

Comparison of Liquid-Liquid Extraction and Solid-Phase Extraction Coupled with GC/MS for Determination of Priority Pollutants in Water

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액체 추출법과 고체상 추출법에 의한 수질 중 유해물질 농축법 비교

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Abstract : Two extraction methods, liquid-liquid extraction(LLE) and solid-phase extraction(SPE), coupled with GC/MS were compared as preconcentration procedures for priority pollutants in water. Among the semi-volatile priority pollutants, 11 acid and 44 base/neutral compounds were spiked in reagent water. With LLE, which is a modification of EPA Method 625, the overall mean recovery of the 54 compounds was 91% with a mean relative standard deviation(RSD) of 4.6%. With SPE, the overall mean recovery of the 52 compounds was 63% with a mean RSD of 8.9%. The detection limits of both methods were in the range of 1~5 μ g/l.

요약 : 수질에서 유해물질을 농축하는 방법으로 액체 추출법과 고체상 추출법을 GC/MS를 검출기로 사용하여 비교하였다. 비휘발성 유해물질 중 11종의 산과 44종의 염기/중성 화합물들을 reagent water에 첨가하여 분석한 결과, 액체추출법은 54종의 화합물에 대해 91%의 평균회수율과 4.6%의 평균상대표준편차를 나타내었으며, 고체상 추출법은 52종의 화합물에 대해 63%의 평균회수율과 8.9%의 평균상대표준편차를 보였다. 두 방법의 검출한계는 1~5 μ g/l였다.

Key words : LLE, SPE, GC/MS, priority pollutant

1. INTRODUCTION

The methods for the preconcentration of organic compounds in water are largely classified to

liquid-liquid extraction(LLE)¹⁻⁶ and solid-phase extraction(SPE)⁶⁻¹⁵. LLE with methylene chloride followed by gas chromatography/mass spectrometry(GC/MS) analysis is the U. S. Environ-

mental Protection Agency(EPA) Method 625 for the determination of extractable organic pollutants in water¹⁶. LLE has been widely used for a variety of compounds with excellent recoveries. But, this method requires large volumes of expensive and toxic organic solvents. In addition, there are problems of losses and contaminations due to sample transportation and storage.

From mid 1980s, SPE has been a rapidly growing technique. The solid supports mostly used in the SPE are bonded phase silicas⁶⁻¹² and various polymeric resins.¹²⁻¹⁵ Among these, octadecyl(C₁₈) bonded silica has been the most popular and exhibited least bias toward acidic or basic compounds in water.⁸ The commercial availability of various packings of disposable cartridges offer big advantages over LLE due to their portability and ease of handling. This technique has recently become a method of choice for a variety of pesticides in water.^{10-11, 17-19} In 1988, EPA adopted SPE and GC/MS as Method 525 for the determination of organics in drinking water.²⁰ However there has been a few examples of application to semi-volatile priority pollutants. The number of compounds investigated in those applications was further limited.

The purpose of this report was to present data which can evaluate the two preconcentration methods. The compounds selected for study were 11 acid and 44 base/neutral(B/N) compounds among the semi-volatile priority pollutants. With GC/MS as a detector, LLE and SPE were compared in terms of mean recovery, mean relative standard deviation(RSD) and method detection limit(MDL).

EXPERIMENTAL

Instrumentation

The GC-MS system utilized was a Hewlett-Packard 5890 A gas chromatograph directly interfaced with a JMS-DX 303 double focusing mass spectrometer(JEOL, Tokyo, Japan) equipped with a

JMA-DA 5000 mass data system.

Separations were performed on a 0.25 μ m, 30m \times 0.25mm I. D. SPB-5 fused-silica capillary GC column(Supelco, Bellefonte, PA, U. S. A.), using a helium flow-rate of 1ml/min. The oven temperature was programmed from 40 $^{\circ}$ C to 290 $^{\circ}$ C at 10 $^{\circ}$ C/min and then held for 30 min. A 1 μ l of sample was injected manually applying the splitless injection technique with the purge time of 0.4 min.

The MS was operated in the electron ionization (EI) mode and following conditions were employed : 70eV electron energy, selected ion monitoring (SIM) mode and 0.1 sec/decade high speed magnetic field switching, 50~500 a. m. u. mass range and 250 $^{\circ}$ C ion source temperature.

Chemicals and reagents

The standard compounds were obtained from Chem Service(Westchester, PA, U. S. A). Methylene chloride, acetone, methanol and benzene were pesticide grade solvents(Baxter Healthcare Corp., Burdick & Jackson Division, Muskegon, MI, U. S. A.). Reagent water was prepared by passing tap water through a RO-20 (Micropore, Taiwan) and a Milli-Q purifier system(Millipore, Bedford, MA, U. S. A.). Anhydrous sodium sulfate(Merck, Darmstadt, F. R. G.) and sodium chloride(Junsei, Tokyo, Japan) were GR grade and heated at 400 $^{\circ}$ C for 4 h. Whatman No. 1 filter papers and boiling chips were Soxhlet-extracted with methylene chloride prior to use. Supelclean cartridges containing 1g of C₁₈ bonded phase silica adsorbents were obtained from Supelco(Cat. No. 57055). Acid surrogates, viz. 2-fluorophenol, phenol-d₅, and 2, 4, 6-tribromophenol, were prepared by diluting the Acid Surrogate Standard Mix-CLP(Supelco, Cat. No. 4-8875). Base/neutral surrogates, viz. nitrobenzene-d₅, 2-fluorobiphenyl and 4-terphenyl-d₁₄ were prepared similarly from Base-Neutrals Surrogate Standard Mix-CLP(Supelco, Cat. No. 4-8925). As internal standards, viz. 1, 4-dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrys-

ene-d₁₂ and perylene-d₁₂, Supelprime-HC Internal Standards Mix(Supelco, Cat. No. 4-8902) was used. These standard solutions were stored at -20°C in screw-cap amber vials with Teflon liners.

Preparation of standard solutions

Stock solution of each individual compound at the 5000µg/ml concentration was prepared by dissolving the standard in methanol, or methylene chloride, or benzene. The stock solutions were stored at -20°C. Primary dilution standard solutions were prepared by combining aliquots of individual stock solutions and diluting the mixture with methanol at 100µg/ml. These solutions were also kept at -20°C. Working standard solutions were made from primary dilution standard solutions by diluting further with acetone at appropriate concentrations on the working day.

Liquid-liquid extraction

The LLE procedure used was a modification of EPA Method 625. Acid and B/N analytes were spiked and analyzed separately. Two l aliquots of reagent water were placed in two separatory funnels. To one aliquot was added 1.0ml of the mixed standard solution containing 10µg/ml of acid analytes and acid surrogates in acetone. B/N analytes and B/N surrogates were added similarly to the other aliquot. After being mixed, pH of the solution spiked with acid analytes and acid surrogates was adjusted to pH<2 with sulfuric acid(1+1). The pH of B/N spiking solution was also adjusted to pH>11 with 10 N sodium hydroxide. Each l of solution was then extracted three times with 60ml aliquots of methylene chloride. The extracts were combined for a total of approximately 180ml methylene chloride. Anhydrous sodium sulfate was added to the extract and then removed by gravity filtration. The dried extract was rotary evaporated to 1ml in a water bath maintained at 30°C. Five µl of internal standards (1000µg/ml) in methylene chloride was added to

the concentrated extract. One µl aliquot of the extract was analyzed by GC/MS.

Solid-phase extraction

The extraction procedure of B/N compounds was as follows. Water sample was prepared by adding 1ml of the mixed standard solution containing B/N analytes (10~120µg/ml) and B/N surrogates(10µg/ml) in acetone to 500ml of reagent water. The cartridge was conditioned sequentially with 10ml of methylene chloride, 10ml of methanol and 10ml of reagent water. All operations with the cartridges used an aspirator vacuum. The water sample was then passed through the cartridge at a flow rate of approximately 5ml/min. The cartridge was washed with reagent water and the vacuum left on for 5 min to dry the solid phase. The analytes were eluted with two 5ml portions of methylene chloride. The eluate was dried with anhydrous sodium sulfate and concentrated to 1ml by rotary evaporation. Internal standards were added to the concentrated eluate and 1µl of the eluate was injected in GC/MS.

For the recovery study of acids, 1ml of the mixed standard solution of acid analytes(10~150µg/ml) and acid surrogates(10µg/ml) was spiked to 500ml of reagent water. The water sample was then adjusted to pH 2 with 1 N-HCl. To this, 75g of NaCl was added and dissolved completely. The cartridge was conditioned with 10ml of methanol, followed by 10ml of reagent water acidified with HCl (pH 2) and saturated with 15% (w/v) NaCl. After the sample had passed through, the solid phase was dried for 5 min. The acid analytes were eluted with two 5ml portions of methanol. The methanol eluate was dried, concentrated and analyzed as described above.

RESULTS AND DISCUSSION

Tables I and II show the retention time, quanti-

Table I. Retention Time, Quantitation Ions and Internal Standard References for Acid Analytes and Acid Surrogates

Compound	Retention Time(min:sec)	Quantitation ion(m/z)	Internal Standard Reference
<u>Internal Standards</u>			
1, 4-dichlorobenzene-d ₄	6 : 39	150	1
naphthalene-d ₈	9 : 29	136	2
acenaphthene-d ₁₀	13 : 56	164	3
phenanthrene-d ₁₀	17 : 42	188	4
<u>Acid Surrogates</u>			
2-fluorophenol	4 : 28	112	1
phenol-d ₅	6 : 05	99	2
2, 4, 6-tribromophenol	15 : 59	332	4
<u>Acid Analytes</u>			
phenol	6 : 06	94	1
2-chlorophenol	6 : 18	128	1
2-nitrophenol	8 : 39	139	2
2, 4-dimethylphenol	8 : 51	122	2
2, 4-dichlorophenol	9 : 14	162	2
4-chloro-3-methylphenol	11 : 05	142	2
2, 4, 6-trichlorophenol	12 : 05	196	3
2, 4-dinitrophenol	14 : 12	184	3
4-nitrophenol	14 : 31	139	3
4, 6-dinitro-2-methylphenol	15 : 37	198	4
pentachlorophenol	17 : 26	266	4

Table II. Retention Time, Quantitation Ions and Internal Standard References for Base/Neutral Analytes and Surrogates

Compound	Retention Time(min:sec)	Quantitation ion(m/z)	Internal Standard Reference
<u>Internal Standards</u>			
1, 4-dichlorobenzene-d ₄	6 : 39	150	1
naphthalene-d ₈	9 : 29	136	2
acenaphthene-d ₁₀	13 : 56	164	3
phenanthrene-d ₁₀	17 : 42	188	4
chrysene-d ₁₂	24 : 36	240	5
perylene-d ₁₂	28 : 59	264	6

B/N Surrogates

nitrobenzene- ₅	7 : 53	128	3
2-fluorobiphenyl	12 : 17	172	3
4-terphenyl-d ₁₄	21 : 56	244	5

B/N Analytes

N-nitrosodimethylamine	2 : 55	74	1
bis(2-chloroethyl)ether	6 : 15	93	1
1, 3,-dichlorobenzene	6 : 34	146	1
1, 4,-dichlorobenzene	6 : 42	146	1
1, 2,-dichlorobenzene	7 : 05	146	1
bis(2-chloroisopropyl)ether	7 : 23	121	1
N-nitroso-di-n-propylamine	7 : 40	70	1
hexachloroethane	7 : 44	201	1
nitrobenzene	7 : 56	123	2
isophorone	8 : 29	82	2
bis(2-chloromethoxy)methane	9 : 05	93	2
1, 2, 4-trichlorobenzene	9 : 25	180	2
naphthalene	9 : 33	128	2
hexachlorobutadiene	10 : 03	225	2
hexachlorocyclopentadiene	11 : 52	237	3
2-chloronaphthalene	12 : 27	162	3
dimethylphthalate	13 : 29	163	3
acenaphthylene	13 : 31	152	3
2, 6-dinitrotoluene	13 : 35	165	3
acenaphthene	14 : 00	154	3
2, 4-dinitrotoluene	14 : 34	165	3
diethylphthalate	15 : 18	149	3
fluorene	15 : 17	166	3
4-chlorophenylphenylether	15 : 22	204	3
N-nitrosodiphenylamine	15 : 41	169	4
4-bromophenylphenylether	16 : 37	248	4
hexachlorobenzene	16 : 56	284	4
phenanthrene	17 : 44	178	4
anthracene	17 : 50	178	4
de-n-butylphthalate	19 : 33	149	4
fluoranthene	20 : 50	202	4
benzidine	21 : 16	184	5
pyrene	21 : 23	202	5
butylbenzylphthalate	23 : 23	149	5
benz(a)anthracene	24 : 33	228	5
3, 3' -dichlorobenzidine	24 : 37	252	5
chrysene	24 : 39	228	5
-bis(2-ethylhexyl)phthalate	-25 : 03	-149	-5
di-n-octylphthalate	26 : 47	149	6
benzo(b)fluoranthene	27 : 39	252	6

benzo(k)fluoranthene	27 : 45	252	6
benzo(a)pyrene	28 : 46	252	6
dibenz(a, h)anthracene	34 : 03	278	6
benzo(g, h, i)perylene	35 : 15	276	6

tation ion and internal standards used for identification and quantitation of acid and B/N compounds.

Liquid-Liquid Extraction(LLE). Blank tests were carried out for the LLE procedure with three 1l aliquots of reagent water. The blank solutions were all free of analytes except for traces(0.46 $\mu\text{g}/\text{l}$ and 0.47 $\mu\text{g}/\text{l}$, respectively) of di-n-butylphthalate and bis(2-ethylhexyl)phthalate. The average blank value was subtracted from the respective water sample measurements.

The mean recoveries of acid (Table III) and B/N analytes(Table IV) from the LLE are given. Except for phenol and 4-nitrophenol, all other acid analytes show excellent recoveries in Table III. The

low recovery of these two compounds had been improved considerably by the continuous liquid-liquid extraction.⁴ As seen from the excellent recoveries of B/N surrogates, nitrobenzene-d₅, 2-fluorobiphenyl and 4-terphenyl-d₁₄, in Table IV, the recovery and precision data of B/N analytes were better than² or comparable to the data^{3, 4} reported in the literature.

The recovery in each step of extraction, drying and concentration was evaluated for the selected priority pollutants. Table V shows the mean recovery from three measurements. Except for relatively volatile analytes, concentration by rotary evaporation was nearly quantitative in the first column of Table V. In the comparison of the first column

Table III. Recoveries of Acid Priority Pollutants from Liquid-Liquid Extraction

Compound	Amount spiked, $\mu\text{g}/\text{l}$	Mean % recovery ^a	RSD, %	MDL, $\mu\text{g}/\text{l}$ ^b
2-fluorophenol ^c	10	65	10	2.2
phenol	10	50	8.9	1.5
2-chlorophenol	10	92	8.0	2.4
2-nitrophenol	10	98	8.2	2.7
2, 4-dimethylphenol	10	97	5.6	1.8
2, 4-dichlorophenol	10	99	7.3	2.4
phenol-d ₅ ^c	10	51	15	2.5
4-chloro-3-methylphenol	10	98	2.9	1.0
2, 4, 6-trichlorophenol	10	97	3.8	1.2
2, 4-dinitrophenol	125	93	7.0	27
4-nitrophenol	150	48	11	26
4, 6-dinitro-2-methylphenol	10	93	7.6	2.4
pentachlorophenol	10	94	7.9	2.5
2, 4, 6-tribromophenol ^c	10	96	4.0	1.3

^a Mean value from six extractions.

^b Method detection limit is the minimum concentration that can be measured with 99% confidence that the concentration is greater than zero.²¹

^c Surrogate standard.

Table IV. Recoveries of Base/Neutral Priority Pollutants from Liquid-Liquid Extraction

Compound	Amount spiked, $\mu\text{g}/l$	Mean % recovery ^a	RSD, %	MDL, $\mu\text{g}/l^b$
N-nitrosodimethylamine	20	44	14	4.1
bis(2-chloroethyl)ether	10	93	2.5	0.8
1, 3-dichlorobenzene	10	76	2.8	0.7
1, 4-dichlorobenzene	10	77	2.6	0.7
1, 2-dichlorobenzene	10	79	2.8	0.7
bis(2-chloroisopropyl)ether	10	94	2.8	0.9
N-nitroso-di-n-propylamine	10	85	3.8	1.1
hexachloroethane	10	69	3.3	0.8
nitrobenzene	10	99	2.3	0.8
isophorone	10	101	4.6	1.5
nitrobenzene- d_5^c	10	99	4.6	1.5
bis(2-chloroethoxy)methane	10	98	3.1	1.0
1, 2, 4-trichlorobenzene	10	89	2.9	0.9
naphthalene	10	95	2.0	0.6
hexachlorobutadiene	10	73	5.2	1.3
hexachlorocyclopentadiene	10	71	3.1	0.7
2-chloronaphthalene	10	98	6.2	2.0
2-fluorobiphenyl ^c	10	97	4.2	1.3
dimethylphthalate	10	76	7.1	1.8
acenaphthylene	10	96	3.6	1.1
2, 6-dinitrotoluene	10	100	4.3	1.4
acenaphthene	10	97	2.5	0.8
2, 4-dinitrotoluene	10	96	2.4	0.8
diethylphthalate	10	76	4.9	1.3
fluorene	10	94	1.6	0.5
4-chlorophenylphenylether	10	96	2.7	0.9
N-nitrosodiphenylamine	10	98	3.7	1.2
4-bromophenylphenylether	10	96	3.0	1.0
hexachlorobenzene	10	97	4.6	1.5
phenanthrene	10	97	3.3	1.1
anthracene	10	99	3.4	1.1
di-n-butylphthalate	10	91	4.2	1.3
fluoranthene	10	95	3.1	1.0
benzidine	100	113	8.4	32
pyrene	10	97	3.1	1.0
butylbenzylphthalate	10	95	5.9	1.9
4-terphenyl- d_{14}^c	10	99	4.5	1.5
benz(a)anthracene	10	97	5.2	1.7
3, 3'-dichlorobenzidine	10	102	7.2	2.5
chrysene	10	96	6.5	2.1
bis(2-ethylhexyl)phthalate	10	97	5.0	1.6
di-n-octylphthalate	10	95	3.7	1.2
benzo(b)fluoranthene	10	96	4.9	1.6
benzo(k)fluoranthene	10	94	3.5	1.1

benzo(a)pyrene	10	94	4.7	1.5
dibenz(a, h)anthracene	10	88	4.7	1.4
benzo(g, h, i)perylene	10	92	2.8	0.9

^a Mean value from six extractions.

^b Method detection limit is the minimum concentration that can be measured with 99% confidence that the concentration is greater than zero.²¹

^c Surrogate standard.

Table V. Mean % Recoveries^a of Selected Priority Pollutants in Each Procedure of Liquid-Liquid Extraction

Compound	Evaporation ^b	Drying and evaporation ^c	Extraction, drying and evaporation ^d
phenol	94	97	50
2-chlorophenol	93	85	92
1, 2-dichlorobenzene	92	82	79
hexachloroethane	91	79	69
nitrobenzene-d ₅ ^e	97	95	99
1, 2, 4-trichlorobenzene	95	87	89
naphthalene	97	88	95
hexachlorobutadiene	95	86	73
2-fluorobiphenyl ^e	97	97	97
2-chloronaphthalene	99	96	98
acenaphthylene	98	96	96
diethylphthalate	94	91	76
4-nitrophenol	—	98	48
hexachlorobenzene	99	97	97
pentachlorophenol	96	97	94
anthracene	96	95	99
di-n-butylphthalate	94	93	91
fluoranthene	97	95	95
pyrene	95	97	97
4-terphenyl-d ₁₄ ^e	97	98	99
benz(a)anthracene	99	98	97

^a Mean value from three experiments.

^b One ml of selected compound mixture(10 μ g/ml) was added to 200ml of methylene chloride.

^c One ml of selected compound mixture(10 μ g/ml) was added to a mixture of 1ml water and 199ml methylene chloride.

^d Data taken from Tables III and IV.

^e Surrogate standard.

with the second one of Table V, it is found that approximately 10% of 1, 2-dichlorobenzene, hexachloroethane, 1, 2, 4-trichlorobenzene and hexachlorobutadiene were lost during the drying with sodium sulfate and filter paper. This may have

been due to their volatility or sorption to sodium sulfate. Other analytes were recovered quantitatively in the drying procedure.

A comparison between the second and the third column in Table V yields the recovery obtained

from the solvent extraction with methylene chloride. Hexachloroethane, hexachlorobutadiene and diethylphthalate gave the extraction recovery of 88, 86 and 84%, respectively. As mentioned earlier, phenol and 4-nitrophenol were only extracted about 50%. The values of 2-chlorophenol and naphthalene were seemed to be in experimental error. The remaining analytes were extracted nearly 100%. Therefore, it can be concluded that with the exception of few compounds, most of acid and B/N priority pollutants were quantitatively extracted, dried and concentrated in the LLE procedure.

Solid-Phase Extraction(SPE). Blank test for the SPE procedure was carried out with 500ml of reagent water. The test was done in triplicate. The mean blank values determined were 1.2, 9.1 and 1.1 $\mu\text{g}/\text{l}$ for di-n-butylphthalate, butylbenzylphthalate and bis(2-ethylhexyl)phthalate, respectively. These blank values were subtracted as background from the spiked water measurements.

The mean recovery data of acid and B/N analytes from the SPE are given in Tables VI and VII. The method accuracy and precision of the two extraction procedures are presented in Table VIII. The analytes are grouped by their structures or other common features². With LLE, the mean recoveries of acid and B/N analytes were 87 and 91% with mean RSDs of 7.1 and 4.0%. With SPE, the mean recoveries of acid and B/N analytes were 69 and 62% with mean RSDs of 12 and 8.2%. With LLE, the overall mean recovery of 54 analytes was 91% with a mean RSD of 4.6%. With SPE, the overall mean recovery of 52 analytes was 63% with a mean RSD of 8.9%. Overall, LLE is qualitatively superior to SPE.

Comparing the analytes by group in Table VIII, it is seen that substituted benzenes gave lower mean recovery than the overall mean recovery with both extraction methods. The low recovery of substituted benzenes was particularly apparent with

Table VI. Recoveries of Acid Priority Pollutants from Solid-Phase Extraction

Compound	Amount spiked, $\mu\text{g}/\text{l}$	Mean % recovery ^a	RSD, %	MDL, $\mu\text{g}/\text{l}$ ^b
2-fluorophenol ^c	20	28	23	4.3
phenol	40	26	24	8.3
2-chlorophenol	20	53	13	4.8
2-nitrophenol	20	49	16	5.4
2, 4-dimethylphenol	20	99	4.6	3.0
2, 4-dichlorophenol	20	95	5.5	3.6
phenol-d ₅ ^c	20	31	27	5.6
4-chloro-3-methylphenol	20	97	4.4	2.9
2, 4, 6-trichlorophenol	20	88	6.3	3.7
2, 4-dinitrophenol	250	27	23	52
4-nitrophenol	300	56	17	97
4, 6-dinitro-2-methylphenol	20	84	9.2	5.2
pentachlorophenol	20	87	5.5	3.2
2, 4, 6-tribromophenol ^c	20	83	8.6	4.8

^a Mean value from six experiments.

^b Method detection limit is the minimum concentration that can be measured with 99% confidence that the concentration is greater than zero.²¹

^c Surrogate standard.

Table VI. Recoveries of Base/Neutral Priority Pollutants from Solid-Phase Extraction

Compound	Amount spiked, $\mu\text{g}/l$	Mean % recovery ^a	RSD, %	MDL, $\mu\text{g}/l^b$
N-nitrosodimethylamine	240	0.7	7.4	44
bis(2-chloroethyl)ether	20	5.2	20	0.7
1, 3-dichlorobenzene	20	42	9.6	2.7
1, 4-dichlorobenzene	20	45	7.9	2.4
1, 2-dichlorobenzene	20	52	9.3	3.2
bis(2-chloroisopropyl)ether	20	65	6.7	2.9
N-nitroso-di-n-propylamine	20	57	3.3	1.3
hexachloroethane	20	26	8.4	1.5
nitrobenzene	20	12	9.6	0.7
isophorone	20	85	5.9	3.4
nitrobenzene- d_5^c	20	12	9.9	0.8
bis(2-chloroethoxy)methane	20	40	9.1	2.4
1, 2, 4-trichlorobenzene	20	55	8.0	3.0
naphthalene	20	73	7.2	3.5
hexachlorobutadiene	20	18	11	1.3
hexachlorocyclopentadiene	20	25	15	2.4
2-chloronaphthalene	20	80	7.7	4.1
2-fluorobiphenyl ^e	20	80	6.9	3.7
dimethylphthalate	20	81	6.6	3.6
acenaphthylene	20	80	3.4	1.8
2, 6-dinitrotoluene	20	68	7.6	3.5
acenaphthene	20	87	4.5	2.6
2, 4-dinitrotoluene	20	66	7.5	3.3
diethylphthalate	20	89	7.0	4.2
fluorene	20	84	5.1	2.9
4-chlorophenylphenylether	20	83	4.9	2.8
N-nitrosodiphenylamine	20	90	5.6	3.4
4-bromophenylphenylether	20	85	4.9	2.8
hexachlorobenzene	20	43	12	3.4
phenanthrene	20	84	4.1	2.3
anthracene	20	65	8.1	3.6
di-n-butylphthalate	20	84	7.2	4.0
fluoranthene	20	69	10	4.7
benzidine	200	120	5.8	47
pyrene	20	61	8.9	3.6
butylbenzylphthalate	60	72	6.6	9.5
4-terphenyl- d_{14}^c	20	46	9.8	3.0
benz(a)anthracene	20	43	11	3.0
3, 3'-dichlorobenzidine	20	83	7.0	3.9
chrysene	20	37	13	3.4
bis(2-ethylhexyl)phthalate	20	45	12	3.6
di-n-octylphthalate	20	38	16	4.1
benzo(b)fluoranthene	20	40	9.7	2.6
benzo(k)fluoranthene	20	42	9.4	2.6

benzo(a)pyrene	20	39	7.1	1.8
dibenz(a, h)anthracene	40	60	8.6	6.9
benzo(g, h, i)perylene	40	69	13	12

^a Mean value from six experiments.

^b Method detection limit is the minimum concentration that can be measured with 99% confidence that the concentration is greater than zero.²¹

^c Surrogate standard.

Table VII. Accuracy and Precision for Analyses of Priority Pollutants with LLE and SPE

Group of compound	LLE			SPE		
	No. of cmpds.	Mean % recovery	Mean % RSD	No. of cmpds.	Mean % recovery	Mean % RSD
Phenols	11	87	7.1	11	69	12
Substituted benzenes	8	89	3.1	7 ^a	53	8.8
PAHs	15	95	3.7	15	62	8.2
Phthalic acid esters, N-nitroso cmpds. and isophorone	9 ^b	90	4.8	9 ^b	71	7.8
Miscellaneous halogenated cmpds. and substituted biphenyls	11	91	4.3	10 ^c	62	8.0
TOTAL	54	91	4.6	52	63	8.9

^a Excluded nitrobenzene.

^b Excluded N-nitrosodimethylamine.

^c Excluded bis(2-chloroethyl)ether.

SPE. This is attributed to their volatility which leads to losses during the water pass through the cartridge and elution with an aspirator vacuum.

Polycyclic aromatic hydrocarbons (PAHs) showed the highest mean recovery among the compounds extracted with LLE. But, with SPE, the mean recovery of higher molecular weight PAHs was lower than the overall mean recovery whereas that of lower molecular weight PAHs was relatively good. This means that higher molecular weight PAHs were poorly retained on the cartridge. Therefore, it indicates the limited capacity of 1g cartridge.

N-nitrosodimethylamine gave the lowest mean recovery with both extraction methods. A major source of low recovery is its volatility. It is practi-

cally impossible to measure N-nitrosodimethylamine with the SPE method. The extremely low recovery of bis(2-chloroethyl)ether with SPE can be also explained on the same reason. The poor recovery of hexachlorocyclopentadiene with the two methods may have been due to thermal decomposition in the inlet of GC and photochemical decomposition.^{2, 20} Phenol and nitro-phenols were recovered less efficiently by the SPE than chloro- and methylphenols were. Small breakthrough volume of polar compounds is assumed to be the reason.^{8, 22} The recoveries of phenol and nitro-phenols are therefore expected to be increased as the water volume is decreased.

Fig. 1 shows the distribution of mean recoveries of analytes with LLE and SPE. Of the 55 analytes

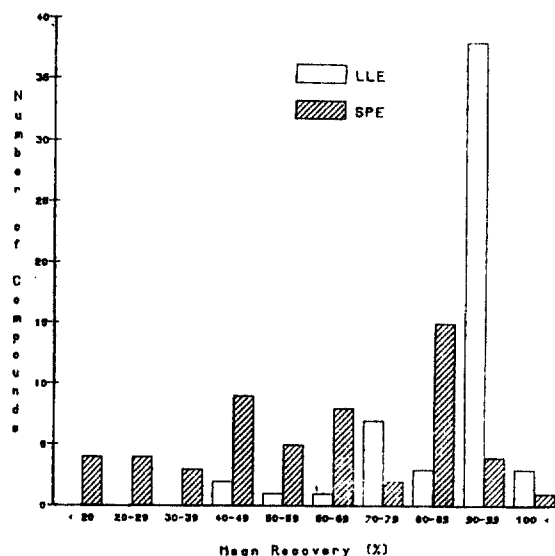


Fig. 1. Distribution of mean recoveries of LLE and SPE.

tested with LLE, 51(93%) had mean recoveries of 70% or greater. With SPE, 22 analytes(40%) had mean recoveries of 70% or greater (and 30 analytes (55%) had mean recoveries of 60% or greater).

Fig. 2 shows the distribution of relative standard deviations(RSD) of the mean recoveries with LLE and SPE. Of the 55 analytes tested with LLE, 53 (96%) had RSD of 10% or less. With SPE, 41

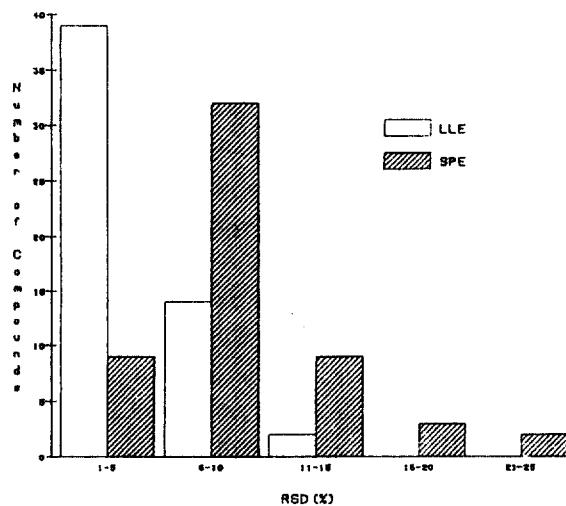


Fig. 2. Distribution of relative standard deviations of mean recoveries of LLE and SPE.

(75%) had RSD of 10% or less.

Comparison of method detection limits(MDL) given in Tables III ~ IV and Tables VI ~ VII shows that, with exceptions of a few analytes, LLE and SPE are in the range of 1~3 and 1~5 $\mu\text{g/l}$, respectively. But, 500ml of water sample was extracted with SPE and so the MDLs of SPE are approximately twice that of LLE. With the extraction of 1l of sample with SPE, the MDLs would be in the same range as obtained with LLE.

CONCLUSION

Liquid-liquid extraction coupled with GC/MS is confirmed as a proper analytical method for the determination of a variety of semi-volatile priority pollutants in water sample.

Solid-phase extraction, which was examined the possibility as a another preconcentration method, is qualitatively inferior to LLE. Since the same drying and concentration procedures were used in both extraction methods, losses due to drying and concentration are not considered. Then, a major source of low recovery is that 500ml of sample volume is greater than the breakthrough volume of most of analytes. Another source is the variability in the size of vacuum which affects the flow rate of sample and also causes the analyte losses during the sorbent drying prior to elution. It is therefore concluded that with the commercial availability of larger capacity cartridges which should be sufficient to extract a full liter of sample without compound breakthrough and with the use of a vacuum manifold which can maintain constant pressure, the improved performance of SPE is expected.

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