ACID/NEUTRAL CONTINUOUS LIQUID/LIQUID EXTRACTION OF PRIORITY POLLUTANTS AND HAZARDOUS SUBSTANCE LIST COMPOUNDS

ENVIRONMENTAL PROTECTION AGENCY,
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Acid/Neutral Continuous Liquid/Liquid Extraction of Priority Pollutants and Hazardous Substance List Compounds

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Environmental Protection Agency

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Abstract

Continuous liquid-liquid extraction was compared to manual extractions per EPA Method 625, but employing an acid-neutral scheme. The results from EPA performance evaluation (quality control) wastewater, Superfund, and RCRA samples are compared using the two extraction techniques. Continuous liquid-liquid extractions following an acid-neutral scheme were compared to those following a base-neutral scheme. The acid-neutral continuous extraction scheme was determined to be effective elegant and labor saving. Emulsion formation was reduced and the recoveries of phenol, 4-nitrophenol, pentachlorophenol and benzoic acid were significantly improved by using the continuous extractor. The acid-neutral scheme as opposed to the Method 625 base-neutral extraction was found to greatly improve the recovery of dimethyl-, diethyl-, di-n-butyl-, and n-butyl benzyl phthalate esters. The levels of target and additional compounds extracted using a continuous extractor from the environmental samples tested equaled or exceeded those obtained from manually extracted samples. The distribution of target compounds in the acid-neutral and base fraction was determined by analyses of performance evaluation samples. All identifications and quantitations were performed using GC/MS systems with fused capillary columns.

*Presented August 6, 1986 at the Rocky Mountain Conference, Denver, Colorado.
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Introduction

The EPA procedure for the analysis of water samples for the National Pollution Discharge Elimination System (NPDES) includes the extraction of certain priority pollutants into methylene chloride. A detailed description of this Method 625 may be found elsewhere (1). The procedure details the extraction of a water sample after adjustment to a pH>11. The extraction is repeated after the sample pH is re-adjusted to pH<2. The separate extracts resulting from these extractions are dried with sodium sulfate, concentrated by Kuderna-Danish (KD) evaporation and analyzed separately using a GC/MS system. This extraction procedure was designed to allow for the recovery of basic, neutral and acidic organic compounds. In addition, this extraction scheme resulted in two extracts which were kept separate to facilitate packed column gas chromatography. Because of the large number of compounds involved and the diversity of polarities, two different packed GC columns were required (2). A column of medium polarity with a stationary phase of SP-2250 (50% methyl, 50% phenyl silicone) was employed for the basic and neutral compounds and a second column using SP-1240 was employed for the acidic compounds. This extraction scheme was adopted by the EPA for the Superfund Contract Laboratory Program (CERCLA) except that the extracts, after the concentration step, are combined and analyzed using a single fused silica capillary column (FSCC). This relatively new column technology provided much improved separation and allowed the increased efficiency of a single mixed extract. Additional refinements have been proposed (3) to Method 625 which involved the initial adjustment of the sample pH to 7. In this proposed scheme: the sample was extracted at pH 7, the pH re-adjusted to 2, the final extracts were combined before concentrating,

and a single analysis was performed on a FSCC. This extraction scheme recovered chlorinated hydrocarbon pesticides found to extract poorly by Method 625. The poor recovery of Method 625 was attributed to chemical reactions occurring among organic compounds in aqueous solutions under strongly basic (pH>11) conditions (4).

The EPA Method 625 includes the optional use of a continuous liquid/ liquid extractor which is recommended when an emulsion is formed during manual extraction (separatory funnel). The term "continuous extractor" in the EPA method, as well as in this report, refers to a batch type extractor (5,6) employing a fixed volume of sample and solvent. The sample is continuously extracted as boiling solvent, methylene chloride (specific gravity 1.355^{15}_{4}), condenses and drips through the sample. The solvent returns via a siphon tube to the boiling solvent flask.

The purpose of this report was to document the extraction efficiencies obtainable for a broad category of organic compounds with a simple extractor (Figure 1) as well as to relate the effect of reversing the pH scheme employed in Method 625. In this acid/neutral extraction, the sample pH was first adjusted to pH<2 thus resulting in an acid/neutral extract (A/N). The sample pH was subsequently readjusted to pH>11 and again extracted, resulting in a base extract. The priority pollutant and hazardous substance (HS) list compounds tested by this extraction procedure were those defined by the EPA for the Superfund program (7) including such HS compounds as: benzoic acid; 2-methylphenol; 4-methylphenol; 2-methylnaphthalene; and 3-nitroaniline. In addition, extraction efficiencies

were measured and compared using the continuous acid/neutral and the manual (separatory funnel) acid/neutral extraction schemes for other (non-target) compounds present in sewage, river water, industrial effluents and ground water.

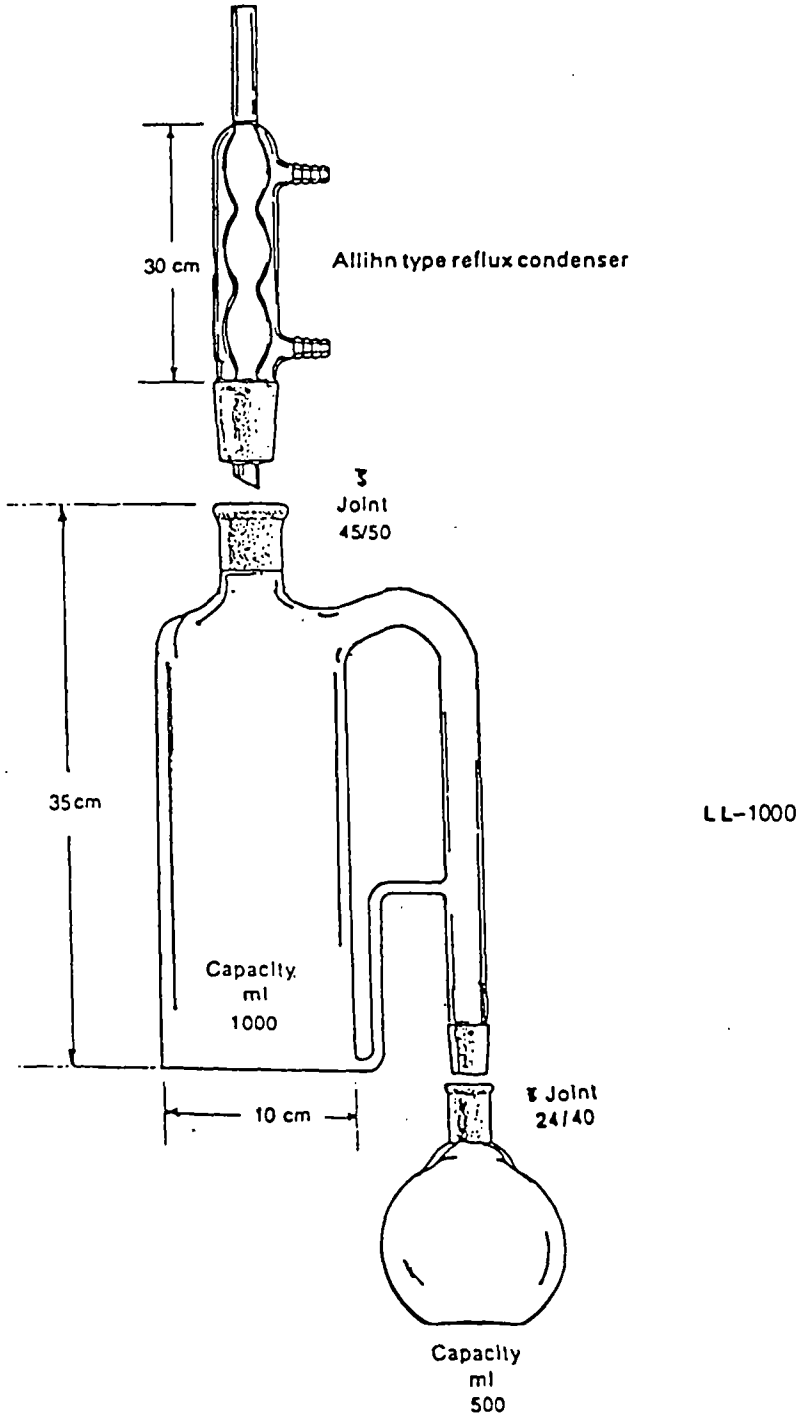
Experimental Section

I. Procedures

A. Continuous Extraction

The continuous extractor (CE) was a simple, inexpensive, all glass design obtained from Perpetual Systems, Rockville, MD. The extractor (Figure 1) stands 35 cm tall and is 10 cm in diameter. Cool water for the Allihn condenser was provided by a re-circulating chiller (Neslab Coolflow 75). The CE itself was first loaded with approximately 300 mL of CH_2CL_2 and 350 mL of CH_2CL_2 was placed in the solvent flask. One liter of spiked laboratory pure water or environmental sample was then placed in the extractor. For the acid/neutral extraction scheme, the pH was first adjusted to pH<2 with 6N H_2SO_4 using Colorphast^R (MCB Reagent, Gibbstown, NJ) test strips on drops of sample removed with a large glass stirring rod. The condenser was placed on the apparatus and the solvent flask was heated to boiling. A rheostat was employed to adjust the boiling rate to give a solvent flow of approximately 6 mL/minute. The extraction was carried out for 24$\pm$2 hours and then the aqueous pH was re-adjusted to pH>11 with 6N NaOH. A fresh flask of methylene chloride was then attached and extracted for 24$\pm$2 hours. In the

FIGURE 1. LIQUID-LIQUID EXTRACTOR



Perpetual Systems Corporation
Scientific Division
2283 Lewis Avenue
Rockville, Maryland 20851
(301) 770-0390

experiments with laboratory pure water spikes, the two solvent extracts were kept separate and GC/MS analyzed separately. In the experiments with environmental samples, the extracts were combined before concentration. The extract(s) were dried through sodium sulfate and concentrated to 1 mL by KD-evaporation with a water bath at 60-65°C as per EPA Method 625 (1). A reagent blank of laboratory pure water was carried through this procedure with each experiment. In the case of the base/neutral extraction scheme (Method 625), the sample pH adjustment for the first extraction was performed at pH>11.

Four separate spiking experiments were performed with laboratory pure water. These included:

I. A priority pollutant cocktail spike.

II. Additional compounds mixture spike.

III. Basic compound spikes.

IV. Pesticide spike.

A detailed description of these spiking materials is provided in the Materials Section.

B. Manual Extraction

For each extraction, a 1-liter aliquot of sample or spiked laboratory pure water was placed in a 2-L separatory funnel. The procedure employed was essentially that outlined by EPA Method 625 (1) with the exception that this manual acid/neutral scheme involved the initial adjustment of the sample to pH<2. In brief, after the pH

adjustment the extraction was carried out by shaking 60 mL of methylene chloride with the sample for 2 minutes. The solvent was dried through sodium sulfate and collected directly in a KD apparatus. This procedure was repeated three times and then the sample pH was readjusted to pH>11 and the process repeated. As with the continuous extractor, the A/N and base extracts were concentrated to 1 mL separately for the laboratory pure water spiking experiments. In the environmental sample experiments, the extracts were combined before concentration and analyzed as a single extract. The same four spiking experiments in laboratory pure water were conducted employing manual extraction except that the following compounds were not included: benzyl alcohol; dibenzofuran; 2-methylphenol, 4-methylphenol, 2,4-dinitrophenol; N-nitrosodiphenylamine.

Throughout this work every effort was made to perform the sodium sulfate drying and KD concentration steps as uniformly as possible since losses during these steps would affect the measured recoveries.

C. GC/MS Systems

The analyses were performed with Finnigan Model 4023 and 4500 mass spectrometer systems interfaced to Finnigan Model 9610 gas chromatographs. The fused silica capillary columns employed were 30 m x 0.32 mm i.d. x 1.0 um film thickness Supelco SPB-5 (5% diphenyl-/94% dimethyl-/1% vinyl-polysiloxane). The columns were connected directly into the spectrometer ion sources. The injections were performed with Grob-type injectors in the splitless mode with

sweep (15 mL/minute) and split (25 mL/minute) flows stopped for 30 seconds during injection. The carrier gas was ultrapure helium with a linear velocity of 38 cm/sec at 100°C. The injector temperature was 270°C and the temperature of the ion source was 270°C. The GC oven was programed at 30°C for 2 minutes followed by a 10°C/minute ramp to 300°C. Cryogenic cooling was provided by GC-regulated liquid nitrogen flow. The scan rate of the spectrometer was controlled by a Data General Nova 3 computer and was set at 35 to 450 AMU at 0.8 seconds per scan. The ionization mode employed was electron impact at 70 eV.

II. Materials

The materials employed were of the quality specified by EPA Method 625 (1). The boiling stones employed were silcon carbide granules (Carborundum^R #12 granules, Hengar Co., Philadelphia, PA), which were found to be less porous and absorptive than ceramic boiling aids. All glassware, glass wool and sodium sulfate were fired at 500°C employing a Blue M Model CFD 20F oven (Blue M Electric Co., Blue Island, Illinois). This oven allowed a gradual temperature change which was less stressful to fragile glassware.

A. Priority Pollutant Mixture

Three quality control (QC) standards WP482 #1 and #3 (non-phenolics in acetone) and WP881 #1 (phenolics in methanol) were obtained from EPA, Environmental Monitoring and Support Laboratory (EMSL) Cincinnati.

A synthetic sample was prepared by adding 1-mL of each of these OC standards to a single 1-liter volume of laboratory pure water.

B. Basic Compounds

Stock solutions of: benzidine (EC 26-01-02 in methanol); 3,3'-dichlorobenzidine (EC 5-01-02 in methanol); and anilines (C075 in benzene) were obtained from the EPA Quality Assurance Materials Bank, Research Triangle Park (RTP), NC.

C. Pesticides

A stock solution (C043 in toluene-hexane) was obtained from EPA (RTP).

D. Additional Compounds

The following extractable priority pollutants and hazardous substance list (HSL) compounds were obtained as neat materials from Chem Service, Inc., West Chester, PA: benzyl alcohol (HSL); dibenzofuran (HSL); 2-methylnaphthalene (HSL); 2,4,5-trichlorophenol (HSL); N-nitrosodiphenylamine. Stock solutions at 1,000 ng/uL were prepared in methanol (MeOH). In addition, the following compounds were obtained as stock solutions from the EPA Quality Assurance Materials Bank (RTP) and were analyzed separately:

N-nitrosodimethylamine (5000 ug/ml MeOH)

hexachlorocyclopentadiene (5000 ug/mL MeOH)

acenaphthylene (5000 ug/mL MeOH)

indeno(1,2,3-cd) pyrene (500 ug/mL acetone)

2-methylphenol (HSL) (5000 ug/mL MeOH)

4-methylphenol (HSL) (5000 ug/mL MeOH)

2,4-dinitrophenol (5000 ug/mL MeOH)

E. Daily Standard(s)

Standards for the target compounds were prepared at 20 ng/uL, 50 ng/uL, and 80 ng/uL from EPA (RTP) stock solutions (C039, C040, C041, C044) in methylene chloride and 1 uL was analyzed daily. In addition standards of the basic compounds, anilines and benzidenes (EC 26-01-02, EC 5-01-02, and C075), were analyzed daily at 50 ng/uL (50 ng injected).

F. Internal Standard(s)

Stock solutions of the following internal standards were purchased from Supelco, Bellefonte, PA (Supelpreme Internal Standards, 4000 ng/uL in methylene chloride): D4-1,4-dichlorobenzene; D8-naphthalene; D10-acenaphthene; D10-phenanthrene; D12-chrysene; D12-perylene. This solution was spiked (10 uL) into each 1 mL extract concentrate and standard solution just prior to GC/MS analysis.

G. Laboratory Pure Water (reagent water)

Laboratory pure water was obtained by passing the effluent of a Milli-R015 system (Millipore Co., Bedford, Mass.) through a 45 cm x 9 cm diameter glass/stainless steel cylinder containing charcoal.

III. Partition Experiment

A priority pollutant mixture spiking experiment was performed at pH<2 with a continuous extractor that had a stopcock in the solvent siphon line (return line). To the extractor was added: 300-350 mL of methylene chloride; 1000 mL of spiked laboratory water containing 1 mL of WP482 #1,

WP482 #3, and WP881 #1; sulfuric acid to pH<2, and the stopcock closed. One flask (350 mL methylene chlorine) of solvent was boiled over in 53 minutes. The temperature of the aqueous sample was 29°C. The heat was removed and the stopcock opened to collect all of the solvent. This solvent was Na_2SO_4 dried and KD concentrated to 1 mL.

IV. Quantitation

Concentrations were determined against a single 50 ng standard in the spiking experiments and against a three point standard curve for the environmental samples. Response factors were computed from quantitation ion peak areas ($Area_x$) versus the closest eluting internal standard as:

$$\text{Response factor} = \frac{(Area_x)}{(Conc._x)} \; \frac{(\text{Conc. Int. Std.})}{(\text{Area Int. Std.})}$$

The quantitation ion selected for each compound was that specified in the EPA Superfund (CERCLA) Program (7).

In the spiking experiments, a reference solution was prepared using the same material in the same amount as that spiked into the laboratory pure water (synthetic sample), but diluted to 1 mL in methylene chloride. The reference solution was added to a 2 mL teflon septum vial and stored in a freezer (-20°C) until the extraction was completed. At that time each sample extract and reference solution was spiked with 10 uL of the internal standards solution. The recoveries reported for the spiking experiments were calculated as:

$$\% \text{ recovery} = 100 \times \frac{\text{GCMS measured concentration with extraction}}{\text{GCMS measured concentration with direct injection of reference solution}}$$

The quality control sample of the phenolic compounds was in methanol (WP881 #1). This reference mixture was observed to give split chromatographic peaks on FSCC. The areas of the peaks were combined to give the total area used in the % recovery calculations.

For environmental samples, the concentration of the target compounds (CERCLA) were determined against a three point standard curve consisting of: a plot of $area_x$/area of internal standard vs. concentration. This response ratio was determined relative to the closest internal standard.

On occasion an environmental sample was analyzed which had target compound concentrations ranging from trace to macro amounts. In these instances an alternate quantitation ion (less abundant ion) was selected for the quantitation of the compounds(s) present in high concentration to allow a greater dynamic range. Some sample extracts required dilution and re-analysis to bring the very high level contaminant target and or non-target compounds to within the standard curve working range. In all cases the quantitation procedures used were the same for the extraction schemes being compared.

With the exception of closely eluting target compound isomers (dichlorobenzenes; methylphenols; phenanthrene and anthracene; benzo(A)anthracene and chrysene; benzo(B)fluoranthene and benzo(K)fluoranthene), the search for the quantitation ions in a relative retention time window and calculations of concentration were performed automatically by the Finnigan AutoQU program. The exceptions

required manual determination of the chromatographic peak areas and manual calculation of analyte concentration. All target identifications were verified by a review of the mass spectra.

For target compounds, in general, a "J" recorded next to a numerical value indicates a concentration value below the level of accurate quantitation. The presence of the compound has been verified by mass spectral information but the quantity reported is an estimate. An "ND" value denotes values which were not detected.

In addition, for environmental samples, compounds other than the target list (for which standards were analyzed daily) were searched against the EPA-NIH National Standard Reference Data System. This is a specral library of 38,750 compounds commonly called the "NBS Library". Quantitation of these "tentatively identified compounds" was based on an assumed response factor of 1.0 relative to the nearest eluting internal standard. All calculations of the concentrations of these compounds were performed with an automatic program entitled Cmixed. This Fortran program is available from the authors.

V. Quality Control

Before the analysis of any sample extracts the mass spectrum of bis(perfluorophenyl)phenylphosphine (DFTPP) was measured and found to be within EPA criteria (Method 625) or the necessary instrument adjustments were performed. At least one standard for all target

compounds was analyzed daily to verify acceptable spectrometer and chromatographic performance. Reagent blanks were routinely analyzed to assure the lack of background contamination.

Results and Discussion

I. Priority Pollutant Cocktail Spiking Experiment

A. Acid/Neutral Extraction Scheme Employing the Continuous Extractor

A single mixture of forty-eight priority pollutants was created by spiking three quality control samples into laboratory pure water. This mixture was extracted in four separate replicate extractions using continuous extractors employing an acid/neutral extraction scheme. The total ion chromatogram of the mixture is illustrated in Figure 2, which also includes six internal standards. The effort was to create a complex mixture to allow possible chemical reactions to occur under extractor conditions. The compounds represented broad classes including phenolics, polynuclear aromatics, ethers, and phthalate esters. The average recovery obtained for each compound ranged from 88.8% for hexachloroethane to 118% for pentachlorophenol (Table 1 and Figures 3 and 4). The true values listed in this table were those provided with the quality control samples. With the exception of 2-methyl-4,6-dinitrophenol (MDNP) all of the recoveries obtained were within the QC (quality control) limits listed for Method 625. The average recovery obtained for MDNP was 108% and the required QC acceptance limit was 53-100%. The standard deviations of the recoveries for these forty-eight

RIC DATA: ACEAN2 #499 SCANS 600 TO 3200
05/19/86 13:28:00 CALI: CAL0324 #3
SAMPLE: CE
CONDS.: 4500 30C 2 MIN TO 300C AT 10C/MIN
RANGE: G 1,3400 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

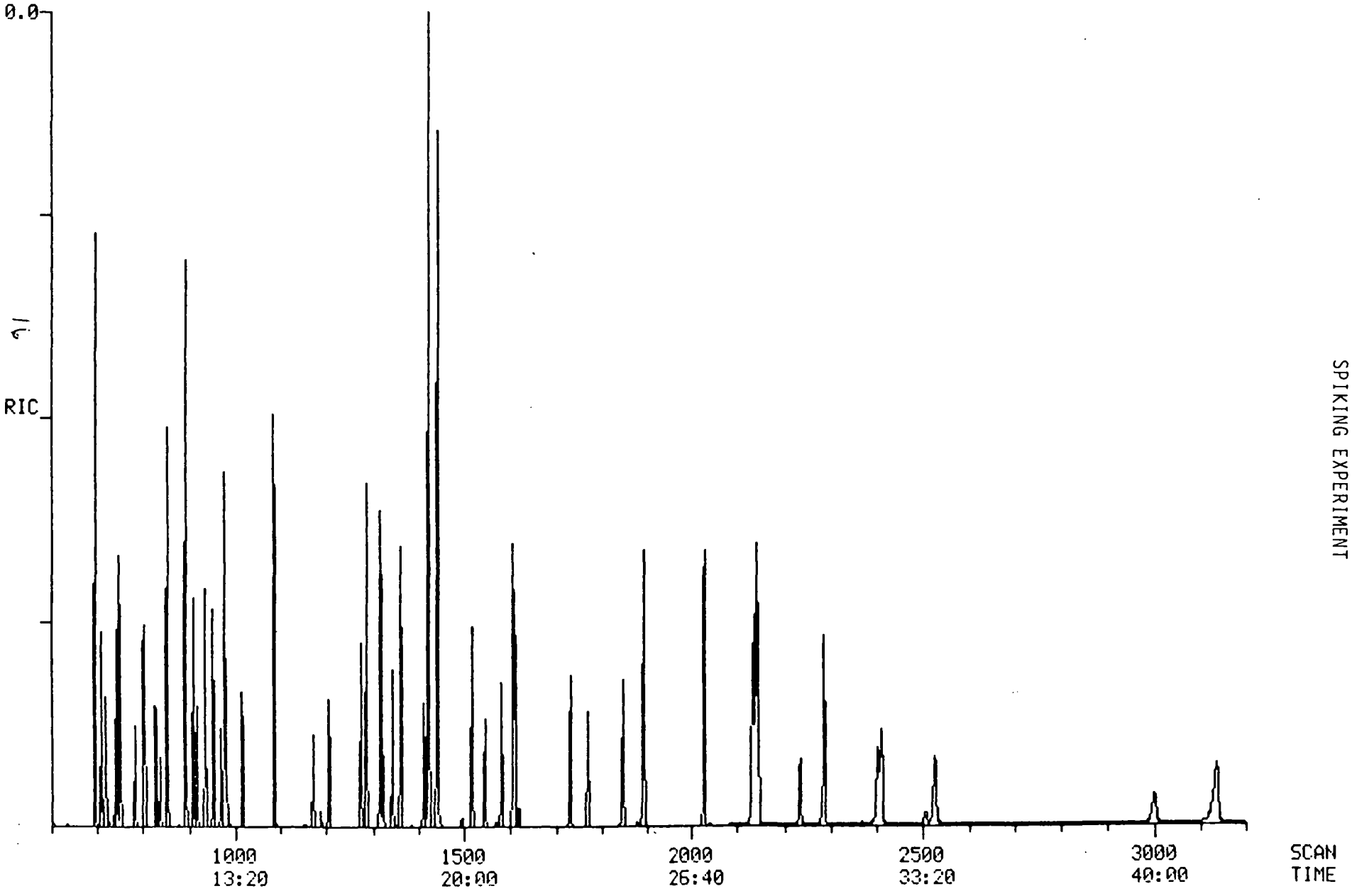


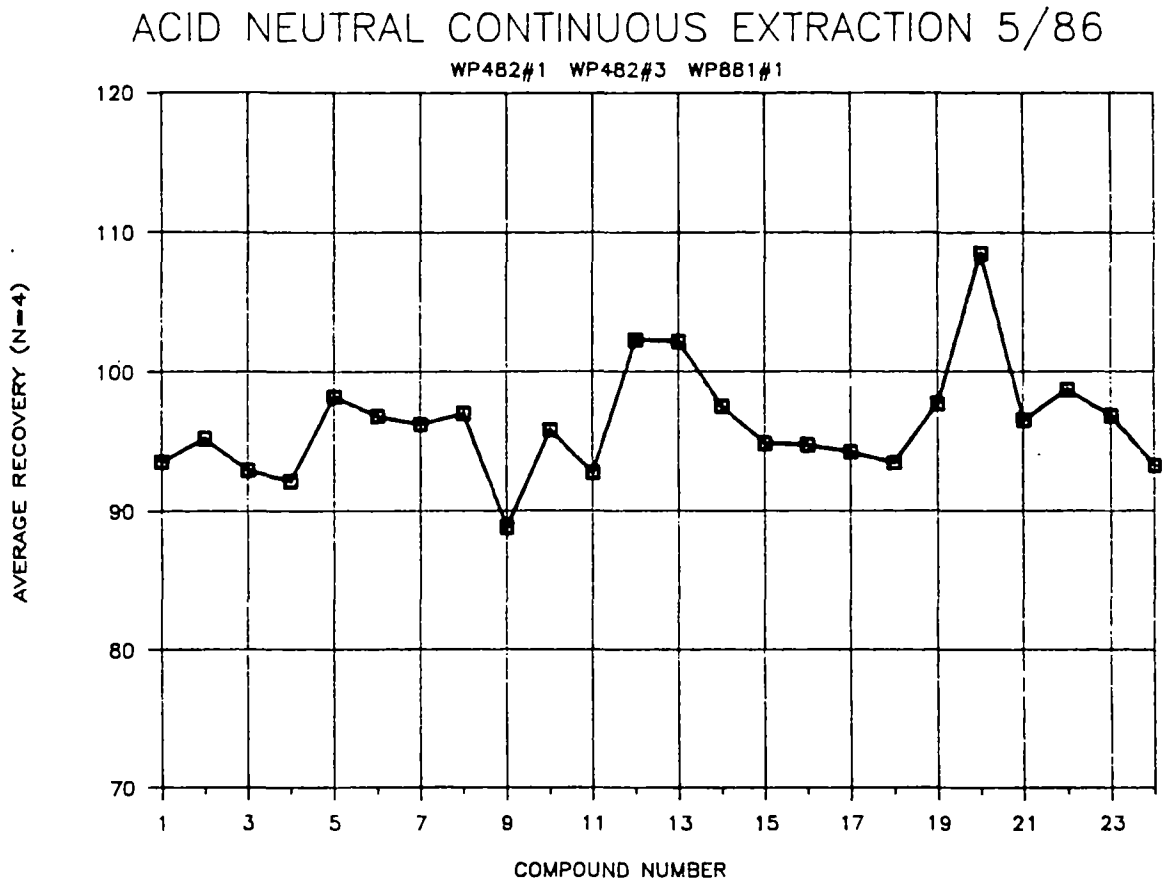
FIGURE 2. PRIORITY POLLUTANT COCKTAIL SPIKING EXPERIMENT

TABLE 1.

ACID NEUTRAL CONTINUOUS EXTRACTION 5/86
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

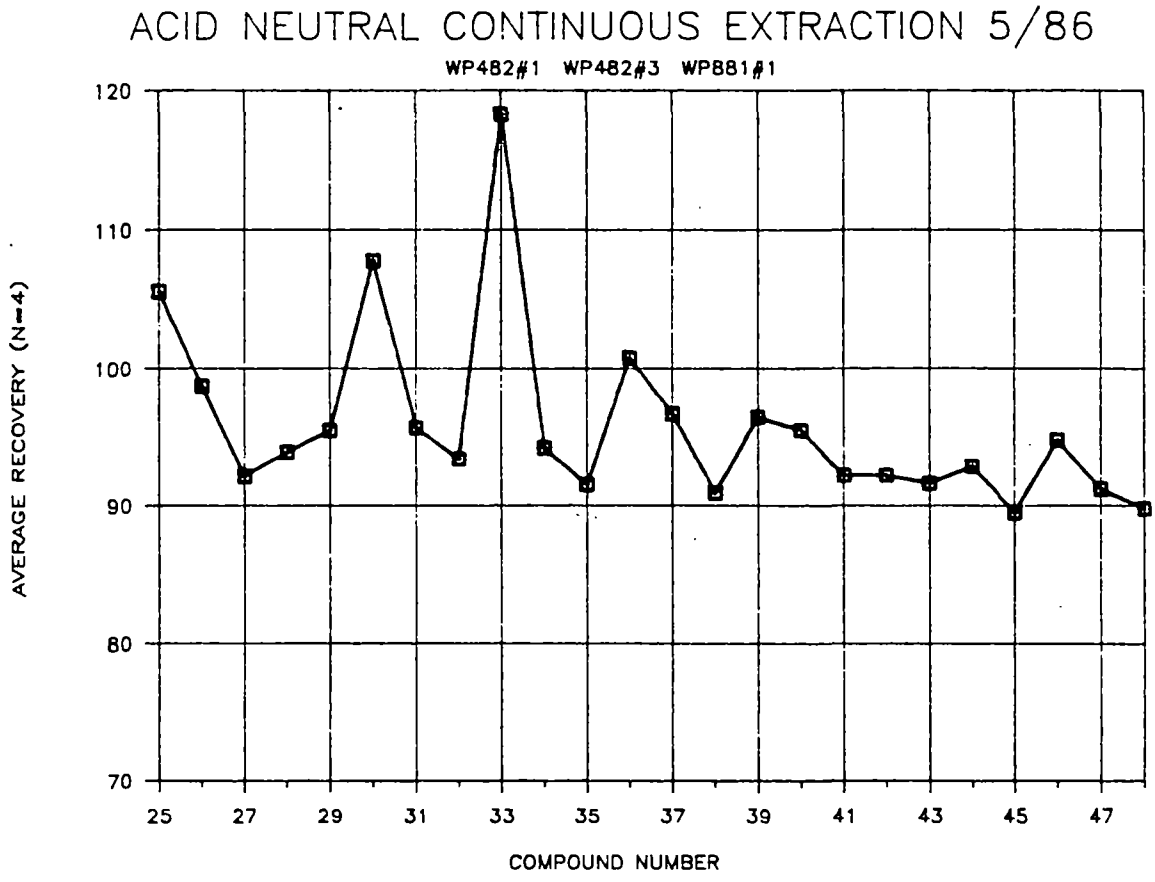
NO.	compound	ppb true value	% RECOVERY #1	#2	#3	#4	AVERAGE RECOVERY	STD. DEV.	EPA 625 REQUIRED RECOVERY
1	phenol	100	94.5	93.5	94.8	91.3	93.5	1.6	16.6-100
2	1,1-oxybis(2-chloroethane)	48.2	93.8	97.5	93	96.6	95.2	2.2	42.9-126
3	2-chlorophenol	30	94.5	91.3	94.3	91.6	92.9	1.7	36.2-120
4	1,3-dichlorobenzene	52	89	92.6	92	94.6	92.1	2.3	16.7-154
5	1,4-dichlorobenzene	24.8	98.2	100	96.4	98.2	98.2	1.5	37.3-106
6	1,2-dichlorobenzene	24.7	98.2	100	92.9	95.9	96.8	3.1	48.6-112
7	bis(2-chloroisopropyl)ether	38.8	97	101	91.8	94.8	96.2	3.9	62.8-139
8	N-nitroso-di-n-propylamine	34.8	95.4	99.5	95.8	97.2	97	1.9	13.6-198
9	hexachloroethane	30	89.5	92.4	85.8	87.5	88.8	2.8	55.2-100
10	nitrobenzene	76.5	96.1	98.4	93.1	95.4	95.8	2.2	54.3-158
11	3,5,5-trimethyl-2-cyclohexen-1-one	76.7	89.8	92.4	93.1	95.4	92.7	2.3	46.6-180
12	2-nitrophenol	50	105	103	102	99	102.3	2.5	45.0-167
13	2,4-dimethylphenol	30	109	103	102	94.8	102.2	5.8	41.8-109
14	bis(2-chloroethoxy)methane	48.6	94.8	99	96.2	100	97.5	2.4	49.2-165
15	2,4-dichlorophenol	50	96.7	94.1	95.3	93	94.8	1.6	52.5-122
16	1,2,4-trichlorobenzene	25.3	92.7	97.6	92.4	96	94.7	2.5	57.3-129
17	naphthalene	24.8	93.2	97.6	91.9	94.2	94.2	2.4	35.6-120
18	1,1,2,3,4,4-hexachloro-1,3-butadiene	49.6	90.9	94.5	92.8	95.4	93.4	2	37.8-102
19	4-chloro-3-methylphenol	75	101	96.7	98.2	94.9	97.7	2.6	40.8-128
20	2,4,6-trichlorophenol	25	116	106	106	106	108.5	5	52.4-129
21	2-chloronaphthalene	25.4	96	96.8	94.8	98.4	96.5	1.5	64.5-114
22	dimethylphthalate	40	100	101	93.6	100	98.7	3.4	D-100
23	2,6-dinitrotoluene	76.5	95.5	95.8	95.7	100	96.8	2.2	68.1-137
24	1,2-dihydroacenaphthylene	19.5	92.9	96.9	90.8	92.2	93.2	2.6	60.1-132
25	4-nitrophenol	50	111	105	107	99.4	105.6	4.8	13.0-107
26	2,4-dinitrotoluene	73.8	91.5	103	96.4	104	98.7	5.9	47.5-127
27	diethylphthalate	25.1	88.2	92	91.4	96.7	92.1	3.5	D-100
28	1-chloro-4-phenoxybenzene	76.7	94	92.2	91.8	97.5	93.9	2.6	38.4-145
29	9H-fluorene	51.2	94.8	95.2	93.1	98.8	95.5	2.4	71.6-108
30	2-methyl-4,6-dinitrophenol	250	107	114	107	103	107.8	4.6	53-100
31	4-bromophenyl-phenylether	41.5	99.8	99.8	86.9	96.4	95.7	6.1	64.9-114
32	hexachlorobenzene	35.7	93.8	94	88.3	97.3	93.4	3.7	7.8-142
33	pentachlorophenol	75	115	117	123	118	118.3	3.4	38.1-152
34	phenanthrene	40.2	92.9	94.3	94	95.4	94.2	1	65.2-109
35	anthracene	40	90.5	93.1	91	91.2	91.5	1.1	43.4-118
36	di-n-butylphthalate	24.9	99.6	103	99.6	101	100.8	1.6	8.4-111
37	fluoranthene	29.8	94	99.3	98.9	94.4	96.7	2.8	42.9-121
38	pyrene	60.2	88.2	90.2	91.7	93.6	90.9	2.3	69.6-100
39	n-butyl benzyl phthalate	51.3	95.8	101	94.9	94.1	96.5	3.1	D-140
40	bis(2-ethylhexyl)phthalate	29.1	97.5	101	91.3	92.3	95.5	4.6	28.9-137
41	benzo(a)anthracene	73.9	90.8	95.3	90.7	92	92.2	2.1	41.8-133
42	chrysene	69.9	91.4	91.5	91.4	94.4	92.2	1.5	44.1-140
43	di-n-octylphthalate	43.9	88.7	92.7	89.6	95.2	91.6	3	18.6-132
44	benzo(b)fluoranthene	40	90.8	95.3	89.5	96.1	92.9	3.3	42.0-140
45	benzo(k)fluoranthene	45.7	91.4	91.5	86.3	88.6	89.5	2.5	25.2-146
46	benzo(a)pyrene	24.9	94.6	98	92.6	94	94.8	2.3	31.7-148
47	dibenzo(a,h)anthracene	40.7	91.9	92.9	87.2	92.6	91.2	2.7	D-200
48	benzo(ghi)perylene	80.4	90.3	83.6	91.1	94.3	89.8	4.5	D-195

FIGURE 3.



NO.	COMPOUND	ppb	NO.	COMPOUND	ppb
1	phenol	100	13	2,4-dimethylphenol	30
2	1,1-oxybis(2-chloroethane)	48.2	14	bis(2-chloroethoxy)methane	48.6
3	2-chlorophenol	30	15	2,4-dichlorophenol	50
4	1,3-dichlorobenzene	52	16	1,2,4-trichlorobenzene	25.3
5	1,4-dichlorobenzene	24.8	17	naphthalene	24.8
6	1,2-dichlorobenzene	24.7	18	1,1,2,3,4,4-hexachloro-1,3-butadiene	49.6
7	bis(2-chloroisopropyl)ether	38.8			
8	N-nitroso-di-n-propylamine	34.8	19	4-chloro-3-methylphenol	75
9	hexachloroethane	30	20	2,4,6-trichlorophenol	25
10	nitrobenzene	76.5	21	2-chloronaphthalene	25.4
11	3,5,5-trimethyl-2-cyclohexen-1-one	76.5	22	dimethylphthalate	40
			23	2,6-dinitrotoluene	76.5
12	2-nitrophenol	50	24	1,2-dihydroacenaphthylene	19.5

FIGURE 4.



NO.	COMPOUND	ppb	NO.	COMPOUND	ppb
25	4-nitrophenol	50	37	fluoranthene	29.8
26	2,4-dinitrotoluene	73.8	38	pyrene	60.2
27	diethylphthalate	25.1	39	n-butyl benzyl phthalate	51.3
28	1-chloro-4-phenoxybenzene	76.7	40	bis(2-ethylhexyl)phthalate	29.1
29	9H-fluorene	51.2	41	benzo(a)anthracene	73.9
30	2-methyl-4,6-dinitrophenol	250	42	chrysene	69.9
31	4-bromophenyl-phenylether	41.5	43	di-n-octylphthalate	43.9
32	hexachlorobenzene	35.7	44	benzo(b)fluoranthene	40
33	pentachlorophenol	75	45	benzo(k)fluoranthene	45.7
34	phenanthrene	40.2	46	benzo(a)pyrene	24.9
35	anthracene	40	47	dibenzo(a,h)anthracene	40.7
36	di-n-butylphthalate	24.9	48	benzo(ghi)perylene	80.4

compounds ranged from 1.0% for phenanthrene (40.2 ug/L spike level) to 6.1 % for 4-bromophenylphenyl ether (41.5 ng/L spike level). No compounds were detected in the base extract after the acid neutral extraction. In addition the solvent below the aqueous sample was analyzed after the completion of the experiment and no compounds were detected.

B. Acid/Neutral Continuous Extraction vs. Acid/Neutral Manual Extraction

The results of the manual (separatory funnel) extraction of the laboratory pure water spiked with a priority pollutant cocktail are listed in Table 2. A comparison of the average recoveries by these two extraction schemes is presented in Figure 5 in which the difference in the % recovery (continuous minus manual extraction recovery) was plotted for each compound. There was good agreement between the two extraction schemes as can be seen by the differences in % recovery oscillating near zero in Figure 5. However, there are five notable exceptions (detailed in Table 3): phenol; 2-chlorophenol; 1,1,2,3,4,4-hexachloro-1,3-butadiene; 4-nitrophenol; and pentachlorophenol. The recoveries of three hydrophilic phenolics (phenol, 4-nitrophenol and pentachlorophenol) were observed to improve when employing continuous extraction. The recoveries of all of the phenolic compounds have been compiled in Table 4.

TABLE 2.

CONTINUOUS VS. MANUAL A/N EXTRACTION
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

NO.	compound	ppb true value	% RECOVERY CONT. EXT. (AVE.5/86)	% RECOVERY MAN EXT. (10/84 QA)
1	phenol	100	93.5	44.1
2	1,1-oxybis(2-chloroethane)	48.2	95.2	101
3	2-chlorophenol	30	92.9	110
4	1,3-dichlorobenzene	52	92.1	86.1
5	1,4-dichlorobenzene	24.8	98.2	93.2
6	1,2-dichlorobenzene	24.7	96.8	87.7
7	bis(2-chloroisopropyl)ether	38.8	96.2	108
8	N-nitroso-di-n-propylamine	34.8	97	102
9	hexachloroethane	30	88.8	80.1
10	nitrobenzene	76.5	95.8	104
11	3,5,5-trimethyl-2-cyclohexen-1-one	76.7	92.7	98.3
12	2-nitrophenol	50	102	110
13	2,4-dimethylphenol	30	102	99
14	bis(2-chloroethoxy)methane	48.6	97.5	97.5
15	2,4-dichlorophenol	50	94.8	106
16	1,2,4-trichlorobenzene	25.3	94.7	86.3
17	naphthalene	24.8	94.2	96.2
18	1,1,2,3,4,4-hexachloro-1,3-butadiene	49.6	93.4	78.3
19	4-chloro-3-methylphenol	75	97.7	101
20	2,4,6-trichlorophenol	25	109	100
21	2-chloronaphthalene	25.4	96.5	93.9
22	dimethylphthalate	40	98.7	95.9
23	2,6-dinitrotoluene	76.5	96.8	98.6
24	1,2-dihydroacenaphthylene	19.5	93.2	99
25	4-nitrophenol	50	106	41.8
26	2,4-dinitrotoluene	73.8	98.7	101
27	diethylphthalate	25.1	92.1	97.1
28	1-chloro-4-phenoxybenzene	76.7	93.9	95.8
29	9H-fluorene	51.2	95.5	95.7
30	2-methyl-4,6-dinitrophenol	250	108	100
31	4-bromophenyl-phenylether	41.5	95.7	95.5
32	hexachlorobenzene	35.7	93.4	97.4
33	pentachlorophenol	75	118	67.1
34	phenanthrene	40.2	94.2	95.4
35	anthracene	40	91.5	96
36	di-n-butylphthalate	24.9	101	104
37	fluoranthene	29.8	96.7	100
38	pyrene	60.2	90.9	97.3
39	n-butyl benzyl phthalate	51.3	96.5	99.7
40	bis(2-ethylhexyl)phthalate	29.1	95.5	95.1
41	benzo(a)anthracene	73.9	92.2	95.4
42	chrysene	69.9	92.2	99.7
43	di-n-octylphthalate	43.9	91.6	95.1
44	benzo(b)fluoranthene	40	92.9	95.1
45	benzo(k)fluoranthene	45.7	89.5	91.1
46	benzo(a)pyrene	24.9	94.8	94.5
47	dibenzo(a,h)anthracene	40.7	91.2	93.1
48	benzo(ghi)perylene	80.4	89.8	87.4

FIGURE 5.

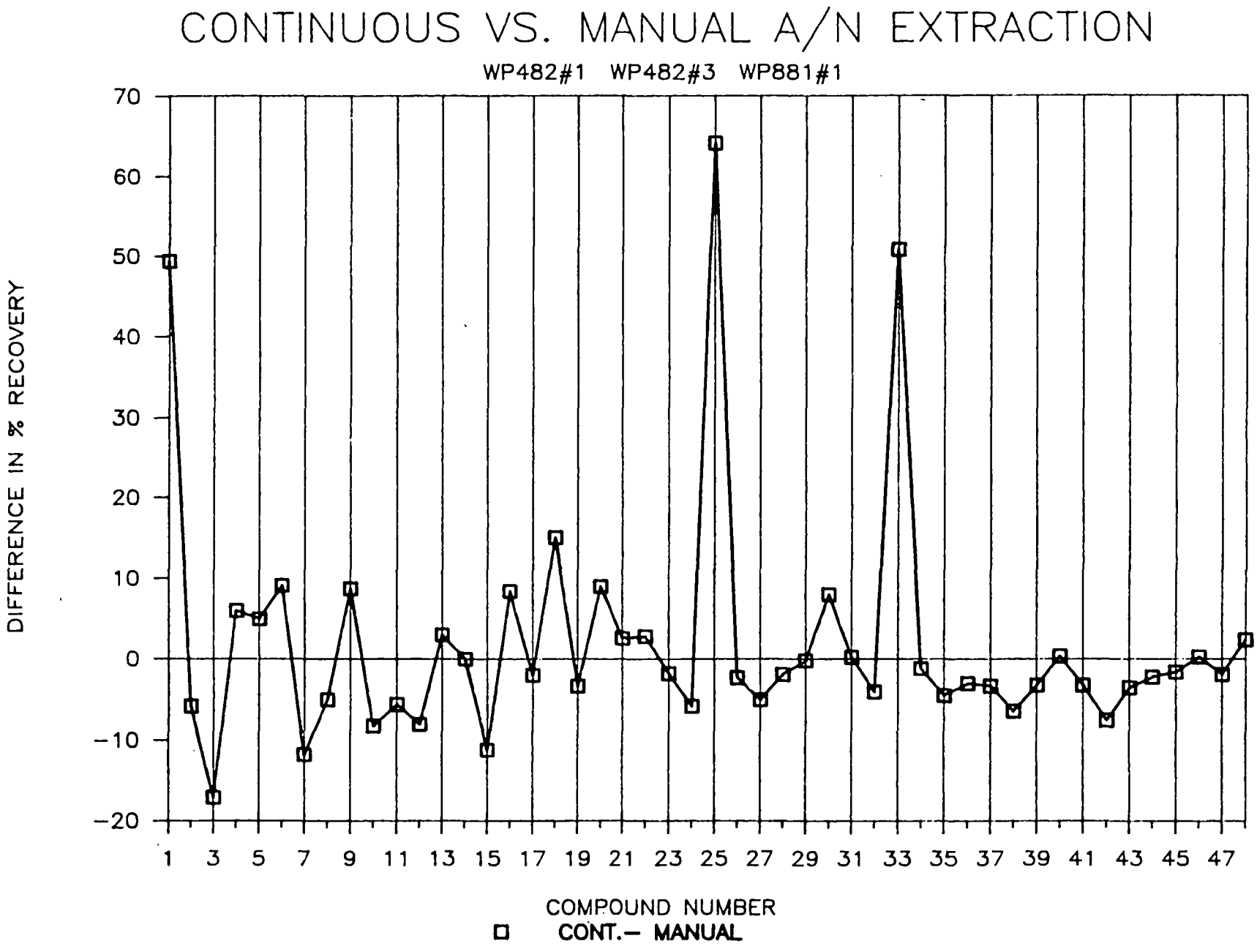

CONTINUOUS VS. MANUAL A/N EXTRACTION
WP482#1 WP482#3 WP881#1
DIFFERENCE IN % RECOVERY
70
60
50
40
30
20
10
0
-10
-20
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37 39 41 43 45 47
COMPOUND NUMBER
CONT.– MANUAL

TABLE 3.

CONTINUOUS VS. MANUAL EXTRACTION
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

NO.	COMPOUND	TRUE VALUE PPB	% RECOVERY CONT. EXT. (AVE.5/86)	% RECOVERY MAN. EXT. (10/84 QA)	DIFF.
1	PHENOL	100	93.5	44.1	49.4
3	2-CHLOROPHENOL	30	92.9	110	-17.1
18	1,1,2,3,4,4-HEXACHLORO-1,3-BUTADIENE	49.6	93.4	78.3	15.1
25	4-NITROPHENOL	50	106	41.8	64.2
33	PENTACHLOROPHENOL	75	118	67.1	50.9

TABLE 4.

CONTINUOUS VS. MANUAL EXTRACTION
EXTRACTION SCHEMES
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

NO.	COMPOUND	TRUE VALUE PPB	% RECOVERY CONT. EXT. (AVE.5/86)	% RECOVERY MAN. EXT. (10/84 QA)	DIFF.
1	PHENOL	100	93.5	44.1	49.4
3	2-CHLOROPHENOL	30	92.9	110	-17.1
12	2-NITROPHENOL	50	102	110	-8
13	2,4-DIMETHYLPHENOL	30	102	99	3
15	2,4-DICHLOROPHENOL	50	94.8	106	-11.2
19	4-CHLORO-3-METHYLPHENOL	75	97.7	101	-3.3
20	2,4,6-TRICHLOROPHENOL	25	109	100	9
25	4-NITROPHENOL	50	106	41.8	64.2
30	2-METHYL-4,6-DINITROPHENOL	250	108	100	8
33	PENTACHLOROPHENOL	75	118	67.1	50.9

C. Acid/Neutral (A/N) Continuous Extraction vs Base/Neutral (B/N) Continuous Extraction Schemes

The recoveries of replicate extractions of the priority pollutant mixture using the Base/Neutral continuous extraction scheme are listed in Table 5. As indicated, all of the recoveries were within or just exceeded (compound #25 and #30) EPA Method 625 method validation criteria with the exception of dimethylphthalate which was not detected at 40 ppb. A comparison of the A/N and B/N extraction schemes is presented in Table 6 and Figure 6. The A/N recoveries are the average of four replicate extractions and the B/N recoveries are the average of two extractions. The graph is a plot of the difference in percent recovery (A/N minus B/N). The A/N scheme was observed to give comparable or improved recoveries. Significant improvement was observed for the following six compounds:

(#9) hexachloroethane (88.8% A/N, 70.7% B/N)

(#18) 1,1,2,3,4,4-hexachloro-1,3-butadiene (93.4% A/N, 69% B/N)

(#22) dimethylphthalate (98.7% A/N, 0% B/N)

(#27) diethylphthalate (92.1% A/N, 1.7% B/N)

(#36) di-n-butylphthalate (101% A/N, 36% B/N)

(#39) n-butyl benzyl phthalate (96.5% A/N, 32.1 B/N)

The most notable improvement was observed for the phthalate esters. In Table 7 a comparison of the recoveries obtained for all the phthalate esters is presented. The generally poor recovery of phthalate esters by the base/neutral scheme appears to be related to the size and complexity of the ester side chain. This pattern

TABLE 5

BASE NEUTRAL CONTINUOUS EXTRACTION 4/86
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

NO.	compound	ppb true value	% RECOVERY #1	#2	AVERAGE RECOVERY	EPA 625 REQUIRED RECOVERY
1	phenol ********(BASE/N + ACID)	100	87.9	84.5	86.2	16.6-100
2	1,1-oxybis(2-chloroethane)	48.2	94.8	97.6	96.2	42.9-126
3	2-chlorophenol ********(BASE/N+ACID)	30	91.8	90.8	91.3	36.2-120
4	1,3-dichlorobenzene	52	78.3	80.4	79.4	16.7-154
5	1,4-dichlorobenzene	24.8	84.2	86.7	85.5	37.3-106
6	1,2-dichlorobenzene	24.7	82.5	85.1	83.8	48.6-112
7	bis(2-chloroisopropyl)ether	38.8	90.3	94.3	92.3	62.8-139
8	N-nitroso-di-n-propylamine	34.8	87	90	88.5	13.6-198
9	hexachloroethane	30	69.8	71.6	70.7	55.2-100
10	nitrobenzene	76.5	97.9	98.7	98.3	54.3-158
11	3,5,5-trimethyl-2-cyclohexen-1-one	76.7	94.5	94.9	94.7	46.6-180
12	2-nitrophenol	50	100	99.4	99.7	45.0-167
13	2,4-dimethylphenol ********(BASE/N+ACID)	30	89.2	88.6	88.9	41.8-109
14	bis(2-chloroethoxy)methane	48.6	97.7	97.5	97.6	49.2-165
15	2,4-dichlorophenol	50	96.3	94.5	95.4	52.5-122
16	1,2,4-trichlorobenzene	25.3	84.8	83.5	83.5	57.3-129
17	naphthalene	24.8	92.5	102	97.3	35.6-120
18	1,1,2,3,4,4-hexachloro-1,3-butadiene	49.6	68.4	69.6	69	37.8-102
19	4-chloro-3-methylphenol ***(BASE/N+ACID)	75	109	93.2	101.1	40.8-128
20	2,4,6-trichlorophenol	25	103	101	102	52.4-129
21	2-chloronaphthalene	25.4	92.4	92	92.2	64.5-114
22	dimethylphthalate	40	0	0	0	D-100
23	2,6-dinitrotoluene	76.5	95.4	96.1	95.8	68.1-137
24	1,2-dihydroacenaphthylene	19.5	92.8	93.8	93.3	60.1-132
25	4-nitrophenol	50	110	106	108	13.0-107
26	2,4-dinitrotoluene	73.8	96.5	96	96.3	47.5-127
27	diethylphthalate	25.1	2.3	1	1.7	D-100
28	1-chloro-4-phenoxybenzene	76.7	95.9	98.6	97.3	38.4-145
29	9H-fluorene	51.2	96.6	96.9	96.8	71.6-108
30	2-methyl-4,6-dinitrophenol	250	101	104	102.5	53-100
31	4-bromophenyl-phenylether	41.5	94.9	95.4	95.2	64.9-114
32	hexachlorobenzene	35.7	91.4	94.2	92.8	7.8-142
33	pentachlorophenol	75	108	107	107.5	38.1-152
34	phenanthrene	40.2	93.2	96	94.6	65.2-109
35	anthracene	40	90.6	91.8	91.2	43.4-118
36	di-n-butylphthalate	24.9	41.1	30.9	36	8.4-111
37	fluoranthene	29.8	95.3	97.4	96.4	42.9-121
38	pyrene	60.2	96.5	97.5	97	69.6-100
39	n-butyl benzyl phthalate	51.3	35	29.1	32.1	D-140
40	bis(2-ethylhexyl)phthalate	29.1	101	107	104	28.9-137
41	benzo(a)anthracene	73.9	93.6	95.2	94.4	41.8-133
42	chrysene	69.9	94.9	96.3	95.6	44.1-140
43	di-n-octylphthalate	43.9	89.5	92.1	90.8	18.6-132
44	benzo(b)fluoranthene	40	90.6	93.9	92.3	42.0-140
45	benzo(k)fluoranthene	45.7	92.1	92.7	92.4	25.2-146
46	benzo(a)pyrene	24.9	91.6	95	93.3	31.7-148
47	dibenzo(a,h)anthracene	40.7	91.9	97.7	97.7	D-200
48	benzo(ghi)perylene	80.4	99.2	100	99.6	D-195

TABLE 6.

CONTINUOUS EXTRACTION

ACID NEUTRAL VS. BASE NEUTRAL
EXTRACTION SCHEMES
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

NO.	compound	ppb true value	% RECOVERY ACID/N EXT. (AVE.5/86)	BASE/N EXT. (AVE.4/86)	DIFF. %
1	phenol	100	93.5	86.2	7.3
2	1,1-oxybis(2-chloroethane)	48.2	95.2	96.2	-1
3	2-chlorophenol	30	92.9	91.3	1.6
4	1,3-dichlorobenzene	52	92.1	79.4	12.7
5	1,4-dichlorobenzene	24.8	98.2	85.5	12.7
6	1,2-dichlorobenzene	24.7	96.8	83.8	13
7	bis(2-chloroisopropyl)ether	38.8	96.2	92.3	3.9
8	N-nitroso-di-n-propylamine	34.8	97	88.5	8.5
9	hexachloroethane	30	88.8	70.7	18.1
10	nitrobenzene	76.5	95.8	98.3	-2.5
11	3,5,5-trimethyl-2-cyclohexen-1-one	76.7	92.7	94.7	-2
12	2-nitrophenol	50	102	99.7	2.3
13	2,4-dimethylphenol	30	102	88.9	13.1
14	bis(2-chloroethoxy)methane	48.6	97.5	97.6	-0.1
15	2,4-dichlorophenol	50	94.8	95.4	-0.6
16	1,2,4-trichlorobenzene	25.3	94.7	83.5	11.2
17	naphthalene	24.8	94.2	97.3	-3.1
18	1,1,2,3,4,4-hexachloro-1,3-butadiene	49.6	93.4	69	24.4
19	4-chloro-3-methylphenol	75	97.7	101	-3.3
20	2,4,6-trichlorophenol	25	109	102	7
21	2-chloronaphthalene	25.4	96.5	92.2	4.3
22	dimethylphthalate	40	98.7	0	98.7
23	2,6-dinitrotoluene	76.5	96.8	95.8	1
24	1,2-dihydroacenaphthylene	19.5	93.2	93.3	-0.1
25	4-nitrophenol	50	106	108	-2
26	2,4-dinitrotoluene	73.8	98.7	96.3	2.4
27	diethylphthalate	25.1	92.1	1.7	90.4
28	1-chloro-4-phenoxybenzene	76.7	93.9	97.3	-3.4
29	9H-fluorene	51.2	95.5	96.8	-1.3
30	2-methyl-4,6-dinitrophenol	250	108	103	5
31	4-bromophenyl-phenylether	41.5	95.7	95.2	0.5
32	hexachlorobenzene	35.7	93.4	92.8	0.6
33	pentachlorophenol	75	118	108	10
34	phenanthrene	40.2	94.2	94.6	-0.4
35	anthracene	40	91.5	91.2	0.3
36	di-n-butylphthalate	24.9	101	36	65
37	fluoranthene	29.8	96.7	96.4	0.3
38	pyrene	60.2	90.9	97	-6.1
39	n-butyl benzyl phthalate	51.3	96.5	32.1	64.4
40	bis(2-ethylhexyl)phthalate	29.1	95.5	104	-8.5
41	benzo(a)anthracene	73.9	92.2	94.4	-2.2
42	chrysene	69.9	92.2	95.6	-3.4
43	di-n-octylphthalate	43.9	91.6	90.8	0.8
44	benzo(b)fluoranthene	40	92.9	92.3	0.6
45	benzo(k)fluoranthene	45.7	89.5	92.4	-2.9
46	benzo(a)pyrene	24.9	94.8	93.3	1.5
47	dibenzo(a,h)anthracene	40.7	91.2	97.7	-6.5
48	benzo(ghi)perylene	80.4	89.8	99.6	-9.8

FIGURE 6.

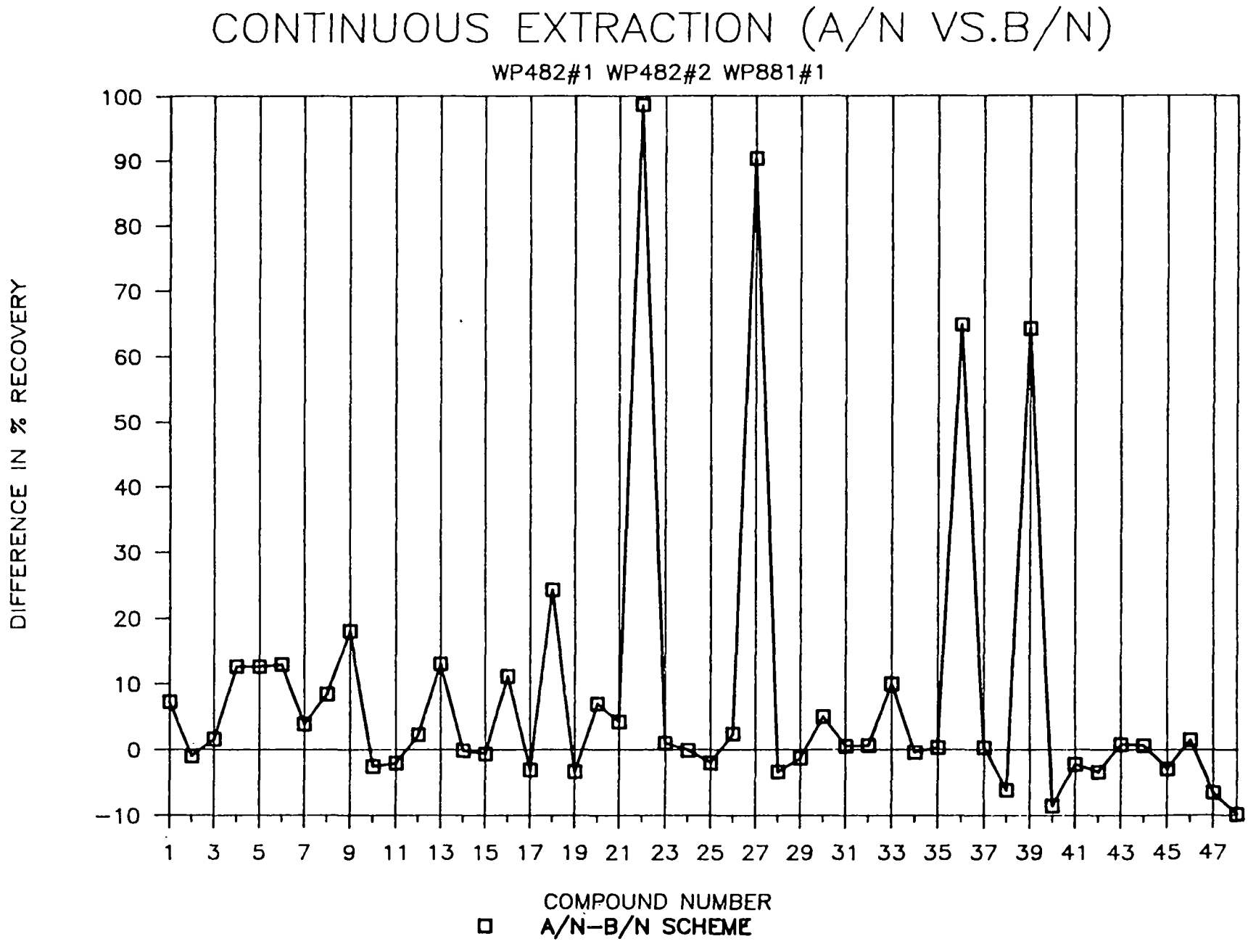

CONTINUOUS EXTRACTION (A/N VS.B/N)
WP482#1 WP482#2 WP881#1
DIFFERENCE IN % RECOVERY
100
90
80
70
60
50
40
30
20
10
0
-10
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37 39 41 43 45 47
COMPOUND NUMBER
A/N-B/N SCHEME

TABLE 7.

CONTINUOUS EXTRACTION

ACID NEUTRAL VS. BASE NEUTRAL
EXTRACTION SCHEMES

PHTHALATE ESTERS

EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

NO.	COMPOUND	TRUE VALUE PPB	% RECOVERY ACID/N EXT. (AVE.5/86)	% RECOVERY BASE/N EXT. (AVE.4/86)	DIFF.
22	DIMETHYLPHTHALATE	40	98.7	0	98.7
27	DIETHYLPHTHALATE	25.1	92.1	1.7	90.4
36	DI-n-BUTYLPHTHALATE	24.9	101	36	65
39	n-BUTYL BENZYL PHTHALATE	51.3	96.5	32.1	64.4
40	BIS-(2-ETHYLHEXYL)PHTHALATE	29.1	95.5	104	-8.5
43	DI-n-OCTYLPHTHALATE	43.9	91.6	90.8	0.8

of recoveries is suggestive of base hydrolysis in which almost complete cleavage occurs with dimethylphthalate resulting in low recovery at the elevated pH. Due to steric hindrance, little hydrolysis occurs for bis(2-ethylhexyl)phthalate. The second order alkaline hydrolysis rate constants (M^{-1} sec^{-1}) listed for phthalate esters in the literature (8) are consistent with this mechanism: dimethyl 6.9×10^{-2}; bis(2-ethylhexyl) 1.1×10^{-4}; diethyl 1.2×10^{-2}; and di-butyl 2.2×10^{-2}. The pH of the B/N extraction scheme was 13.

The recoveries listed for the base/neutral extraction scheme (Table 5) are the sums of the recoveries obtained from the analysis of the base/neutral and acid extracts. The only compounds found in both extracts were phenolics. The distributions of these compounds between the extracts are listed in Table 8. Significant quantities of phenol (8%); 2,4-dimethylphenol (88.9%); and 4-chloro-3-methylphenol (42.9%) were observed to extract (continuous extraction CE) the B/N phase.

II. Basic Compound Spiking Experiment

Acid/Neutral Continuous Extraction vs. Acid/Neutral Manual Extraction

Another group of compounds spiked into laboratory pure water was termed "basic compounds". The measured recoveries obtained using acid/neutral continuous extraction and acid/neutral manual extraction are presented in Table 9. The continuous extractor gave comparable recoveries

TABLE 8.

BASE NEUTRAL CONTINUOUS EXTRACTION 4/86
ACID COMPOUND RECOVERY PATTERN
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

NO.	COMPOUND	TRUE VALUE PPB	% RECOVERY BASE/N EXTRACT	% RECOVERY ACID EXTRACT
1	PHENOL	100	8	78.2
3	2-CHLOROPHENOL	30	2.1	89.2
12	2-NITROPHENOL	50	TRACE	99.7
13	2,4-DIMETHYLPHENOL	30	88.9	0
15	2,4-DICHLOROPHENOL	50	TRACE	95.4
19	4-CHLORO-3-METHYLPHENOL	75	42.9	58.2
20	2,4,6-TRICHLOROPHENOL	25	0	102
25	4-NITROPHENOL	50	0	108
30	2-METHYL-4,6-DINITROPHENOL	250	0	103
33	PENTACHLOROPHENOL	75	0	108

TABLE 9.

CONTINUOUS VS. MANUAL EXTRACTION (QA 10/85)
ACID NEUTRAL + BASE COMBINED
BASIC COMPOUNDS

EPA/RTP C075 (BENZENE) *
EPA/RTP EC26-01-02 (MEOH) **
EPA/RTP EC5-01-02 (MEOH) ***

COMPOUND	CONC. PPB	COMBINED C.E. % RECOVERY	COMBINED MANUAL % RECOVERY (AVE.N=4)	STD. DEV.
* ANILINE	100	113	94.7	3.9
* 4-CHLOROANILINE	100	89.5	97.7	1.8
* 2-NITROANILINE	100	98.1	98.1	0.8
* 3-NITROANILINE	100	94.9	97.5	1.3
* 4-NITROANILINE	100	82.9	95	1.8
** BENZIDINE	100	95	64.4	13.4
***3,3'-DICHLOROBENZIDINE	100	94.2	92.3	7.3

for the listed aniline and benzidine compounds with notable improvement measured for benzidine (95% CE and 64.4% manual). The continuous extractor recoveries reported in this table are the arithmetic sum of the individual acid/neutral extract and base extract recoveries presented in Table 10. Two compounds, aniline and benzidine, were found to extract significantly in the base extract after completion of the acid/neutral extraction. Benzidine was detected only in the base extract and 85.2% of the aniline was detected in this fraction. These proved to be the only target compounds tested in this study to be basic to the extent that they were not completely extracted by the first (acid/neutral) extraction.

The pKa for aniline is 4.63 and the pKa_1 and pKa_2 for benzidine are 4.66 and 3.57, respectively (9). Even though the aniline would be expected to be present at 99.98% as the hydrophilic-charged species during the acid/neutral extraction (pH approximately 1.0), because of the continuous shifting of equilibria in the extractor toward the solvent, 28.1% of the aniline was recovered with the acidic extraction. With this acidic extraction, benzidine would be distributed between the singularly charged and doubly charged hydrophilic species and was not measurably extracted from the aqueous phase. Both aniline and benzidine have been dropped from the EPA Superfund target analyte list (10). Benzidine is a priority pollutant and remains part of EPA Method 625.

A similar spiking experiment using the CE technique was repeated for aniline (100 ug/L) and benzidine (100 ug/L) at pH 7.0 (neutral extraction). This was followed by a separate base extraction (pH>11)

TABLE 10.

ACID NEUTRAL CONTINUOUS EXTRACTION (2/86)
BASIC COMPOUNDS

EPA/RTP C075 (BENZENE) *
EPA/RTP EC26-01-02 (MEOH) **
EPA/RTP EC5-01-02 (MEOH) ***

COMPOUND	CONC. PPB	% RECOVERY A/N	% RECOVERY BASE
* ANILINE (HSL)	100	28.1	85.2
* 4-CHLOROANILINE (HSL)	100	89.5	0
* 2-NITROANILINE (HSL)	100	98.1	0
* 3-NITROANILINE (HSL)	100	94.6	0
* 4-NITROANILINE (HSL)	100	82.9	0
** BENZIDINE	100	0	95
***3,3'-DICHLOROBENZIDINE	100	94.2	0

with the two extract concentrates analyzed separately. These compounds were only detected in the neutral extract (aniline 91.9% recovered, benzidine 99.9% recovered). It was concluded that basic pH conditions were not necessary for the recovery of these compounds. However, aniline and benzidine are weak bases relative to alkylamines, certain pyridines and numerous other organic bases. The basic extraction following the A/N was desirable despite the increased potential for emulsion formation and chemical reactions, to provide a broad pH extraction range. This assured the recovery of the full gamut of organic compounds potentially present in environmental samples.

III. Additional Compounds Spiking Experiment

Acid/Neutral Continuous Extraction vs Acid/Neutral Manual Extraction

Thirteen additional target compounds, not included in the priority pollutant or basic compound mixtures, were spiked separately into laboratory pure water. The recoveries obtained for these analyses, each performed in duplicate, are listed in Table 11. The continuous extractor resulted in 99.6% recovery of N-nitrosodimethylamine. This was the most volatile of all target compounds. Its chromatographic retention time was very near that of the solvent front. Hexachlorocyclopentadiene, a heat labile compound, gave an average recovery of 102% with continuous extraction. All of the "additional compounds" tested were found to extract totally into the A/N extract--none were detected in the base extract. The results of this experiment indicated that, even after 24 hours of extraction with boiling methylene chloride

TABLE 11.

CONTINUOUS VS. MANUAL EXTRACTION (5/86)
ACID NEUTRAL
ADDITIONAL COMPOUNDS

EPA/RTP (MEOH) *
CHEM SERVICE INC.(NEAT MATERIAL INTO MEOH) **

COMPOUND	CONC PPB	C.E. % REC. AVE. N=2	MAN. % REC. AVE. N=2
BENZYL ALCOHOL (HSL) **	50	93.6	NO DATA
DIBENZOFURAN (HSL) **	50	89.6	NO DATA
N-NITROSODIMETHYLAMINE *	50	99.6	38.8
2-METHYLNAPHTHALENE (HSL) **	125	102	92.5
HEXACHLOROCYCLOPENTADIENE *	50	102	69.1
ACENAPHTHYLENE *	50	88.4	90.9
INDENO(1,2,3-CD)PYRENE *	50	94.5	101
2-METHYLPHENOL (HSL)*	100	94.3	NO DATA
4-METHYLPHENOL (HSL) *	100	97.1	NO DATA
2,4,5-TRICHLOROPHENOL (HSL) **	100	95.9	91.6
BENZOIC ACID (HSL) **	100	30.5	0.1
2,4-DINITROPHENOL *	100	118	NO DATA
N-NITROSODIPHENYLAMINE **	50	90.3	NO DATA

at 40°C and a sample temperature (heated slightly by the process) of approximately 29°C, these fragile compounds were little affected. Benzoic acid proved to be the compound with the poorest extraction efficiency of all the target compounds tested. The average continuous extractor efficiency was 30.5% and was quite erratic with a standard deviation of 18 (N=2), Table 12. Similar problems and even poorer recoveries were encountered with manual extraction of benzoic acid, Table 11. Benzoic acid is not a priority pollutant but is a Superfund HSL compound.

IV. Pesticides Spiking Experiment

Acid/Neutral Continuous Extraction

The final category of compounds tested as spikes into laboratory pure water were sixteen priority pollutant pesticides. A single analysis was performed at 50 ug/L each and the recoveries obtained are included in Table 13. This spiking level proved quite low for electron impact mass spectrometry employing single mass quantitation routines. Despite low sensitivity these compounds gave recoveries ranging from 83.7 to 104% and were all within recoveries required by EPA Method 625 (CFR - Table 6 - QC Acceptance Criteria (1)).

V. Environmental Samples

A. Sewage Treatment Plant Influent: Acid/Neutral Continuous Extraction vs. Acid/Neutral Manual Extraction

The reconstructed ion chromatograms (RIC) presented in Figure 7

TABLE 12.

ACID NEUTRAL CONTINUOUS EXTRACTION (5/86)
ADDITIONAL COMPOUNDS

EPA/RTP (MEOH) *
CHEM SERVICE INC.(NEAT MATERIAL INTO MEOH) **

COMPOUND	CONC PPB	ACID/N % REC. #1	ACID/N % REC. #2	ACID/N % REC. AVE.
BENZYL ALCOHOL (HSL) **	50	86.2	101	93.6
DIBENZOFURAN (HSL) **	50	83.7	95.5	89.6
N-NITROSODIMETHYLAMINE *	50	98.1	101	99.6
2-METHYLNAPHTHALENE (HSL) **	125	104	100	102
HEXACHLOROCYCLOPENTADIENE *	50	103	100	101.5
ACENAPHTHYLENE *	50	90.8	85.9	88.4
INDENO(1,2,3-CD)PYRENE *	50	98.4	90.5	94.5
2-METHYLPHENOL (HSL)*	100	86.5	102	94.3
4-METHYLPHENOL (HSL) *	100	94.2	100	97.1
2,4,5-TRICHLOROPHENOL (HSL) **	100	92.9	98.9	95.9
BENZOIC ACID (HSL) **	100	17.7	43.2	30.5
2,4-DINITROPHENOL *	100	110	125	117.5
N-NITROSODIPHENYLAMINE **	50	87.5	93.1	90.3

TABLE 13.

ACID NEUTRAL CONTINUOUS EXTRACTION PESTICIDES (3/86)
EPA/RTP STANDARD C043 (TOLUENE-HEXANE)

NO.	COMPOUND	TRUE VALUE PPB	% RECOVERY	EPA 625 * REQUIRED % RECOVERY
1	ALPHA-BHC	50	97.7	-
2	BETA-BHC	50	95.5	-
3	GAMMA-BHC (LINDANE)	50	98.2	-
4	DELTA-BHC	50	95.7	24-149
5	HEPTACHLOR	50	95.6	D-192
6	ALDRIN	50	101	D-166
7	HEPTACHLOR EPOXIDE	50	97.8	26-155
8	ENDOSULFAN I (ALPHA)	50	92.9	-
9	4,4'-DDE	50	95.3	4-136
10	DIELDRIN	50	97	29-136
11	ENDRIN	50	104	-
12	4,4'-DDD	50	92.1	D-145
13	ENDOSULFAN II (BETA)	50	88.1	-
14	ENDRIN ALDEHYDE	50	85.6	D-209
15	4,4'-DDT	50	88.1	D-203
16	ENDOSULFAN CYCLIC SULFATE	50	83.7	D-107

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* 40 CFR PART 136,VOL.49,NO.49,FRIDAY,OCT. 26,1984

D= DETECTION LIMIT

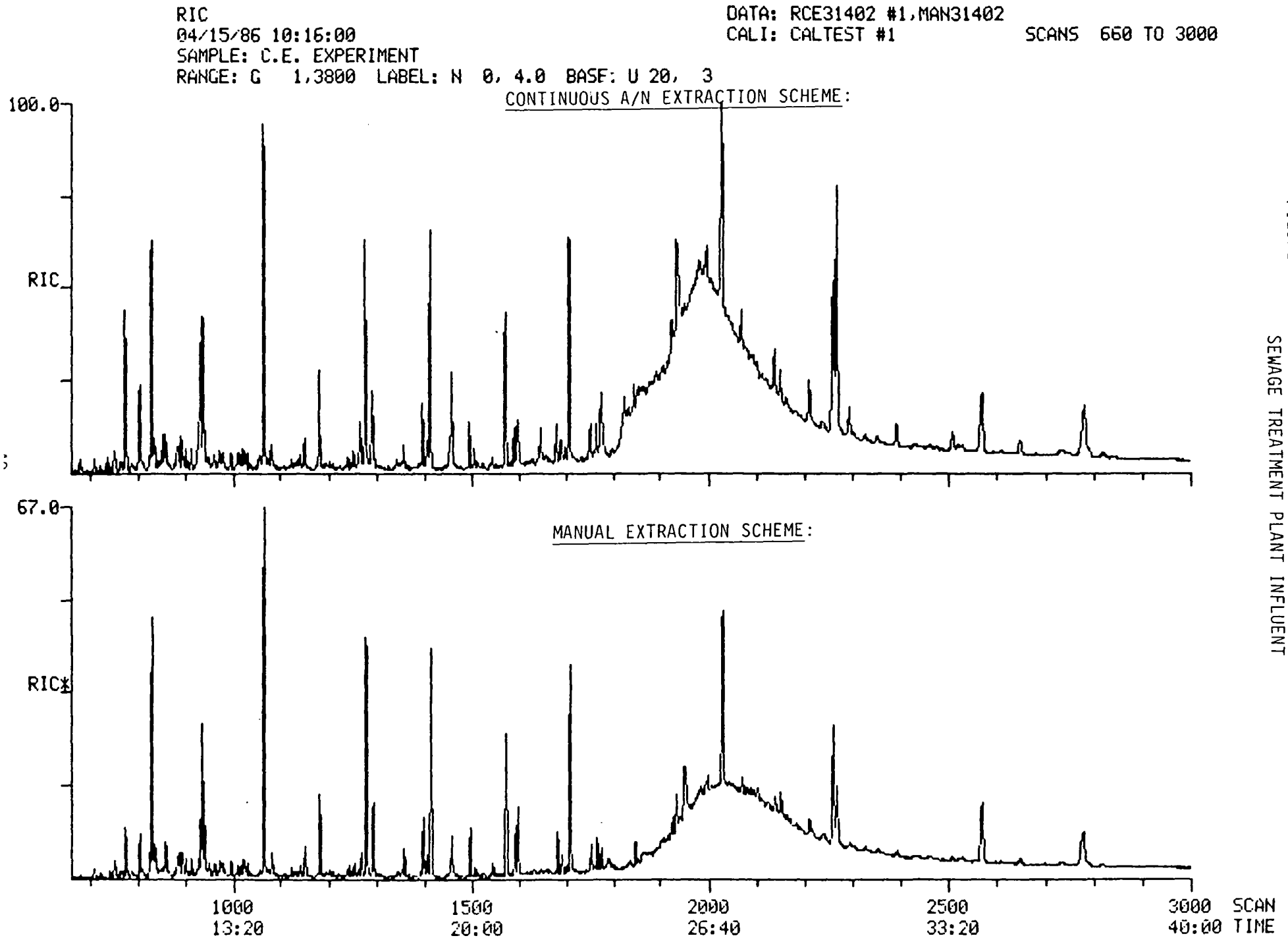


FIGURE 7. RECONSTRUCTED ION CHROMATOGRAMS OF SEWAGE TREATMENT PLANT INFLUENT

were obtained from influent to a waste treatment plant in Virginia. The sample was analyzed as part of EPA's Pre-Treatment Program. The top RIC was obtained after continuous extraction and the bottom graph was from manual extraction. The target compounds detected are listed in Table 14. The CE technique resulted in good agreement with the manual extraction except for bis-(2-ethylhexyl)phthalate in which significantly more was recovered by CE. This compound had been observed to extract equally well in laboratory pure water spiking experiments: 95.5% recovery via CE and 104% manually. This phthalate compound is a common laboratory contaminant, however reagent blanks analyzed with these extractions were free of this compound. Further, the high sample concentration recovered by CE (45.7 ppb) far exceeds any trace (0.1 ppb) level contamination observed during this work.

The non-target analytes (those for which standards were not readily available) and tentatively identified compounds detected in this sample by these extraction schemes are presented in Figure 8. These compounds represent a broad range of aromatic and aliphatic hydrocarbons for which the CE recovery was determined to equal or exceed that observed by separatory funnel extraction. The concentrations are reported as "estimated" in that a response factor of 1.0 has been assumed for each compound relative to the closest eluting internal standard. The manual extraction of this sample resulted in a thick emulsion (heaviest at pH>11). Centrifugation was required after each two minute shaking period with methylene chloride in order to break the emulsion.

TABLE 14.

SEWAGE TREATMENT PLANT INFLUENT

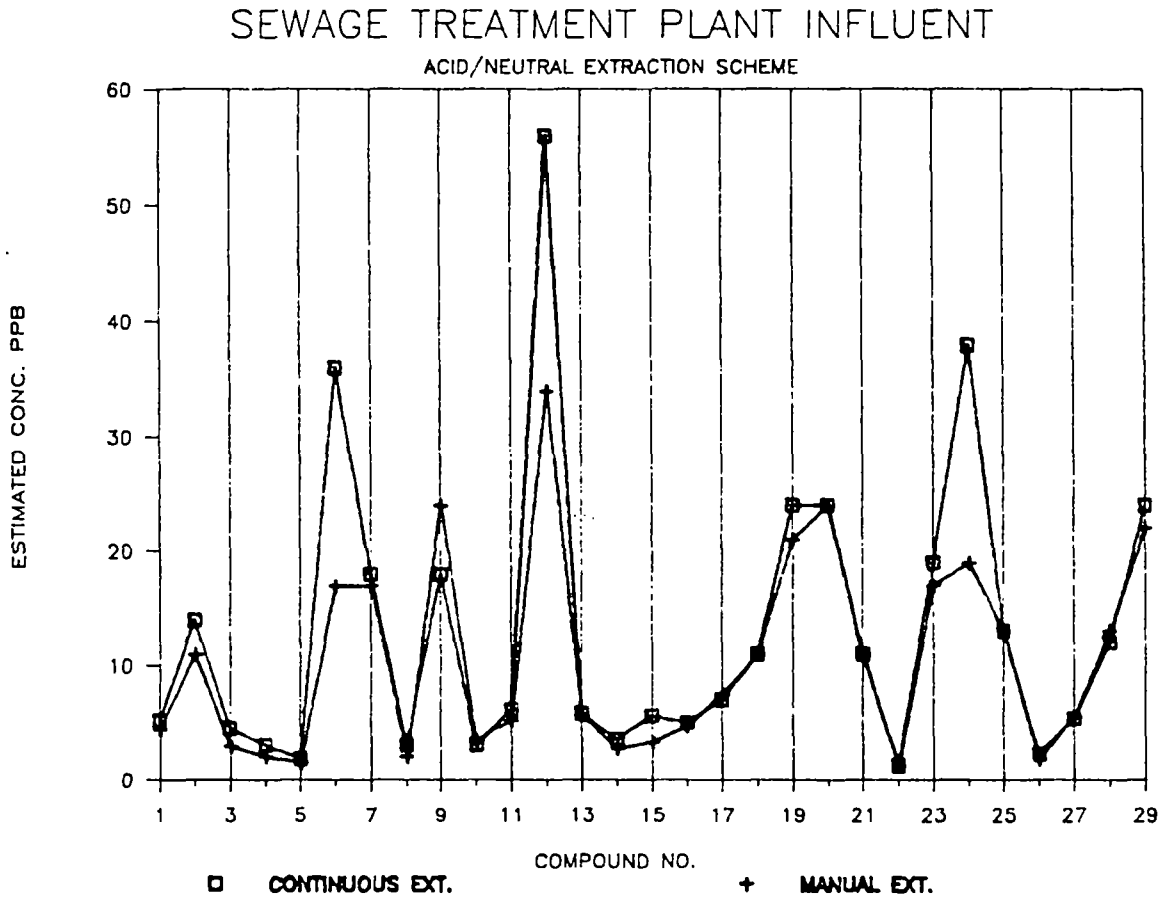
ACID/NEUTRAL EXTRACTION 500 ML

NPDES 24HR COMPOSITE SAMPLE 86031402

TARGET COMPOUNDS

COMPOUND	CONC. PPB CONT. EXT. 4-15-86	CONC. PPB MAN. EXT. 4-15-86
1,4-DICHLOROBENZENE	0.5J	0.3J
1,2-DICHLOROBENZENE	0.6J	0.5J
2-METHYLNAPHTHALENE	0.2J	ND
DIETHYLPHTHALATE	1.8J	1.6J
PHENANTHRENE	0.5J	0.4J
BIS(2-ETHYLHEXYL)-PHTHALATE	45.7	14.2
DIOCTYLPHTHALATE	0.8J	0.8J

FIGURE 8.



TENTATIVE IDENTIFICATION

NO.	COMPOUND	NO.	COMPOUND
1	4-METHYL-2-PROPYL-1-PENTANOL	16	3-METHYLUNDECANE
2	2,3,6-TRIMETHYLHEPTANE	17	6-METHYLDODECANE
3	2,3,7-TRIMETHYLOCTANE	18	2,3,7-TRIMETHYLOCTANE
4	1,2,4-TRIMETHYLBENZENE	19	TRIDECANE
5	(1-METHYLETHYL)BENZENE	20	TETRADECANE
6	DECANE	21	4,7-DIMETHYLUNDECANE
7	5-ETHYL-2-METHYLHEPTANE	22	3,7-DIMETHYLUNDECANE
8	1,2,4-TRIMETHYLBENZENE	23	4,7-DIMETHYLUNDECANE
9	4,6,8-TRIMETHYL-1-NONENE	24	DODECANOIC ACID
10	DECAHYDRONAPHTHALENE	25	HEXADECANE
11	3-ETHYL-2,7-DIMETHYLOCTANE	26	4-(1,1,3,3-TETRAMETHYLBUTYL)PHENOL
12	UNDECANE	27	3,6-DIMETHYLUNDECANE
13	3,7-DIMETHYLNONANE	28	4,7-DIMETHYLUNDECANE
14	1,2,4,5-TETRAMETHYLBENZENE	29	UNKNOWN
15	2-PROPENYLCYCLOHEXANE		

B. River Water from an Industrial Spill:

Acid/Neutral Continuous Extraction vs. Acid/Neutral Manual Extraction

The results of target compounds presented in Table 15 represent the analysis of estuarine river water after a spill by a mothball manufacturer. As indicated by the analysis, this was a chlorinated benzene type of insecticide and extensive quantities of dichloro- and trichlorobenzene isomers were measured. The table indicates close agreement between the results of the two extraction procedures with the exception of 2-chlorophenol. Spikes of this compound into reagent water had given comparable recovery (92.9% by CE and 110% recovery using manual extraction). The ten fold higher value by CE in this sample suggests possible matrix interference for the manual extraction or a positive interference with continuous extraction. The mass spectrum, chromatographic peak shape and relative retention time were clearly indicative of 2-chlorophenol and did not indicate the possibility of a co-eluting compound or false positive identification. A possible mechanism for the formation of this compound under these extraction conditions is unclear and unlikely. Spikes of fifty ppb (ug/L) of 1,4-dichlorobenzene and 1,2,4-trichlorobenzene into seventeen industrial waste and superfund landfill samples have resulted in average recoveries of 71.8% ($\pm$11.9) and 73.9% ($\pm$12.7) respectively by continuous acid neutral extraction. The non-target compounds extracted from this sample matrix by these techniques are presented in Figure 9. As indicated, this sample contained significant quantities of chlorinated benzenes that extracted comparably by both extraction

TABLE 15.

RIVER WATER FROM AN INDUSTRIAL SPILL

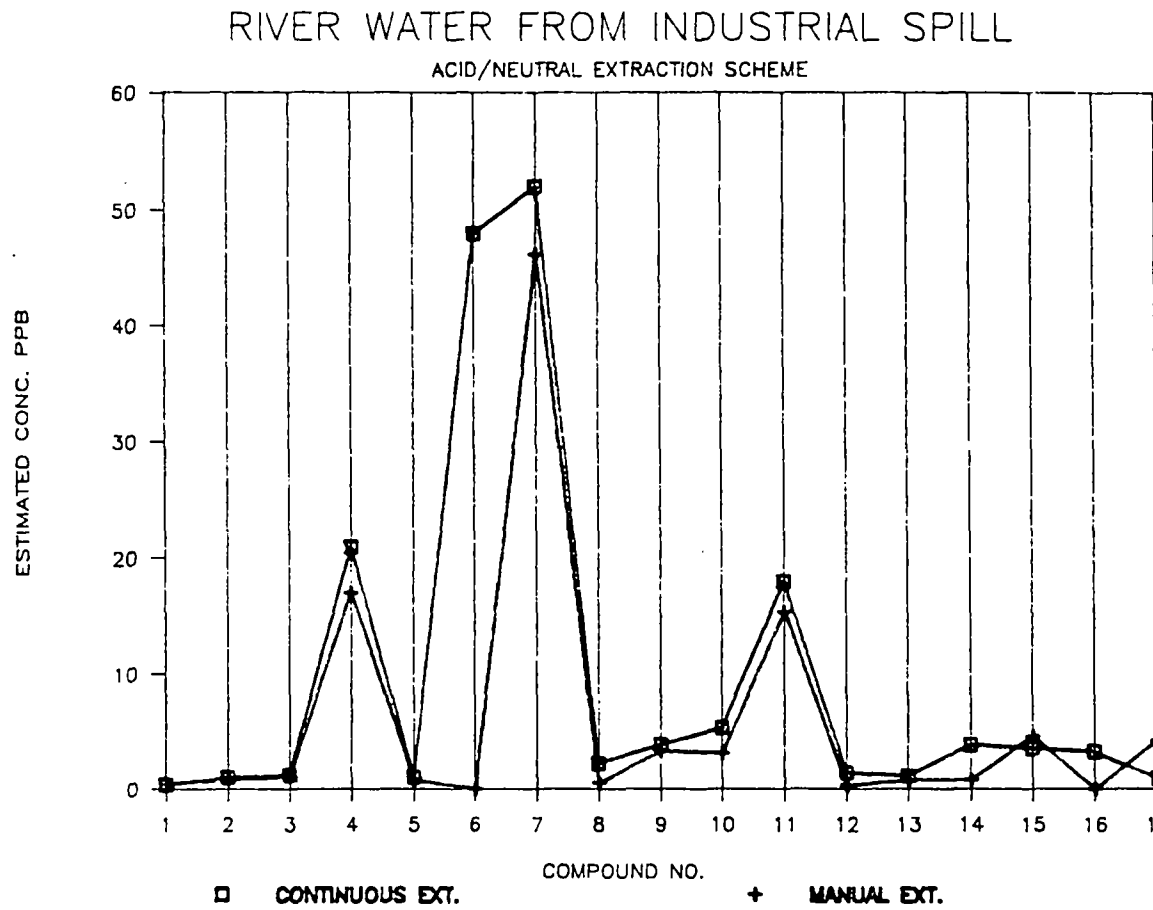
ACID/NEUTRAL EXTRACTION SCHEME 500 ML

MOTHBALL MANUFACTURER

TARGET COMPOUNDS

COMPOUND		CONC. PPB CONT. EXT. 6-02-86	CONC. PPB MAN. EXT. 6-02-86
PHENOL		44	46
2-CHLOROPHENOL		340	24
1,2-DICHLOROBENZENE		46	46
1,4-DICHLOROBENZENE	(55m/z)	1950	1700
1,2-DICHLOROBENZENE	(55m/z)	270	240
2-METHYLPHENOL HSL		12J	10J
NITROBENZENE		33	30
2,4-DIMETHYLPHENOL		31	30
2,4-DICHLOROPHENOL		3.8J	1.4J
1,2,4-TRICHLOROBENZENE		390	320

FIGURE 9.



TENTATIVE IDENTIFICATIONS

NO.	COMPOUND	NO.	COMPOUND
1	(1-METHYLETHYL)BENZENE	9	1,2,3,5-TETRACHLOROBENZENE
2	(METHYLETHYL)BENZENE ISOMER	10	METHYL-ETHYLPROPANOIC ACID ISOMER
3	ETHYL-METHYLBENZENE ISOMER	11	TETRACHLOROBENZENE ISOMER
4	METHYLPHENOL ISOMER	12	1H-BENZOTRIAZOLE
5	1-CHLORO-4-(CHLOROMETHYL)BENZENE	13	PENTACHLOROBENZENE
6	UNKNOWN	14	TETRADECANOIC ACID
7	1,3,5-TRICHLOROBENZENE	15	HEXADECANOIC ACID
8	BUTANOIC ACID,2-PROPENYL ESTER	16	1-(ETHENYLOXY)OCTADECANE
		17	UNKNOWN

schemes. One significant peak was detected by the CE analysis and not by the manual extraction (compound #6). It was not identified because of a poor spectral match with the compounds in the EPA-NIH mass spectral library. This compound had a base peak of 43 m/z and a mass spectrum indicative of an aliphatic hydrocarbon.

C. Ground Water from Superfund Test Wells:

Acid/Neutral Continuous Extraction vs. Acid/Neutral Manual Extraction

Samples from two test wells at a Superfund site in Pennsylvania were extracted and analyzed. The concentrations measured for the target compounds of the more highly comtaminated Well #2 are presented in Table 16. The data indicate significant benzyl alcohol and methyphenol contamination. The CE extraction scheme resulted in target compound concentrations that equaled or exceeded all target compounds detected by manual extraction. The relatively poor benzoic acid recovery by manual extraction was consistent with spiking results in laboratory pure water. The recovery of benzyl alcohol by manual extraction, also low relative to CE in this sample, had not been tested with laboratory pure water spikes.

This sample from Well #2 was extracted as 500 mL of sample (manual and CE) diluted to 1 liter with laboratory pure water. The base peak ions for benzyl alcohol and benzoic acid saturated the electron multiplier and quantitation was performed using an alternate (less intense) ion. This technique afforded a greater dynamic range and allowed the determination of compounds present at trace levels as well as those present in macro amounts by a single GC/MS analysis.

TABLE 16.

GROUND WATER (SUPERFUND)

ACID/NEUTRAL EXTRACTION SCHEME

ENFORCEMENT-REMEDIAL TEST WELL #2

TARGET COMPOUNDS 6-06-86

CONC. PPB

COMPOUND	CONT. EXT.	MAN. EXT.
PHENOL	72	25
1,4-DICHLOROBENZENE	6.5J	6.2J
BENZYL ALCOHOL	4400	1100
1,2-DICHLOROBENZENE	10J	10J
2-METHYLPHENOL	540	450
4-METHYLPHENOL	620	340
2,4-DIMETHYLPHENOL	114	92
BENZOIC ACID	1240	318
2,4-DICHLOROPHENOL	1.1J	0.9J
NAPHTHALENE	13J	12J
PHENANTHRENE	0.1J	0.1J
BUTYLBENZYL-PHTHALATE	55	45
DI-n-OCTYL PHTHALATE	4.7J	1.2J

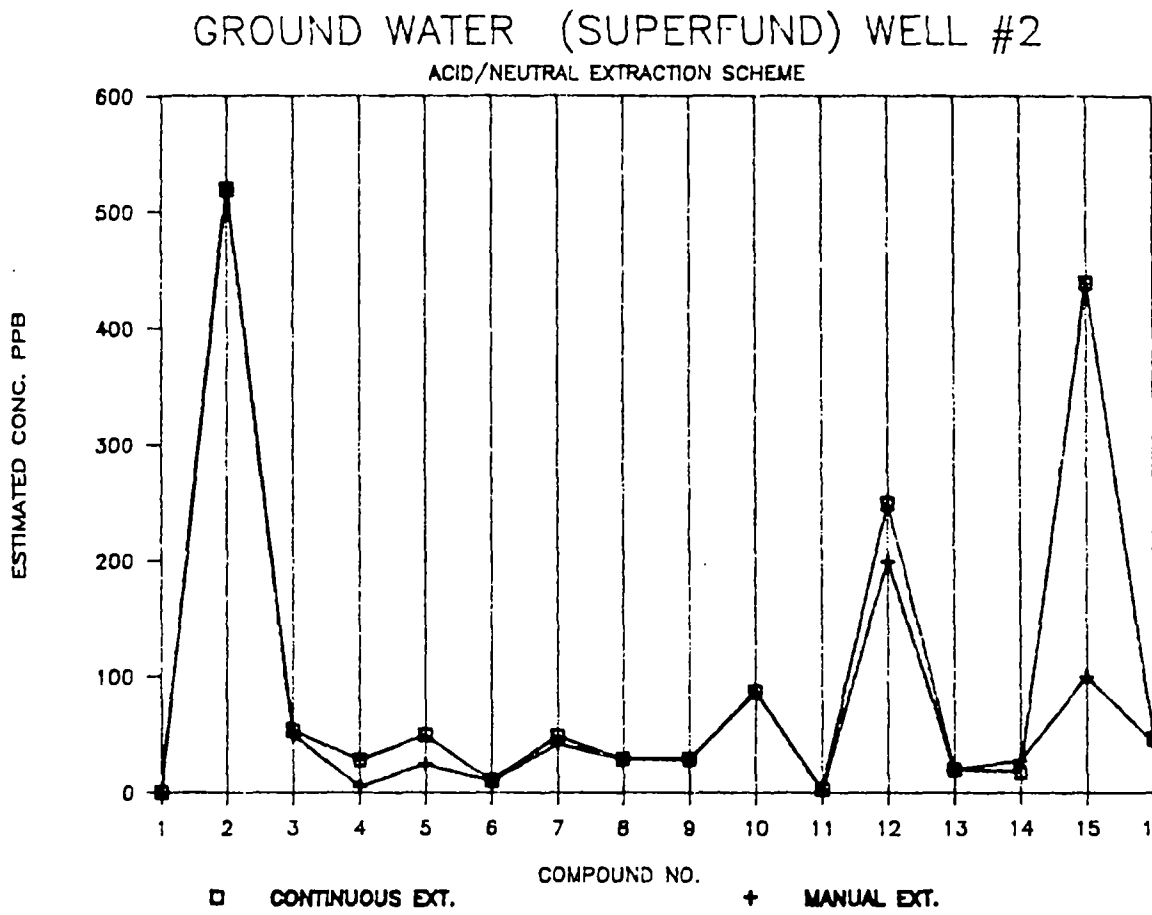
The tentatively identified compounds extracted from this test well are presented in Figures 10 and 11. The compounds are predominantly alkyl substituted aromatics. The recovery of N,N-dimethylbenzenamine followed the pattern established for 4,4'-diaminobiphenyl (benzidine) in lab pure water: much greater quantities were recovered by the continuous extractor (440 ug/L CE and 100 ug/L manual). The recoveries for 3-methylbenzoic acid were much closer (29 ug/L CE and 38 ug/L manual) than those for benzoic acid (1240 ug/L CE and 318 ug/L manual). The benzoic acid recoveries for this sample were similar to those obtained from spikes into laboratory pure water (30.5% CE recovery and 0.1% manual recovery). The phenol recovery was approximately three times larger by continuous extraction (72 ug/L CE and 25 ug/L manual). Test Well #5 was far less contaminated. The target compounds were present in trace concentrations, except for bis(2-ethythexyl)phthalate. Extraction efficiencies (Table 17) were comparable by both extraction schemes. The tentatively identified compounds in this well water (Figure 12) ranged 10 to 200 fold lower in concentration than for test Well #2. The agreement in recoveries obtained using the two extraction schemes was excellent with the exception of: dihydro-2(3H)-furanone (5.6 ug/L CE and not detected by manual extraction); 4,7-dimethyl-undecane (11 ug/L CE and 20 ug/L manual) and (entry #20) unknown hydrocarbon (17.0 ug/L CE and not detected by manual extraction).

D. Industrial Effluents:

Acid/Neutral Continuous Extraction vs. Acid/Neutral Manual Extraction

The final environmental matrix studies were from two metal finishing

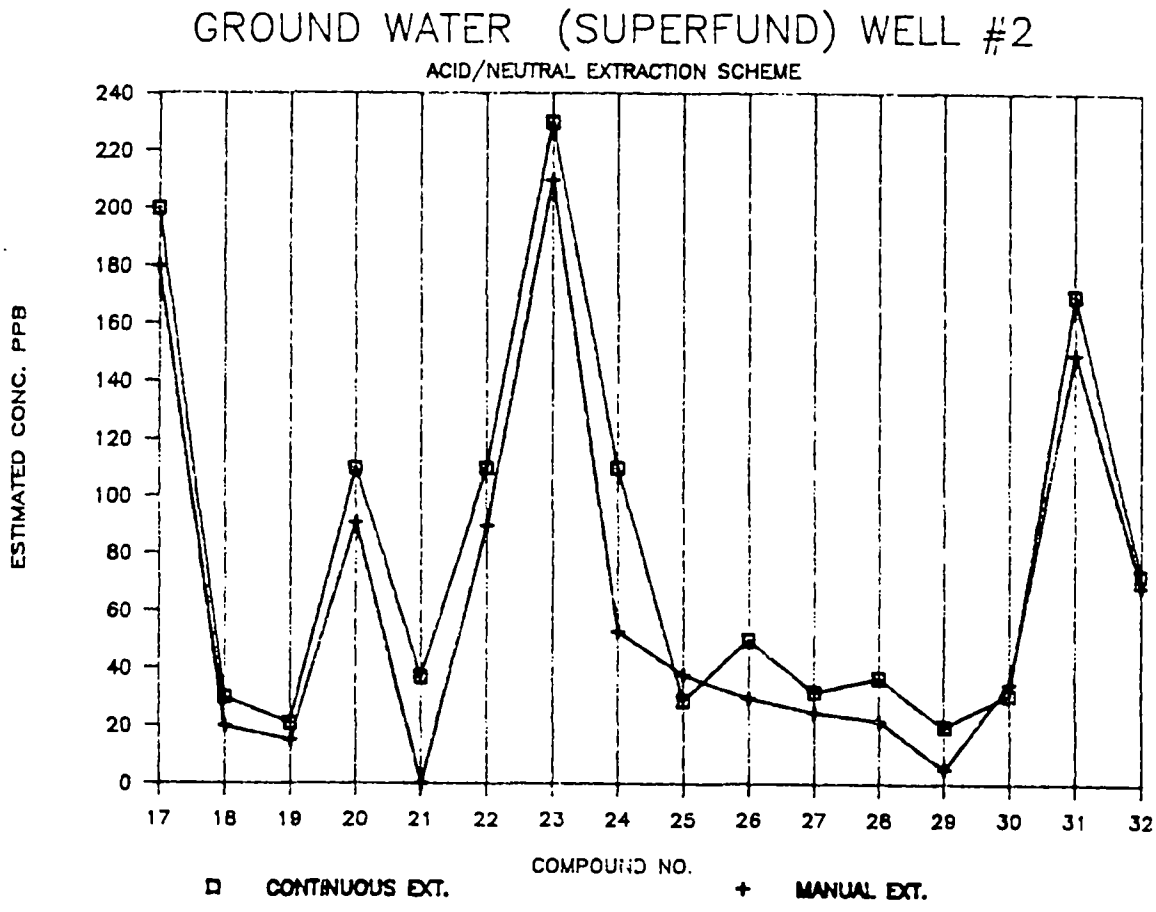
FIGURE 10.



TENTATIVE IDENTIFICATIONS

NO.	COMPOUND	NO.	COMPOUND
1	1,2-DIMETHYLBENZENE	9	1-ETHYL-2-METHYLBENZENE
2	1,3-DIMETHYLBENZENE	10	1,2,4-TRIMETHYLBENZENE
3	1,4-DICHLOROBUTANE	11	(2-METHYLPROPYL)BENZENE
4	DIETHYLDISULFIDE	12	2-ETHYL-1-HEXANOL
5	1-METHYLETHYLBENZENE	13	1-METHYL-3-(1-METHYLETHYL)BENZENE
6	PROPYLBENZENE	14	4-ETHYL-1,2-DIMETHYLBENZENE
7	1-ETHYL-4-METHYLBENZENE	15	N,N-DIMETHYLBENZEAMINE
8	1,2,4-TRIMETHYLBENZENE	16	2,5-DIMETHYLPHENOL

FIGURE 11.



TENTATIVE IDENTIFICATIONS

NO.	COMPOUND	NO.	COMPOUND
17	2-ETHYLHEXANOIC ACID	25	3-METHYLBENZOIC ACID
18	PHOSPHORIC ACID, TRIETHYL ESTER	26	UNKNOWN HYDROCARBON
19	2-ETHYLPHENOL	27	UNKNOWN HYDROCARBON
20	BENZENEACTONITRILE	28	1,3-ISOBENZOFURANDIONE
21	2,2,4-TRIMETHYL-1,3-PENTANEDIOL	29	BENZAMIDE
22	1,7,7-TRIMETHYL-BICYCLO(2.2.1)-HEPTAN-2-ONE	30	1(3H)-ISOBENZOFURANONE
23	3,4-DIMETHYLPHENOL	31	4-(1,1,3,3-TETRAMETHYLBUTYL)-PHENOL
24	BENZENEACETIC ACID	32	UNKNOWN HYDROCARBON

TABLE 17.

GROUND WATER (SUPERFUND)

ACID/NEUTRAL EXTRACTION SCHEME

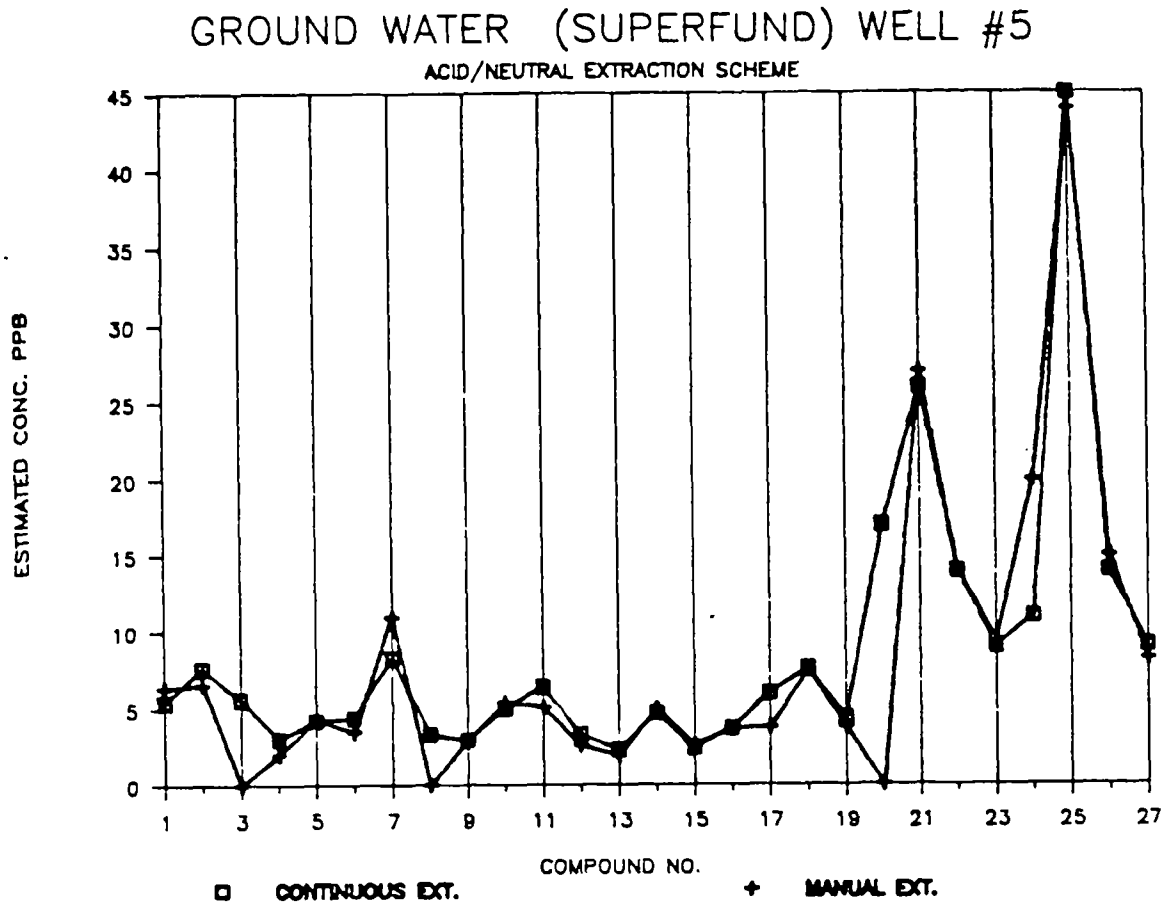
ENFORCEMENT-REMEDIAL TEST WELL #5

TARGET COMPOUNDS 6-06-86

CONC. PPB

COMPOUND	CONT. EXT.	MAN. EXT.
1,4-DICHLOROBENZENE	0.9J	0.6J
1,2-DICHLOROBENZENE	0.5J	0.3J
2-METHYLPHENOL	1.2J	1.0J
BENZOIC ACID	0.2J	ND
2-CHLOROANILINE	1.1J	0.8J
BIS(2-ETHYLHEXYL)-PHTHALATE	45	34

FIGURE 12.



NO.	TENTATIVE IDENTIFICATIONS	NO.	COMPOUND
1	1,2-DIMETHYLBENZENE	15	1,1'-(1,4-PHENYLENE)BIS-ETHANONE
2	1,4-DICHLOROBUTANE	16	2,4,6-TRIMETHYLOCTANE
3	DIHYDRO-2(3H)-FURANONE	17	2,6,11-TRIMETHYLDODECANE
4	2-CHLOROPYRIDINE	18	4,7-DIMETHYLUNDECANE
5	2-ETHYL-1-HEXANOL	19	2,7,10-TRIMETHYLDODECANE
6	DIMETHYLBENZENE METHANOL	20	UNKNOWN HYDROCARBON
7	2-EHTYLHEXANOIC ACID	21	UNKNOWN HYDROCARBON
8	2-(2-BUTOXYETHOXY)ETHANOL	22	2,6,11-TRIMETHYLDODECANE
9	TETRAMETHYLTHIOUREA	23	HEXADECANE
10	2,2,4,4-TETRAMETHYLPENTANE	24	4,7-DIMETHYLUNDECANE
11	BENZOTHIAZOLE	25	UNKNOWN HYDROCARBON
12	N-METHYL-N-PHENYLACETAMIDE	26	HEPTADECANE
13	3,7-DIMETHYLNONANE	27	2,7,10-TRIMETHYLDODECANE
14	1,1'(1,3-PHENYLENE)BIS-ETHANONE		

companies in Pennsylvania. In the first, designated 860227-12, the trace level target compounds detected (phenolics and polynuclear aromatics) were extracted to the same extent by both techniques as indicated by the first and third columns of Table 18. The manual extraction was performed in duplicate. The benzoic acid present in this aqueous sample matrix, which contained primarily alcohols, aldehydes and ketones (Figure 13) was extracted to a greater extent by the continuous extactor (1300 ug/L CE and 775 ug/L manual). As indicated in Table 18, the acid/neutral and base extracts from the continuous extraction were analyzed separately and no target compounds were detected in the base extract. However, the tentatively identified compounds 3-phenyl-2-butanone (3.2 ug/L); 4-methoxy-benzaldehyde (14 ug/L); and 1,2-dimethoxyethylbenzene (3.6 ug/L) were detected in the base CE extract (Table 19). The first two compounds may represent trace carry over since much higher concentrations were measured in the acid/neutral CE extract (170 ug/L and 630 ug/L respectively). The 1,2-dimethoxyethylbenzene measured was at trace levels and may have also been recovered in the acid neutral extract but been below the level of GC/MS detection.

A second industrial effluent was collected from a different metal plating company. The sample was milky-white in color and required repeated centrifugation to break the emulsions formed during the manual extraction. The single target compound detected was benzoic acid which was recovered in trace quantity only from the continuous extractor. The most predominant tentatively identified compound was 3-octadecene. The close agreement of the two extraction schemes is evident in Figure 14.

TABLE 18.

INDUSTRIAL EFFLUENT

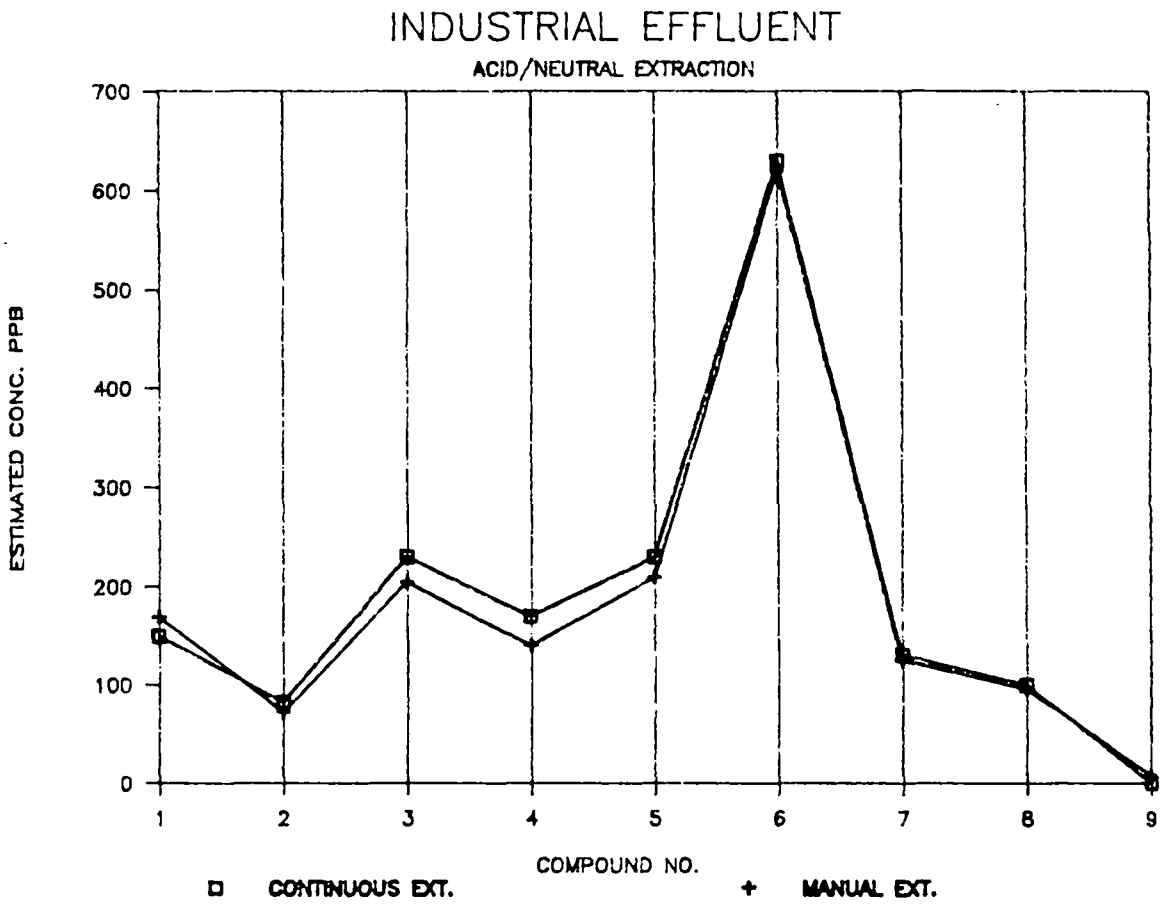
ACID/NEUTRAL EXTRACTION

SAMPLE 860227-12

TARGET COMPOUNDS 3-3-86

			CONC. PPB		
COMPOUND	CONT. A/N	CONT. BASE	AVE. MAN. A/N+BASE	MAN. #1	MAN. #2
PHENOL	6.1J	ND	1.2J	2.4J	ND
2-CHLOROPHENOL	3.2J	ND	ND	ND	ND
BENZOIC ACID	1300	ND	775	770	780
NAPHTHALENE	12	ND	8.4	9.7J	7J
2-METHYLNAPHTHALENE	2.7J	ND	3.9	4.7J	3J
PHENANTHRENE	0.5J	ND	0.1J	0.2J	ND

FIGURE 13.



TENTATIVE IDENTIFICATIONS

NO.	COMPOUND
1	UNDECANE
2	2-CHLOROBENZALDEHYDE
3	2-CHLOROBENZENE METHANOL
4	3-PHENYL-2-BUTANONE
5	3-METHOXYBENZALDEHYDE
6	4-METHOXYBENZALDEHYDE
7	2-BUTOXYETHANOL
8	3,4-DIMETHOXYBENZENE METHANOL
9	1,2-DIMETHOXYETHYLBENZENE

TABLE 19.

INDUSTRIAL EFFLUENT

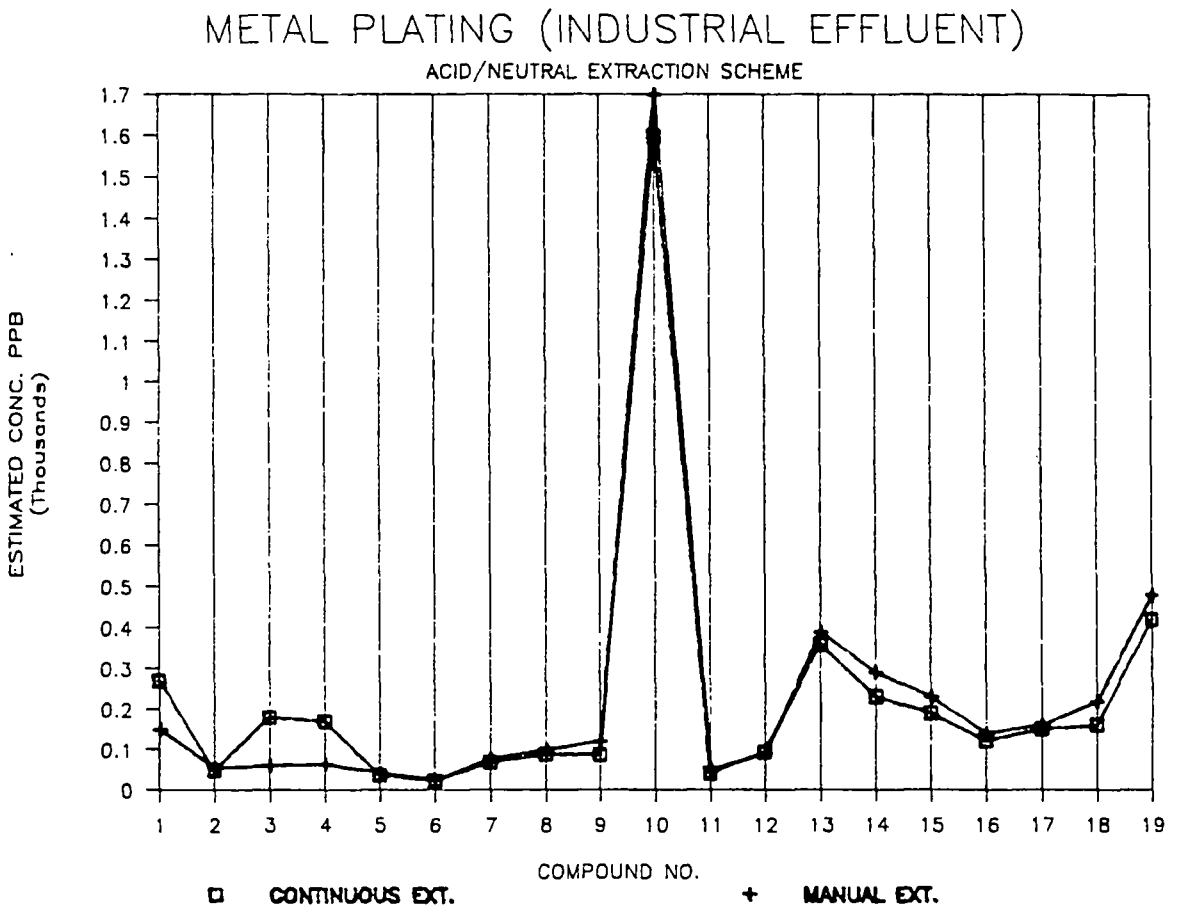
ACID/NEUTRAL EXTRACTION

SAMPLE 860227-12

TENTATIVE IDENTIFICATIONS 3-3-86

NO.	COMPOUND	CONT. EXT. A/N	CONT. EXT. BASE	ESTIMATED CONC. PPB AVE. MAN. EXT. A/N+BASE	MAN. #1	MAN. #2
1	UNDECANE	150	ND	170	140	200
2	2-CHLOROBENZALDEHYDE	82	ND	72.5	79	66
3	2-CHLOROBENZENE - METHANOL	230	ND	205	240	170
4	3-PHENYL-2-BUTANONE	170	3.2	140	160	120
5	3-METHOXYBENZALDEHYDE	230	ND	210	250	170
6	4-METHOXYBENZALDEHYDE	630	14	620	650	590
7	2-BUTOXYETHANOL	130	ND	125	160	90
8	3,4-DIMETHOXYBENZENE-METHANOL	100	ND	96	130	62
9	1,2-DIMETHOXYETHYL-BENZENE	ND	3.6	7.5	5	10

FIGURE 14.



TENTATIVE IDENTIFICATIONS

NO.	COMPOUND	NO.	COMPOUND
1	2-BUTOXYETHANOL	11	3,8-DIMETHYLDECANE
2	1-HYDROXY-2-PROPANONE	12	HEXADECANE
3	1,3-DIHYDRO-2H-INDOL-2-ONE	13	UNKNOWN
4	1,2-DIHYDRO-2H-INDOL-2-ONE	14	2,6,11-TRIMETHYLDODECANE
5	2,4,6-TRIMETHYLOCTANE	15	HEPTACOSANE
6	3,7-DIMETHYLUNDECANE	16	2,7,10-TRIMETHYLDODECANE
7	4,7-DIMETHYLUNDECANE	17	NONADECANE
8	HEXADECANOIC ACID	18	2,6,10-TRIMETHYLDODECANE
9	4,7-DIMETHYLUNDECANE	19	UNKNOWN HYDROCARBON
10	3-OCTADECENE		

VI. Partition Experiment

The recoveries for the priority pollutant mixture obtained from a single 350 mL solvent pass using a stopcock fitted continuous extractor are presented in Table 20. For the purposes of this paper, a "partition ratio" has been defined as the weight of material in the solvent phase relative to the weight of the material in the aqueous phase. This was calculated as:

$$\text{Partition Ratio} = \frac{\text{ng in solvent phase}}{\text{ng in aqueous phase}} = \frac{\text{ng measured in solvent phase}}{\left(\text{ng measured in unextracted reference solution} - \text{ng measured in solvent phase}\right)}$$

The partition ratios ranged from 0.1 for benzo(a)anthracene to 26.5 for pentachlorophenol. The process occurring in the extractor is complicated. Droplets of dense solvent fall rapidly through the sample and a steady state distribution of analytes between the two phases may not be occurring. The extracting solvent is freshly distilled, shifting the analyte distribution in favor of the clean solvent. The solvent/sample interface at the bottom of the extractor would also be expected to be involved in the partition process. As a result of this complexity, the continuous extraction process is difficult to describe in terms of discrete partitions or equilibria. The partition ratios measured represent the extent of extraction that had occurred with 350 mL of CH_2CL_2 passing through the spiked reagent water in 53 minutes at 29°C. These results indicate that a great deal of material had extracted within one hour. Interestingly, even though the late eluting compounds, benzo(a)anthracene through benzo(ghi)perylene, had the lowest partition ratios, the CE recoveries for these compounds after 24 hours were all in excess of 89% (Priority Pollutant Cocktail Spiking Experiment, Table 1.)

TABLE 20.

ACID NEUTRAL CONTINUOUS EXTRACTION 1PASS EXP. 5/86
EPA EMSL AUDITS: WP482#1 WP482#3 WP881#1

		ng Spiked	MEASURED ng solvent	ng aqueous	partition ratio
1	phenol	95.8	49.7	46.1	1.1
2	1,1-oxybis(2-chloroethane)	45.9	37.0	8.9	4.2
3	2-chlorophenol	27.4	21.7	5.7	3.8
4	1,3-dichlorobenzene	46.7	31.3	15.4	2.0
5	1,4-dichlorobenzene	21.1	16.7	4.4	3.8
6	1,2-dichlorobenzene	22.1	16.8	5.3	3.2
7	bis(2-chloroisopropyl)ether	35.4	29.5	5.9	5.0
8	N-nitroso-di-n-propylamine	21.9	13.6	8.3	1.6
9	hexachloroethane	26.2	18.5	7.7	2.4
10	nitrobenzene	69.8	55.8	14.0	4.0
11	3,5,5-trimethyl-2-cyclohexen-1-one	76.4	62.8	13.6	4.6
12	2-nitrophenol	43.3	40.3	3.0	13.4
13	2,4-dimethylphenol	21.3	16.2	5.1	3.2
14	bis(2-chloroethoxy)methane	44.3	36.9	7.4	5.0
15	2,4-dichlorophenol	44.7	39.2	5.5	7.1
16	1,2,4-trichlorobenzene	21.8	17.6	4.2	4.2
17	naphthalene	23.5	18.9	4.6	4.1
18	1,1,2,3,4,4-hexachloro-1,3-butadiene	43.3	31.0	12.3	2.5
19	4-chloro-3-methylphenol	69.8	61.1	8.7	7.0
20	2,4,6-trichlorophenol	18.7	17.7	1.0	17.7
21	2-chloronaphthalene	23.5	18.2	5.3	3.4
22	dimethylphthalate	40.8	32.0	8.8	3.6
23	2,6-dinitrotoluene	75.5	62.4	13.1	4.8
24	1,2-dihydroacenaphthylene	10.0	8.2	1.8	4.6
25	4-nitrophenol	50.7	29.0	21.7	1.3
26	2,4-dinitrotoluene	66.5	55.7	10.8	5.2
27	diethylphthalate	24.2	20.2	4.0	5.1
28	1-chloro-4-phenoxybenzene	78.2	59.8	18.4	3.3
29	9H-fluorene	45.2	35.3	9.9	3.6
30	2-methyl-4,6-dinitrophenol	245.0	241.3	3.7	65.2
31	4-bromophenyl-phenylether	37.1	28.9	8.2	3.5
32	hexachlorobenzene	30.3	18.8	11.5	1.6
33	pentachlorophenol	50.4	48.5	1.9	25.5
34	phenanthrene	36.9	30.2	6.7	4.5
35	anthracene	30.8	30.0	0.8	37.5
36	di-n-butylphthalate	22.7	18.5	4.2	4.4
37	fluoranthene	29.1	21.2	7.9	2.7
38	pyrene	54.6	36.0	18.6	1.9
39	n-butyl benzyl phthalate	47.3	34.4	12.9	2.7
40	bis(2-ethylhexyl)phthalate	25.0	5.5	19.5	0.3
41	benzo(a)anthracene	55.8	7.1	48.7	0.1
42	chrysene	67.3	21.9	45.4	0.5
43	di-n-octylphthalate	39.5	6.7	32.8	0.2
44	benzo(b)fluoranthene	38.7	11.2	27.5	0.4
45	benzo(k)fluoranthene	35.9	7.5	28.4	0.3
46	benzo(a)pyrene	20.5	5.5	15.0	0.4
47	dibenzo(a,h)anthracene	45.3	6.3	39.0	0.2
48	benzo(ghi)perylene	74.6	10.8	63.8	0.2

Conclusions

The acid/neutral continuous extraction scheme is effective, elegant, and labor saving. Its effectiveness derives from both its acid/neutral and continuous aspects. The acid/neutral continuous extraction scheme resulted in recoveries of priority pollutant compounds that satisfied the method validation requirements of EPA Method 625, with the exception of 2-methyl-4,6-dinitrophenol which was recovered at 108% (53-100% required). The continuous extraction scheme provided a safer mode of extraction since the analyst was less exposed to methylene chloride and hazardous sample constituents. In addition the continuous mode of extraction: improved the recoveries of phenol, 4-nitrophenol, pentachlorophenol and benzoic acid. The acid/neutral scheme as opposed to the Method 625 base/neutral extraction was found to greatly improve the recovery of dimethyl-, diethyl-, di-n-butyl-, and n-butylbenzyl phthalate esters. In addition, environmental samples tend to have considerable amounts of dissolved metals (e.g. iron) and fats. These form an insoluble floc and soapy emulsion when extracted using the Method 625 base/neutral extraction scheme employing either manual or continuous extraction. The acid/neutral scheme minimizes this problem. When the sample pH is made first acidic (A/N), emulsion formation is limited. When the sample pH is re-adjusted and made caustic (base extract), all of the target compounds of interest except benzidine and aniline have already been extracted. Interestingly, these compounds have been dropped as target compounds from the EPA Superfund Program (10). All of the current Superfund target compounds are extracted with a single A/N extraction. The results of this work suggest that much time, labor, and expense could be saved by the A/N extraction scheme while not compromising the quality of the analytical

results. The use of a neutral pH following the acid/neutral extraction was found to recover the relatively basic target compounds aniline and benzidine. However, the broad pH extraction range afforded by the acid/neutral and base extraction procedure assures the recovery of more basic organic compounds (non-target compounds) potentially present in environmental samples.

The continuous extractor was found to effectively extract environmental samples including: ground water, sewage influent, and estuarine and industrial effluents. The levels of target and tentatively identified compounds obtained when the CE was used equaled or exceeded those obtained from manually extracted samples. The fact that the continuous extractor resulted in excellent recoveries of complex priority pollutant mixtures (48 compounds) and gave comparable results to manual extraction of environmental samples indicated that the chemical reactions during the CE process were not significant. These reactions were probably minimized by the large volume (350 mL) of solvent employed in all extractor flasks and changing of the solvent with each pH adjustment (24-hour period of exposure to 40°C).

During these experiments, several difficulties were encountered with the continuous extractors. The extractors require approximately twice the volume of methylene chloride as used for manual separatory funnel extraction. Our laboratory is investigating the possibility of re-distilling spent solvent. The extractors require cooling water. The number of condensors in series may be limited by this cooling capacity. A re-circulating chiller was employed in this work. Condensation of room moisture on the cooling

lines etc. may prove annoying in humid climates. Our laboratory has found pipe insulation to be effective in controlling this problem. Finally, the continuous extraction process does not lend itself to quick turnaround time, in that, 48 hours is needed to complete the process. However, the analyst is free to perform other tasks during this period.

The one piece all glass continuous extractor employed in this work was found to have the following advantages:

- The extractor was easy to clean and could be fired at 500°C.
- The flat-bottom design allows the use of a magnetic stirrer. This may be useful for samples containing settleable solids which accumulate at the aqueous/solvent interface.
- Because of the dimensions of the extractor, the solvent dropping from the condenser strikes the aqueous surface and breaks into many small droplets. This increased the surface area of the extracting solvent and aided extraction, yet required no fragile frit or elaborate stirring mechanism.

Acknowledgement

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Registry No. N-Nitrosodimethylamine, 62-75-8; Phenol, 108-95-2; Aniline, 62-53-34; bis(2-Chloroethyl)ether, 111-44-4; 2-Chlorophenol, 95-57-8; 1,3-Dichlorobenzene, 541-73-1; 1,4-Dichlorobenzene, 106-46-7; Benzyl Alcohol, 100-51-6; 1,2-Dichlorobenzene, 95-50-1; 2-Methylphenol, 95-48-7; bis(2-chloroisopropyl)ether, 39638-32-9; 4-Methylphenol, 106-44-5; N-Nitroso-di-n-propylamine, 621-64-7; Hexachloroethane, 67-72-1; Nitrobenzene, 98-95-3; Isophorone, 78-59-1; 2-Nitrophenol, 88-75-5; 2,4-Dimethylphenol, 105-67-9; Benzoic Acid, 65-85-0; Bis(2-Chloroethoxy)methane, 111-91-1; 2,4-Dichlorophenol, 120-83-2; 1,2,4-Trichlorobenzene, 120-82-1; Naphthalene, 91-20-3; 3-Chloroaniline, 106-47-8; Hexachlorobutadiene, 87-68-3; 4-Chloro-3-methylphenol, 59-50-7; 2-Methylnaphthalene, 91-57-6; Hexachlorocyclopentadiene, 77-47-4; 2,4,6-Trichlorophenol, 88-06-2; 2,4,5-Trichlorophenol, 95-95-4; 2-Chloronaphthalene, 91-58-7; 2-Nitroaniline, 88-74-4; Dimethylphthalate, 131-11-3; Acenaphthylene, 208-96-8; 3-Nitroaniline, 99-09-2; Acenaphthene, 83-32-9; 2,4-Dinitrophenol, 51-28-5; 4-Nitrophenol, 100-02-7; Dibenzofuran, 132-64-9; 2,4-Dinitrotoluene, 121-14-2; 2,6-Dinitrotoluene, 606-20-2; Diethylphthalate, 84-66-2; 4-Chlorophenyl phenylether, 7005-72-3; Fluorene, 86-73-7; 4-Nitroaniline, 100-01-6; 4,6-Dinitro-2methylphenol, 543-52-1; 4-Bromophenyl phenylether, 101-55-3; Hexachlorobenzene, 118-74-1; Pentachlorophenol, 87-86-5; Phenanthrene, 85-01-8; Anthracene, 120-12-7; Di-n-butylphthalate, 84-74-2; Fluoranthene, 206-44-0; Benzidine, 92-87-5; Pyrene, 129-00-0; Butylbenzylphthalate, 85-68-7; 3,3'-Dichlorobenzidine, 91-94-1; Benzo(a)anthracene, 56-55-3; Bis(2-ethylhexy)phthalate, 117-81-7; Chrysene, 218-01-9; Di-n-octyl-phthalate, 117-84-0; Benzo(b)fluoranthene, 205-99-2; Benzo(k)fluoranthene, 207-08-9; Benzo(a)pyrene, 50-32-8; Indeno(1,2,3-cd)pyrene, 193-39-5; Dibenzo(a,h)anthracene, 53-70-3; Benzo(g,h,i)perylene, 191-24-2.

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