibration Standard (ACCU Standard 100 ng Z014A,B,D,E,GR,H) With Ultra Sc. Int.
 Supelco CRADA QC SAMPLES

NO. COMPOUND	A1	A2	A3	A4	A5	AVE % REC	STD. DEV.	REQUIRED 625
								RANGE FOR AVERAGE
2 PHENOL *CCC*	90.5	89.7	90.4	89.6	86.9	89.4	1.3	16.6--100
3 ETHANE, 1,1'-OXYBIS(2-CHLORO-	91.5	91.0	91.3	90.2	88.5	90.5	1.1	42.9--126
4 2-CHLOROPHENOL	95.7	94.1	94.9	94.6	91.5	94.2	1.4	36.2--120.4
5 1,3-DICHLOROBENZENE (COELUTES)	78.3	79.6	81.1	80.8	76.8	79.3	1.6	16.7--153.9
7 1,4-DICHLOROBENZENE (COELUTES) *CCC*	84.1	79.8	85.4	84.4	81.0	82.9	2.2	37.3--105.7
8 1,2-DICHLOROBENZENE (COELUTES)	84.3	79.5	86.2	86.6	82.6	83.8	2.6	48.6--112.0
13 1-PROPANAMINE, N-NITROSO-N-PROPYL-	85.1	85.7	84.4	86.0	85.3	85.3	0.5	13.6--197.9
14 ETHANE, HEXACHLORO-	76.9	73.4	77.8	76.0	74.5	75.7	1.6	55.2--100.0
15 BENZENE, NITRO-	91.6	93.7	91.5	90.9	88.0	91.1	1.8	54.3--157.6
16 2-CYCLOHEXEN-1-ONE, 3,5,5-TRIMETHYL- *CCC*	96.0	96.1	95.6	94.6	92.7	95.0	1.3	46.6--180.2
17 2-NITRO-PHENOL	95.2	98.0	94.2	94.0	91.4	94.6	2.1	45.0--166.7
18 PHENOL, 2,4-DIMETHYL-	111.8	99.7	104.9	113.0	111.3	108.1	5.1	41.8--109.0
20 ETHANE, 1,1'-[METHYLENEBIS(OXY)]BIS[2-CHLOR	112.7	113.5	112.9	111.8	108.5	111.9	1.8	49.2--164.7
21 2,4-DICHLORO-PHENOL	95.8	96.7	96.1	94.2	92.5	95.1	1.5	52.5--121.7
22 BENZENE, 1,2,4-TRICHLORO-	85.3	84.5	87.7	87.5	83.7	85.7	1.6	57.3--129.2
24 NAPHTHALENE	96.2	92.3	96.0	94.9	92.8	94.4	1.6	35.6--119.6
25 1,3-BUTADIENE, 1,1,2,3,4,4-HEXACHLORO- *CCC	71.0	74.8	76.2	75.5	73.7	74.2	1.8	37.8--102.2
26 PHENOL, 4-CHLORO-3-METHYL-	98.3	101.7	98.0	95.3	94.7	97.6	2.5	40.8--127.9
29 2,4,6-TRICHLOROPHENOL HSL	96.8	94.9	94.2	93.2	92.1	94.2	1.6	
31 2-CHLORONAPHTHALENE	95.1	90.6	93.2	91.3	89.5	91.9	2.0	64.5--113.5
32 1,2-BENZENEDICARBOXYLIC ACID, DIMETHYLESTER	93.8	90.0	91.0	90.7	89.2	90.9	1.6	0--100
33 2,6-DINITRO-TOLUENE	95.8	95.3	93.0	93.0	92.6	93.9	1.3	68.1--138
36 ACENAPHTHYLENE, 1,2-DIHYDRO- *CCC*	95.4	93.3	95.9	96.1	92.1	94.6	1.6	60.1--132
37 2,4-DINITROPHENOL *SPCC*	76.1	76.0	72.3	72.1	71.4	73.6	2.0	0--172.9
40 4-NITROPHENOL (SEC ION)	91.2	103.4	91.2	85.8	85.2	91.4	6.5	13.0--106.5
41 2,4-DINITRO-TOLUENE	97.8	97.4	94.8	94.3	86.8	94.2	4.0	47.5--126.9
42 1,2-BENZENEDICARBOXYLIC ACID, DIETHYLESTER	95.8	92.0	92.8	93.0	92.6	93.2	1.3	0--100
43 1-CHLORO-4-PHENOXY-BENZENE	114.1	104.8	108.0	111.7	109.6	109.6	3.2	38.4--144.7
44 9H-FLUORENE	99.9	92.9	96.3	97.3	95.6	96.4	2.3	71.6--108.4
45 2-METHYL-4,6-DINITROPHENOL	83.8	76.9	81.6	79.6	79.8	80.3	2.3	53.0--100.0
47 BROMOPHENOXYBENZENE	92.9	89.0	90.7	92.8	91.4	91.4	1.4	64.9--114.4
48 BENZENE, HEXACHLORO- *CCC*	98.6	91.6	93.2	94.8	96.2	94.9	2.4	7.8--141.5
49 PENTACHLOROPHENOL	95.1	101.7	90.3	88.9	91.1	93.4	4.6	38.1--151.8
51 PHENANTHRENE	101.4	94.1	101.1	100.3	99.5	99.3	2.7	65.2--108.7
52 ANTHRACENE	96.1	88.6	95.9	95.9	94.9	94.3	2.9	43.4--118.0
53 1,2-BENZENEDICARBOXYLIC ACID, DIBUTYLESTER	94.7	88.6	96.9	95.5	94.2	94.0	2.8	8.4--111.0
54 FLUORANTHENE CCC*	92.8	93.3	94.1	100.8	98.6	95.9	3.2	42.9--121.3
55 PYRENE	93.0	91.7	92.6	97.0	96.9	94.2	2.3	69.6--100.0
56 N-BUTYL BENZYL PHTHALATE	96.0	96.5	99.5	103.0	98.1	98.6	2.5	0--139.9
57 BIS(2-ETHYLHEXYL)PHTHALATE	94.3	87.5	96.0	101.5	98.0	95.5	4.6	28.9--136.8
59 BENZO/A/ANTHRACENE	95.4	95.5	95.3	94.0	93.7	94.8	0.8	41.8--133
60 CHRYSENE	96.1	92.5	95.5	98.4	95.8	95.7	1.9	44.1--139.9
61 DIOCTYLPHTHALATE *CCC*	95.2	93.6	97.9	97.0	92.2	95.2	2.1	18.6--131.8
62 BENZO/B/FLUORANTHENE	106.5	92.8	92.7	98.1	95.6	97.1	5.1	42.0--140.4
63 BENZO/K/FLUORANTHENE	101.3	112.6	102.3	95.9	96.1	101.6	6.1	25.2--145.7
64 BENZO/A/PYRENE	90.2	83.0	86.6	84.0	83.3	85.4	2.7	31.7--148.0
67 DIBENZO(A,H) ANTHRACENE	94.4	85.0	94.4	93.8	97.0	92.9	4.1	0--199.7
68 BENZO/GHI/PERYLENE	103.7	92.0	105.6	107.7	100.1	101.8	5.5	0--195.0

TABLE 5

GC/MS Method Validation Study (October 30, 1992)
 Performed by Ed Messer, EPA Central Regional (III) Laboratory

TARGET COMPOUNDS	TRUE VALUE	MV1	MV2	MV3	MV4	AVERAGE	RANGE FOR AVG	REQUIRED 625	
								STD DEV	LIMIT STD DEV
2 Phenol	100	82.9	88.3	95.2	94.2	90.2	16.6-100.0	4.9	22.6
3 Bis(2-Chloroethyl)Ether	100	84.1	94.5	102.0	98.6	94.8	42.9-126.0	6.7	55.0
4 2-Chlorophenol	100	85.6	92.1	99.9	96.0	93.4	36.2-120.4	5.3	28.7
5 1,3-Dichlorobenzene	100	61.1	71.3	78.6	74.6	71.4	16.7-153.7	6.5	41.7
7 1,4-Dichlorobenzene	100	66.7	72.0	75.5	72.0	71.6	37.3-105.7	3.1	32.1
8 1,2-Dichlorobenzene	100	65.8	75.0	83.3	78.7	75.7	48.6-112.0	6.4	30.9
13 Nitrosodi-n-propylamine	100	76.6	88.2	92.2	90.5	86.9	13.6-197.9	6.1	55.4
14 Hexachloroethane	100	63.0	68.1	70.1	68.9	67.5	55.2-100.0	2.7	24.5
15 Nitrobenzene	100	98.9	91.6	93.6	96.2	95.1	54.3-157.6	2.7	39.3
16 Isophorone	100	97.9	102.0	104.0	105.0	102.2	46.6-180.2	2.7	63.3
17 2-Nitrophenol	100	96.1	87.3	92.3	97.2	93.2	45.0-166.7	3.9	35.2
18 2,4-Dimethyl Phenol	100	84.7	104.0	102.0	102.0	98.2	41.8-109.0	7.8	26.1
20 Bis(2-Chloroethoxy)Methane	100	112.0	119.0	124.0	125.0	120.0	49.2-164.7	5.1	34.5
21 2,4-Dichlorophenol	100	92.1	92.9	94.8	95.4	93.8	52.5-121.7	1.3	26.4
22 1,2,4-Trichlorobenzene	100	73.8	77.5	82.1	81.2	78.7	57.3-129.2	3.3	28.1
24 Naphthalene	100	85.7	88.7	88.6	89.6	88.2	35.6-119.6	1.5	30.1
25 Hexachlorobutadiene	100	62.9	67.2	69.6	69.0	67.2	37.8-102.2	2.6	26.3
26 4-Chloro-3-Methyl Phenol	100	105.0	108.0	108.0	109.0	107.5	40.8-127.9	1.5	37.2
29 2,4,6-Trichlorophenol	100	95.1	97.8	98.2	95.8	96.7	52.4-129.2	1.3	31.7
31 2-Chloronaphthalene	100	87.9	91.6	95.3	92.8	91.9	64.5-113.5	2.7	13.0
32 Dimethyl Phthalate	100	98.1	97.6	99.3	94.6	97.4	D-100.0	1.7	23.2
33 2,6-Dinitrotoluene	100	87.0	92.3	96.1	94.8	92.6	68.1-136.7	3.5	29.6
36 Acenaphthene	100	94.2	92.4	94.3	91.2	93.0	60.2-132.3	1.3	27.6
37 2,4-Dinitrophenol	100	68.6	61.0	62.5	72.1	66.1	D-172.9	4.5	49.8
40 4-Nitrophenol	100	109.0	114.0	111.0	110.0	111.0	13.0-160.5	1.9	47.2
41 2,4-Dinitrotoluene	100	94.7	100.0	104.0	102.0	100.2	47.5-126.9	3.5	21.8
42 Diethyl Phthalate	100	90.9	96.2	101.0	97.6	96.4	D-100.0	3.6	26.5
43 4-Chlorophenyl Phenyl Ether	100	103.0	105.0	107.0	103.0	104.5	38.4-144.7	1.7	33.4
44 Fluorene	100	91.1	92.2	93.8	90.7	92.0	71.6-108.4	1.2	20.7
45 2-Methyl-4,6-Dinitrophenol	100	80.5	85.9	77.1	79.7	80.8	53.0-100.0	3.2	93.2
47 4-Bromophenyl Phenyl Ether	100	87.8	91.1	90.4	87.8	89.3	64.9-114.4	1.5	23.0
48 Hexachlorobenzene	100	87.0	95.1	95.3	95.8	93.3	7.8-141.5	3.6	24.9
49 Pentachlorophenol	100	94.9	102.0	95.5	101.0	98.4	38.1-151.8	3.2	48.9
51 Phenanthrene	100	86.9	94.1	97.9	94.6	93.4	65.2-108.7	4.0	20.6
52 Anthracene	100	85.7	89.3	89.5	86.2	87.7	43.4-118.0	1.7	32.0
53 Di-n-Butyl Phthalate	100	85.6	87.0	91.0	87.0	87.7	8.4-111.0	2.0	16.7
54 Fluoranthene	100	90.9	95.3	103.0	93.3	95.6	42.9-121.3	4.5	32.8
55 Pyrene	100	84.5	94.3	104.0	93.5	94.1	69.6-100.0	6.9	25.2
56 Benzyl Butyl Phthalate	100	102.0	104.0	108.0	100.0	103.5	D-139.9	3.0	23.4
57 Bis(2-Ethylhexyl)Phthalate	100	83.2	86.7	94.9	86.2	87.8	28.9-136.8	4.3	41.1
59 Benzo(a)Anthracene	100	91.5	99.2	103.0	98.4	98.0	41.8-133.0	4.1	27.6
60 Chrysene	100	86.9	87.8	92.1	86.5	88.3	44.1-139.9	2.2	48.3
61 Di-n-Octyl Phthalate	100	85.6	94.9	98.4	92.7	92.9	18.6-131.8	4.7	31.4
62 Benzo(b)Fluoranthene	100	97.5	96.0	83.0	91.3	92.0	42.0-140.4	5.7	38.8
63 Benzo(k)Fluoranthene	100	87.6	93.2	98.3	94.1	93.3	25.2-145.7	3.8	32.3
64 Benzo(a)Pyrene	100	78.0	79.9	73.2	75.2	76.6	31.7-148.0	2.6	39.0
67 Dibenzo(a,h)Anthracene	100	71.6	71.9	70.4	70.7	71.2	D-199.7	0.6	70.0
68 Benzo(g,h,i)Perylene	100	66.4	65.5	80.6	70.6	70.8	D-195.0	6.0	58.9

Figure 4

MINI vs MACRO EXTRACTION

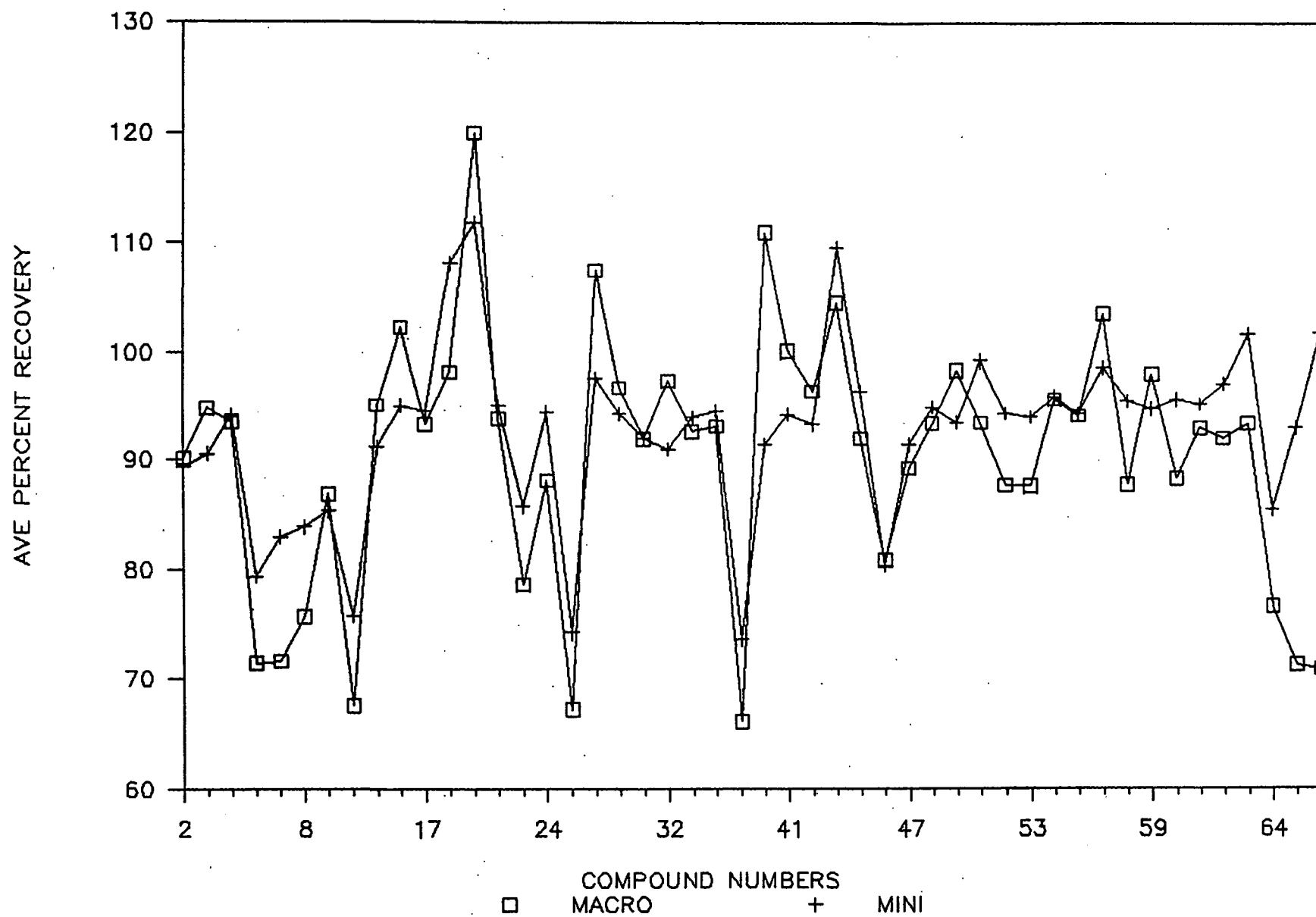


TABLE 6

Recovery of Anilines and Benzidines ("Basic Compounds"):

Min. Cont. Liq/Liq. Extractors (195 mm)

Spikes: 100 ug/L (1.0 mL of 100 ug/mL Working Stock)

Stocks: 5000 mg/L from EPA RTP Repository (MEOH);

Working Stock: diluted 200 uL of each RTP Stock to 10 ML MEOH.

Extraction: 24 hrs; pH >11 (6N NaOH); Chiller 3C;
200 mL Fisher "Optima" CH₂Cl₂; 1L Lab Pure Water.

Recovery: Determined Relative to Direct Analysis of Spike.

Compound ***	Run 1	Run 2	ng or % Recovery		Run 5	Average Recovery	EPA 625 RECOVERY	Std. Dev. (N-1)	EPA 625 Std.Dev.
			Run 3	Run 4					
2-Nitroaniline	96.2	101.3	103.9	100.8	99.4	100.3	-	2.8	-
3-Nitroaniline	101.9	107.8	114	107.6	108.3	107.9	-	4.3	-
Benzidine	92.7	98.7	113.5	101.4	109.9	103.2	-	8.4	-
3,3'-Dichlorobenzidine	100	101.5	116.7	103.8	110.5	106.5	8.2-212	7.0	71.4

*** Aniline was tested as well, but the MEOH/MeOH in the reference solution resulted in multiple peaks (6-8 peaks) in the reference resulting in exaggerated recoveries (>>150% in the extracts (MeOH does not CE extract). This chromatographic problem was not observed for the substituted anilines or benzidines.

TABLE 7

Pesticide Validation (Miniature Continuous Liquid/Liquid Extraction) [FILE : PESTCE.WK1]

100 ug/L Spike into Lab Pure Water (1.0 mL of 500 uL of AccuStandard Z-014C diluted to 10.0 ML with MEOH).

GC/MS ANALYSIS

Compound	% Recovery					40 CFR		Std. Dev. (n-1)
	Run 1	Run 2	Run 3	Run 4	Run 5	Average Recovery	Required Recovery	
Alpha-BHC	96.1	103.6	92.2	101.1	98.4	98.3	37-134	4.42
Delta-BHC	98.8	104	91.8	92	101.2	97.6	19-140	5.49
Gamma-BHC	95.9	103.5	98.8	91	98.9	97.6	32-127	4.59
Beta-BHC	99.1	106.3	105.3	91.7	103.3	101.1	17-147	5.96
Heptachlor	93.5	103.8	109	101.9	100.3	101.7	34-111	5.63
Aldrin (HHDN)	90.9	101.2	101.9	98.2	98.4	98.1	42-122	4.36
Heptachlor Epoxide	89.8	100.4	94.2	96.7	97.7	95.8	37-132	4.00
Endosulfan I	99.2	107.5	108.3	99.9	103.7	103.7	45-153	4.19
4,4'-DDE	96	99.5	96.6	95.3	99.3	97.3	30-145	1.94
Dieldrin	90.9	101	95.6	95.1	98.9	96.3	36-146	3.87
Endrin	86.6	91.2	99	81.3	80.3	87.7	30-147	7.70
4,4'-DDD	95.6	100.7	94.2	94.2	101.5	97.2	31-141	3.58
Endrin Aldehyde	94.5	98.3	92.9	93.3	108.4	97.5	-	6.47
4,4'-DDT	95.9	102.4	86	95.6	105.9	97.2	25-160	7.62
Endosulfan Cyclic Sulfate	91.2	98.2	87.7	97	107.2	96.3	26-144	7.46
Endosulfan II	98.9	103.1	102.7	98.4	108	102.2	D-202	3.87

Figure 5

RIC+MASS CHROMATOGRAM

02/17/93 14:17:00

SAMPLE: FC43

CONDS.: UPGRADE 300 2 MIN TO 300 AT 100/MIN

RANGE: G 1.3575 LABEL: N 1, 4.0 QUAN: A -1, 4.0 J 0 BASE: U 20, 3

DATA: CHLOR02 #1

CALI: CAL0715 #3

SCANS 1700 TO 1860

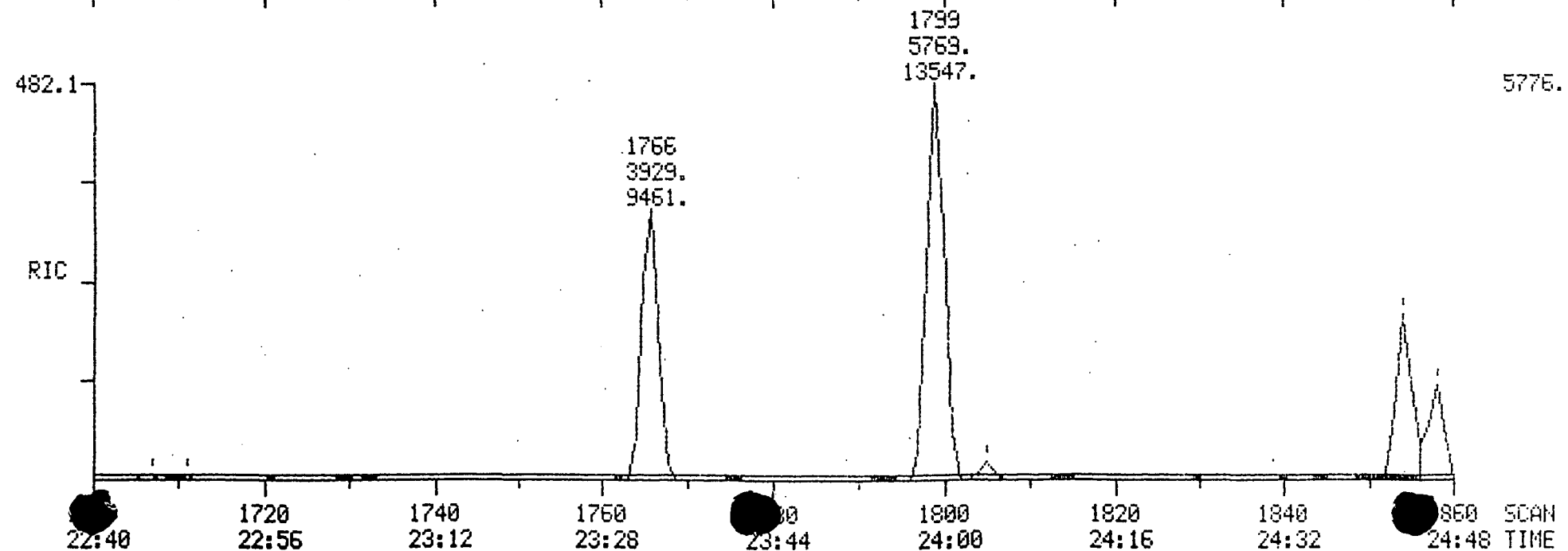
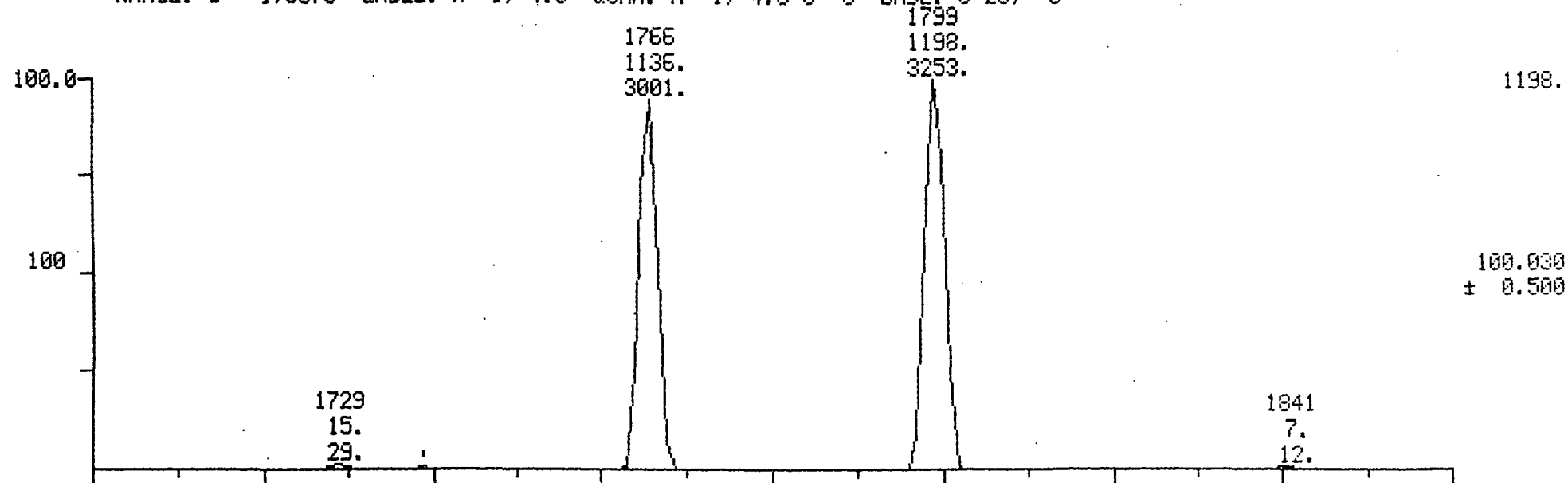


Figure 6

LIBRARY SEARCH
02/17/93 14:17:00 + 23:59
SAMPLE: FC43
CONDS.: UPGRADE 300 2 MIN TO 300 AT 100/MIN
ENHANCED (S 15B 2N 0T)

DATA: CHLOR02 #1799
CALI: CAL0715 # 3

BASE M/Z: 100
RIC: 5000.

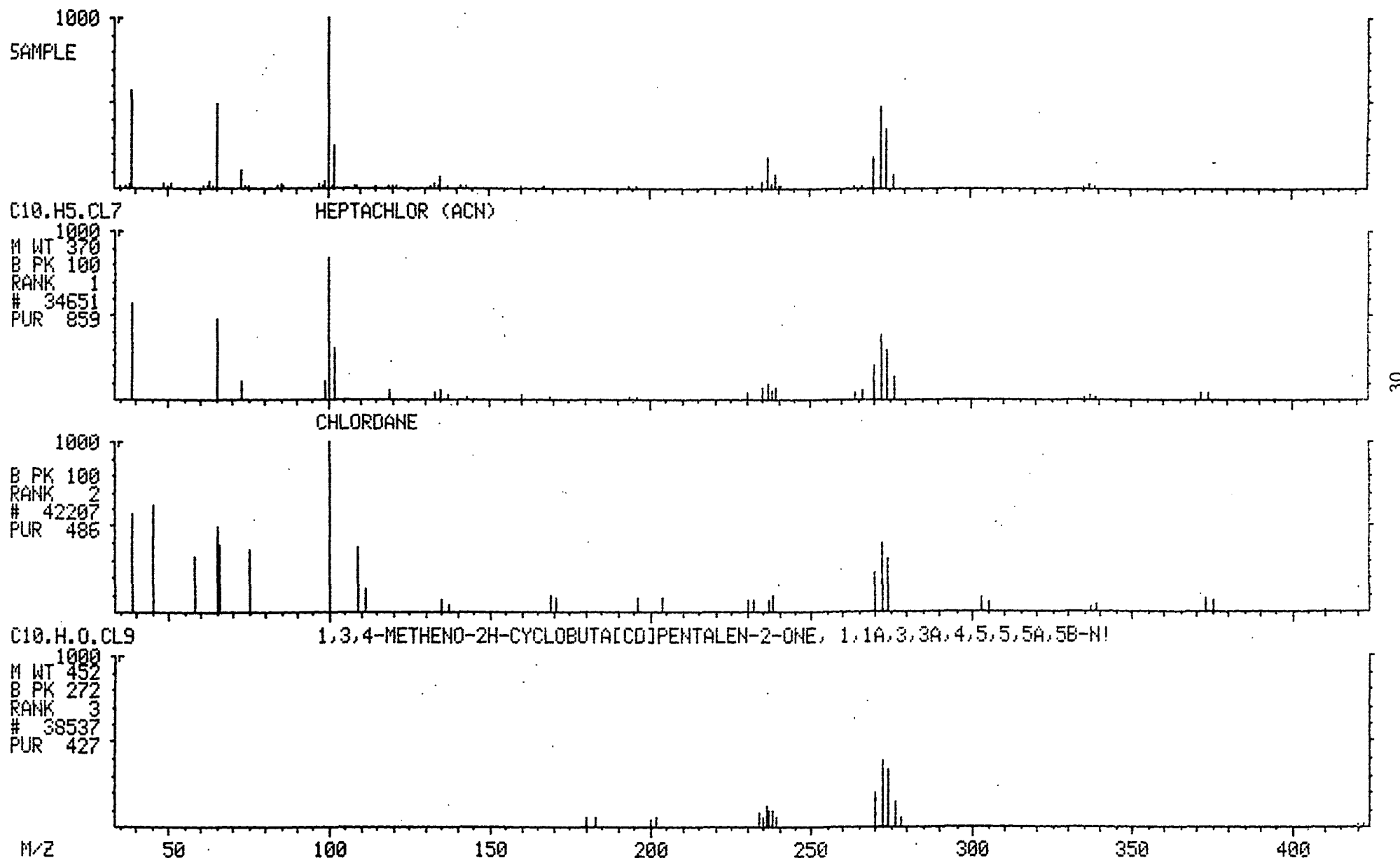


TABLE 8

Miniature Continuous L/L Extraction: Chlordane

50 ug/L spike (Methanol, EPA-RTP), GCMS (100 m/z)

% RECOVERY:					STD. DEV. ug/L (n-1)
Replicate #1	Replicate #2	Replicate #3	Replicate #4	AVE. %	
100	112.1	108	112	108	2.7

608 REQ. (55.2 - 109) 10.0

TABLE 9

PERCENT RECOVERY OF TOXAPHENE via MINIATURE CONTINUOUS EXTRACTION

TARGET CPD #	PERCENT RECOVERY					
	REP-1	REP-2	REP-3	REP-4	REP-5	AVERAGE std (n-1)
1	100	112	108	112	108	108 4.9

TABLE 10

RECOVERY OF PCB-1260 VIA MINIATURE CONTINUOUS EXTRACTION

TARGET CPD #	PERCENT RECOVERY					LIMIT	
	PCB1242-2	PCB1242-3	PCB1242-4	PCB1242-5	AVE	std (n-1)	STD DEV
1	94	100	101	105	100	4.6	12

TABLE 11

RECOVERY OF PCB-1242 VIA MINIATURE CONTINUOUS EXTRACTION

TARGET CPD #	PERCENT RECOVERY					
	1260CE1	1260CE2	1260CE3	1260CE4	1260CE5	AVERAGE std (n-1)
1	91	100	101	95	101	97.6 4.6

Figure 7 PCB 1260

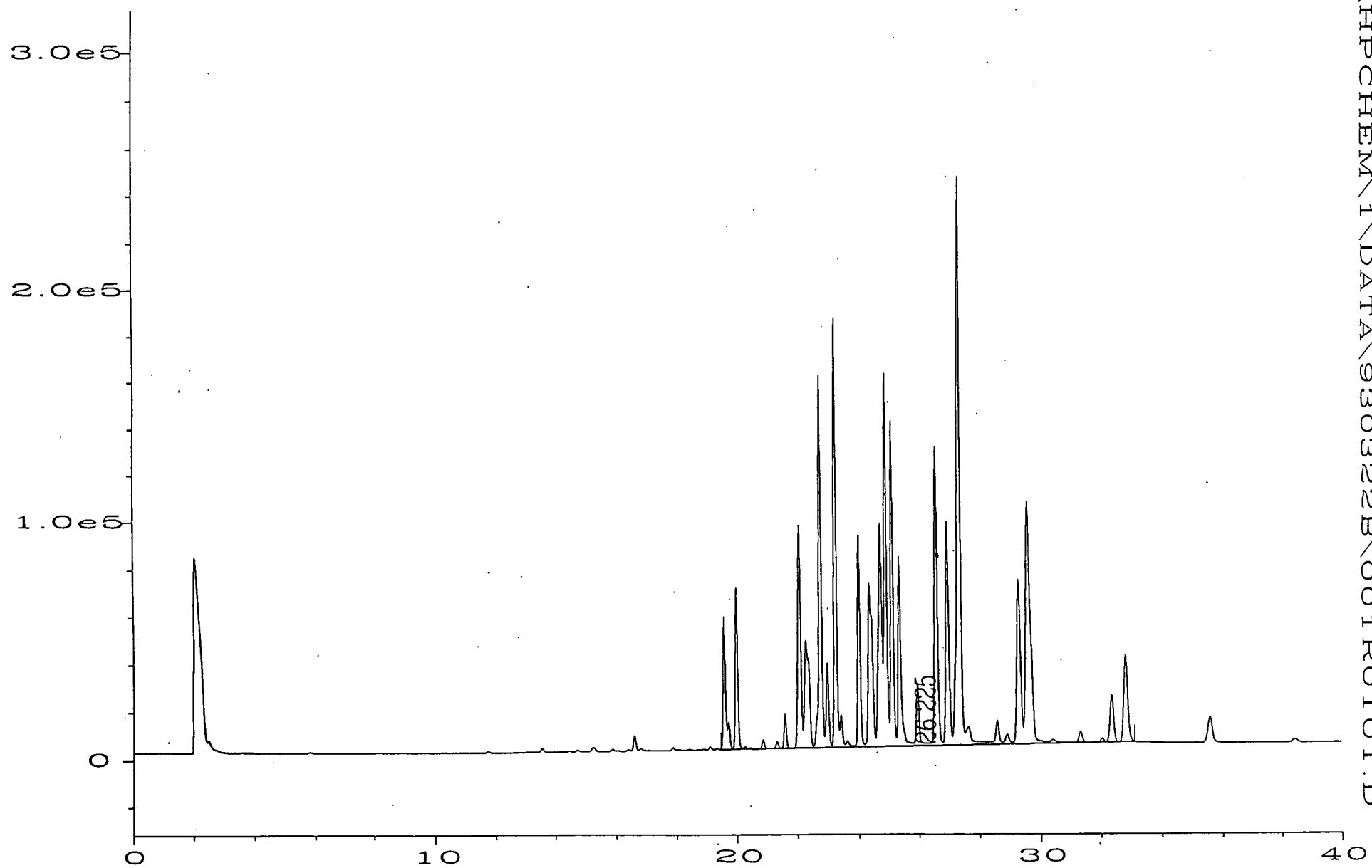


TABLE 12

Surrogate Recovery (Miniature & Macro- Continuous Liquid/Liquid Extraction)

50 ug/L Spike into Secondary Effluent (100 uL of 500 ug/mL of USEPA RTP Repository Standard).

Compound	% Recovery				CLP Limits
	Min. CE Run 1	Min. CE Run 2	Mac. CE Run 1	Mac. CE Run 2	
2-Fluorophenol	85.3	85.7	75.3	74.2	(21-100)
D5-Phenol	89.5	89.8	80.3	76.7	(10-94)
D5-Nitrobenzene	91.8	92.2	81.6	78.7	(35-114)
2-Fluoro-1,1'-biphenyl	88.6	87.7	79.9	79.3	(43-116)
2,4,6-Tribromophenol	96.8	94.8	82.7	84.8	(10-123)
D14-p-Terphenyl	92.6	92.3	79.6	80.8	(33-141)

TABLE 13

Continuous Extraction of Secondary Effluent

Miniature (MIN.) vs. Macro- CEs

Quantitation Based on Assumed Response Factor = 1.

Qualitative Identifications Based Upon EPA-NIH Mass Spectral Library Match.

Scan	Compound Name	Estimated Concentration (ug/L)	
		MIN. CE	Max. CE
413	dimethyl disulfide	4.5	3.7
680	sulfonylbismethane	4	4.2
794	1-(2-methoxy-1-methylethoxy)-2-propanol	3.3	2.9
815	1-(2-methoxypropoxy)-2-propanol	4.6	4.2
948	2-(methylthio)pyridine	0.7	0.6
1012	4,4,5-trimethyl-2-hexene	0.6	1.3
1103	2-(2-hydroxypropoxy)-1-propanol	8.4	7.5
1106	3-Ethyl-4-Methyl-1H-pyrrole-2,5-dione	0.7	0.6
1125	2-methyl-2-(1-methylethoxy)propane	0.7	0.7
1393	N,N-diethyl-1,2-ethanediamine	2.6	2.5
1404	2,6-bis(1,1-dimethylethyl)-4-methylphenol	1.9	1.7
1583	4-(dimethylamino)-3-methyl-2-butanone	7.6	8
1743	Caffeine	2.9	2.5
1755	4-(dimethylamino)-3-methyl-2-butanone	2.9	4.2
1911	methoxycyclobutane	0.7	1.5

Appendix:

- ** Calibration standards and Spiking Solutions/Procedures.**
- ** Hydrophobic Membranes--possible mode of extract drying with minimum use of rinsing solvents.**
- ** Possible "Solvent Effect" associated with methanol.**

**Calibration Standards and
Spiking Solutions/Procedures:**

Spiking Solutions (General):

The spiking cocktails were methanol or acetone (miscible with water). Additions were made using volumetric pipets, or calibrated uL pipets. A "reference standard" was prepared using the same volume as was the spike into a volumetric flask of the same volume as the final K-D volume (final extract volume).

Calibration Standards (GC/MS):

Calibration standards (10, 20, 50, 100 ng/uL in MeCl₂) for all of the tested semivolatile compounds (excluding pesticides and PCBs) were prepared volumetrically from AccuStandard (New Haven, CT) stock solutions (ampules at 2 mg/mL in MeCl₂). The procedure was as follows:

AccuStd. (Stock ID)	Content (in MeCl ₂)	Conc. (ng/uL)
Z-014A	Base Neutral Mix 1	2000
Z-014B	Base Neutral Mix 2	2000
Z-014D	Tox. Sub. Mix 1	2000
Z-014E	Tox. Sub. Mix 2	2000
Z-014G-R	PNA Mix	2000
Z-014P	Phenols Mix	2000
Z-014A	Int. Std. Mix	4000

Vol. (uL) AccuStd. Stock ^a	10.0	20.0	50.0	50.0
Vol. (uL) AccuStd. Int. Std. ^b	20.0	20.0	20.0	10.0
Final Vol. (mL) ^c	2.0	2.0	2.0	1.0
Final Conc. (ng/uL)	10.0	20.0	50.0	100.0

^a 50 uL syringe. ^b 20 uL syringe. ^c Volumetric flask (Class "A").

The compound names are delineated in Table #4. The final concentrations of the internal standards were 40 ng/uL.

Internal Standards:

AccuStandard Internal Standard Mix (Z-014J) was employed, which consisted of 4000 ng/uL (in methylene chloride) of each of the following: d10-acenaphthene; d12-chrysene; d4-1,4-dichlorobenzene; d8-naphthalene; d12-perylene; and d10-phenanthrene. Because of concern for the stability of d10-perylene in solution, it was not employed as an internal standard (quantitation).

All extracts were spiked with the internal standards mix just prior to GC/MS analysis.

Superfund CLP "Matrix Spikes" (MS):

Stock solutions (ampules) at 5000 ng/uL were in methanol were obtained from the EPA Quality Assurance Materials Bank in RTP, North Carolina. These were diluted 10 fold with methanol to give 500 ng/uL spiking solutions. One hundred uL spikes were performed directly into 1 L of the aqueous samples (deionized water) prior to continuous extraction (50 ug/L spike). The compounds included: 1,2-dichlorobenzene; N-nitroso-n-propylamine; 2,4-dinitrotoluene; di-n-butylphthalate; acenaphthene; 1,2,4-trichlorobenzene; pyrene; 4-nitrophenol; pentachlorophenol; 4-chloro-3-methylphenol; phenol; and 2-chlorophenol.

This spiking cocktail was used during the design/re-design phases of this work, in which a relatively simple mixture, with a wide range of chemical qualities could be accurately measured via GC/FID (a means of quickly screening different CE designs, without costly GC/MS analyses).

Superfund CLP "Surrogate Compound" Spikes:

Stock solutions (ampules at 5000 ng/uL in methanol) were obtained from the EPA Quality Assurance Materials Bank in RTP, North Carolina. These were diluted 5 fold to give 1000 ng/uL spiking solutions. One hundred uL spikes were placed directly into 1 L of the aqueous samples prior to continuous extraction (100 ug/L spike). The compounds included: 2-fluorophenol; d5-phenol; d5-nitrobenzene; 2-fluoro-1,1'-biphenyl; 2,4,6-tribromophenol; and d14-p-terphenyl.

BNA QC Spiking Solution:

Quality Control solutions (CRADA ampules) were obtained from Supelco Inc., Bellefonte, PA. Base/Neutral #1, Base/Neutral #2 ampules were in acetone and contained 37 target semivolatile target priority pollutant (base/neutral) compounds. Acid #1 ampules contained 11 priority pollutant (acid) compounds in methanol. All compounds were at a concentration of 100 ng/uL. These were added as 1.0 mL (class A volumetric pipets) into 1000 mL of aqueous

sample (deionized water) to result in a 100 ug/L spike for each compound. The compound names are delineated in Table # 4.

Benzidine/s and Aniline/s Spikes:

Stock solutions (ampules) were obtained from the EPA Quality Assurance Materials Bank, RTP, North Carolina. C-075 and 62-53-3 (aniline) at 5000 ng/uL in benzene were diluted 50 fold (200 uL to 10 mL in methanol) to result in a working stock of 100 ng/uL. The excessive dilution was performed to maximize the quantity of methanol (hydrophilic solvent). This mixed stock solution was added as 1.0 mL (class "A" volumetric pipet) into 1000 mL of aqueous sample (deionized water) to result in a 100 ug/L spike for each compound. The compounds are delineated in Table # 6.

Pesticide Spikes:

Single Component Analytes:

Stock solutions (ampules) were obtained from Accustandard Z-014C at 2000 ng/uL in 1:1 toluene/hexane. These were diluted 500 uL to 10 mL in methanol (to maximize the hydrophilic solvent). This stock solution was added as 1.0 mL (class "A" volumetric pipet) into 1000 mL of aqueous sample (deionized water) to result in a 100 ug/L spike for each compound. The compound names are delineated in Table # 7.

Toxaphene:

Stock solutions (ampules) were obtained from the EPA Quality Assurance Materials Bank, RTP, North Carolina. These were as 1000 ng/uL solutions in methanol. Spikes were prepared by the addition of 50 uL of the stock solutions to 1000 mL of aqueous sample (deionized water) to result in a 50 ug/L spike for this compound. The resulting CE extracts were exchanged to hexane (as per method 608/508).

Chlordane:

Stock solutions (ampules) were obtained from the EPA Quality Assurance Materials Bank, RTP, North Carolina. These were as 1000 ng/uL solutions in methanol. Spikes were prepared by the addition of 50 uL of the stock solutions to 1000 mL of aqueous sample (deionized water) to result in a 50 ug/L spike for this compound.

PCBs:

Stock solutions (ampules) were obtained from Supelco, Inc. (CRADA QC material) for Aroclor 1260 and 1242. These solutions were in acetone at 50 ng/uL. Spikes were prepared by the addition of 1 mL (class "A" volumetric pipet) to 1000 mL of aqueous sample (deionized water) to result in a 50 ug/L spike for these compounds. The resulting extracts were exchanged to hexane (as per method 608/508).

Hydrophobic Membranes

[filters2.wk1]

EXPERIMENT: Validation of the hydrophobic filters. 60 mL of methylene chloride spiked with the list below and gravity filtered.

"Extracts were concentrated via K-D (EPA 625) and GC/MS analysis was performed vs. a "reference spike".

COMPOUND	Percent Recoveries			
	T073101	T073102	AVERAGE	STD. DEV.
1 METHANAMINE, N-METHYL-N-NITROSO-				
2 PHENOL *CCC*	85.500	90.268	87.884	2.4
3 ETHANE, 1,1'-OXYBIS(2-CHLORO-	93.354	92.885	93.120	0.2
4 2-CHLOROPHENOL	92.498	96.790	94.644	2.1
5 1,3-DICHLOROBENZENE (COELUTES)	90.780	95.814	93.297	2.5
6 *** D4-1,4-DICHLOROBENZENE ***INTERNAL STD.***				
7 1,4-DICHLOROBENZENE (COELUTES) *CCC*	91.007	92.881	91.944	0.9
8 1,2-DICHLOROBENZENE (COELUTES)	86.060	87.442	86.751	0.7
9 BENZENEMETHANOL HSL	85.535	89.520	87.528	2.0
10 2-METHYLPHENOL HSL	86.503	88.717	87.610	1.1
11 BIS(2-CHLOROISOPROPYL)ETHER	82.977	82.477	82.727	0.3
12 4-METHYLPHENOL HSL	89.216	97.299	93.258	4.0
13 1-PROPANAMINE, N-NITROSO-N-PROPYL-	84.193	86.212	85.203	1.0
14 ETHANE, HEXACHLORO-	83.023	86.868	84.946	1.9
15 BENZENE, NITRO-	97.464	91.929	94.697	2.8
16 2-CYCLOHEXEN-1-ONE, 3,5,5-TRIMETHYL- *CCC*	98.508	92.175	95.342	3.2
17 2-NITROPHENOL	96.241	99.470	97.856	1.6
18 PHENOL, 2,4-DIMETHYL-	104.924	107.665	106.295	1.4
19 BENZOIC ACID HSL	100.037	71.771	85.904	14.1
20 ETHANE, 1,1'-[METHYLENEBIS(OXY)]BIS[2-CHLORO-	95.042	96.104	95.573	0.5
21 2,4-DICHLOROPHENOL	90.548	97.734	94.141	3.6
22 BENZENE, 1,2,4-TRICHLORO-	93.348	96.470	94.909	1.6
23 *** D8-NAPHTHALENE ***INTERNAL STD.***				
24 NAPHTHALENE	91.623	90.906	91.265	0.4
25 1,3-BUTADIENE, 1,1,2,3,4,4-HEXACHLORO- *CCC*	93.790	98.902	96.346	2.6
26 PHENOL, 4-CHLORO-3-METHYL-	92.721	95.399	94.060	1.3
27 NAPHTHALENE, 2-METHYL- HSL	90.745	93.457	92.101	1.4
28 1,2,3,4,5,5-HEXACHLORO-1,3-CYCLOPENTADIENE *SPCC*	64.775	66.911	65.843	1.1
29 2,4,6-TRICHLOROPHENOL *CCC*	84.823	93.313	89.068	4.2
30 2,4,5-TRICHLOROPHENOL HSL	80.859	92.302	86.581	5.7
31 2-CHLORONAPHTHALENE	83.988	86.651	85.320	1.3
32 1,2-BENZENEDICARBOXYLIC ACID, DIMETHYLESTER	85.173	92.398	88.786	3.6
33 2,6-DINITROTOLUENE	76.472	87.642	82.057	5.6
34 ACENAPHTHYLENE	81.324	88.287	84.806	3.5
35 *** D10-PHENANTRENE ***INTERNAL STD.***				
36 ACENAPHTHYLENE, 1,2-DIHYDRO- *CCC*	82.432	87.826	85.129	2.7
37 2,4-DINITROPHENOL *SPCC*	69.712	83.007	76.360	6.6
38 PHENOL, 4-NITRO- *SPCC*	67.536	75.770	71.653	4.1
39 DIBENZOFURAN HSL	84.284	87.618	85.951	1.7
40 4-NITROPHENOL (SEC ION)	81.055	95.171	88.113	7.1
41 2,4-DINITROTOLUENE	77.978	84.672	81.325	3.3
42 1,2-BENZENEDICARBOXYLIC ACID, DIMETHYLESTER	81.574	86.406	83.990	2.4
43 1-CHLORO-4-PENOXYBENZENE	87.701	96.009	91.855	4.2
44 9H-FLOURENE	87.246	92.556	89.901	2.7
45 2-METHYL-4,6-DINITROPHENOL	80.430	89.049	84.740	4.3

Hydrophobic Membranes (cont'd)

46	NO STD. AVAILABLE ***N-PHENYLBENZENEAMINE DECOMP. OF NNDPA	78.500	82.387	80.444	1.9
47	BROMOPHENOXYBENZENE	79.194	87.924	83.559	4.4
48	BENZENE, HEXACHLORO- *CCC*	78.996	89.361	84.179	5.2
49	PENTACHLOROPHENOL	79.313	92.561	85.937	6.6
50	*** D10-PHENANTHRENE ***INTERNAL STD.***				
51	PHENANTHRENE	82.499	89.901	86.200	3.7
52	ANTHRACENE	79.466	87.524	83.495	4.0
53	1,2-BENZENEDICARBOXYLIC ACID, DIBUTYLESTER	86.907	93.386	90.147	3.2
54	FLUORANTHENE CCC*	91.250	107.378	99.314	8.1
55	PYRENE	89.885	103.851	96.868	7.0
56	N-BUTYL BENZYL PHTHALATE	97.158	106.327	101.743	4.6
57	BIS(2-ETHYLHEXYL)PHTHALATE	103.051	108.143	105.597	2.5
58	*** D12-CHRYSENE***INTERNAL STD.***				
59	BENZ/A/ANTHRACENE	87.408	91.997	89.703	2.3
60	CHRYSENE	94.722	97.892	96.307	1.6
61	DIOCTYLPHTHALATE *CCC*	74.639	93.802	84.221	9.6
62	BENZO\B\FLUORANTHENE	74.949	86.738	80.844	5.9
63	BENZO\K\FLUORANTHENE	82.893	92.354	87.624	4.7
64	BENZO/A/PYRENE	83.144	90.382	86.763	3.6
65	*** D12-PERYLENE ***INTERNAL STD.***				
66	INDENO(1,2,3-CD)PYRENE	89.225	90.171	89.698	0.5
67	DIBENZO(A,H) ANTHRACENE	92.429	99.621	96.025	3.6
68	BENZO\GHI\PERYLENE	88.329	96.353	92.341	4.0

Possible "Solvent Effect"
(Methanol)

MATRIX SPIKE % RECOVERY MICRO--REFERENCE CONTAINING 200 UL OF METHANOL

- (1) PHENOL
- (2) 2-CHLOROPHENOL
- (3) 1,4-DICHLOROBENZENE
- (4) N-NITROSO-N-PROPYL-1-PROPANAMINE
- (5) 1,2,4-TRICHLOROBENZENE
- (6) PHENOL-4-CHLORO-3-METHYL-
- (7) ACENAPHTHENE
- (8) 4-NITROPHENOL
- (9) 2,4-DINITROTOLUENE
- (10) PENTACHLOROPHENOL
- (11) 1,2-BENZENEDICARBOXYLICACID,DIBUTYLESTER
- (12) PYRENE

SAMPLE	1	2	3	4	5	6	7	8	9	10	11	12
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TARGET % WATER

	(12-89)	(27-123)	(36-97)	(41-116)	(39-98)	(23-97)	(46-118)	(10-80)	(24-96)	(9-103)	(11-117)	(26-127)
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30C(initial temp.) via GC/MS: 30M SPB-5, 1uM FILM, 0.32 mm ID

921101-01	83.7	87.7	74.4	82.7	77.4	86.6	92.5	146.0	95.6	212.1	95.3	99.0
921101-02	78.3	84.2	72.7	78.5	75.2	83.1	91.3	142.6	93.2	229.9	94.2	95.9
921101-03	77.2	82.8	69.2	77.1	75.9	82.1	90.1	142.6	95.3	221.6	94.0	97.7
921101-04	84.5	91.0	77.1	84.3	80.8	88.1	96.8	151.7	97.1	216.5	93.6	93.8
REF.#1	91.9	96.4	97.3	94.4	97.9	95.1	98.4	77.0	97.0	100.1	97.3	101.2
REF.#2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
REF.#3	97.8	99.0	101.0	99.3	102.3	93.7	101.5	106.1	97.7	90.8	96.8	98.9
AVE. SAMPLES	80.9	86.4	73.4	80.7	77.3	85.0	92.7	145.7	95.3	220.0	94.3	96.6
STD.DEV.SAMPLE	3.7	3.7	3.3	3.4	2.5	2.8	2.9	4.3	1.6	7.6	0.7	2.3
AVE. REF.	96.6	98.5	99.4	97.9	100.1	96.3	100.0	94.4	98.2	97.0	98.0	100.0
STD.DEV.REF.	4.2	1.9	1.9	3.1	2.2	3.3	1.6	15.3	1.6	5.3	1.7	1.2

50C(initial temp.)GC/MS 30M SPB-5, 1uM FILM, 0.32 mm ID

921101-01	79.6	81.5	68.8	80.9	74.0	81.5	91.1	91.7	93.4	207.3	90.3	84.2
921101-02**												
921101-03	78.7	82.8	73.5	83.9	76.6	84.5	93.1	92.6	98.7	241.5	92.9	91.1
921101-04	81.5	87.4	77.8	87.0	78.1	85.6	92.3	94.3	97.9	251.4	96.0	91.1
REF.#1	91.3	92.8	88.5	95.5	97.9	97.2	97.2	93.7	89.4	92.0	90.5	92.1
REF.#2 **												
REF.#3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
AVE. SAMPLES	79.9	83.9	73.4	83.9	76.2	83.9	92.2	92.9	96.7	233.4	93.1	88.8
STD.DEV.SAMPLE	1.4	3.1	4.5	3.1	2.1	2.1	1.0	1.3	2.9	23.1	2.9	4.0
AVE. REF.	95.7	96.4	94.3	97.8	99.0	98.6	98.6	96.9	94.7	96.0	95.3	96.1
STD.DEV.REF.	6.2	5.1	8.1	3.2	1.5	2.0	2.0	4.5	7.5	5.7	6.7	5.6

Possible "Solvent Effect"

(Methanol)

Cont'd

(initial temp.) GC/FID: 60M SPB-5, 0.25µM FILM, 0.32mm ID

921101-01	85.5	84.1	69.9	77.1	74.1	87.4	88.0	109.7	90.4	130.1	94.9	94.7
921101-02	87.0	86.1	75.9	77.9	78.1	87.8	86.1	111.2	87.8	129.7	90.9	92.2
921101-03	81.6	81.3	73.5	73.7	77.4	81.9	85.3	98.4	86.2	120.4	88.7	89.8
921101-04	82.6	82.2	74.2	74.7	78.0	83.3	86.2	101.4	87.4	127.4	90.8	90.7
REF.#1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
REF.#2	94.4	94.7	95.8	94.8	95.0	95.2	95.5	96.4	95.8	102.3	95.7	96.2
REF.#3	92.8	93.2	93.9	92.3	93.4	93.3	93.8	91.1	94.6	91.6	93.4	94.0

AVE. SAMPLES	84.2	83.4	73.4	75.9	76.9	85.1	86.4	105.2	88.0	126.9	91.3	91.9
STD.DEV.SAMPLE	2.5	2.1	2.5	2.0	1.9	2.9	1.1	6.2	1.8	4.5	2.6	2.1
AVE. REF.	95.7	96.0	96.6	95.7	96.1	96.2	96.4	95.8	96.8	98.0	96.4	96.7
STD.DEV.REF.	3.8	3.6	3.1	3.9	3.4	3.5	3.2	4.5	2.8	5.6	3.4	3.0

Solvent minimization in the continuous liquid/liquid
extraction of aqueous samples for semivolatile
organics

OC:35112543