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## SELECTIVE PRECONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS AND POLYCHLORINATED BIPHENYLS BY *IN SITU* METAL HYDROXIDE PRECIPITATION

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### SUMMARY

An investigation of selective concentration of analytes from aqueous samples by *in situ* magnesium hydroxide precipitation, as described by Faltusz, has yielded the following results: (1) the method is selective for polycyclic aromatic hydrocarbons and polychlorinated biphenyls of higher molecular weight: it discriminates strongly against acidic molecules, and other neutral and basic molecules are only partially recovered; (2) a variety of metal hydroxides could evidently be used in this method, but magnesium appears to have practical advantages over some of the others; (3) the reproducibility of analyses on pure water samples is acceptable (*ca.* 20% relative standard deviation), but the results from natural samples show lower recovery and wider variability; (4) a preliminary test, in which this method was used to discriminate against major amounts of interfering solutes, shows promise that this technique might have unique advantages in certain situations.

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### INTRODUCTION

Analysis of aqueous samples for trace organic compounds requires concentration of analytes in most cases. In many situations, complex matrices require selective concentration of target analytes to produce extracts above the instrumental limit of detection. Typically, liquid-liquid extraction is followed by evaporation to a convenient volume for analysis. An interesting alternate, selective concentration method was developed by Faltusz<sup>1</sup>, in which polycyclic aromatic hydrocarbons (PAHs) were concentrated by adsorption onto magnesium hydroxide, precipitated *in situ*. The precipitate was removed by centrifugation and redissolved in a small volume of acidic buffered solution for analysis.

Several questions regarding Faltusz's procedure are addressed in the present study. (1) Is the technique selective for a specific group of analytes? (2) Are the analyses repeatable with any degree of precision? (3) Would hydroxides other than

that of magnesium also concentrate analytes? (4) Does the method appear to have any unique advantage for use with environmental samples?

## EXPERIMENTAL

The analytical instruments used were a Hewlett-Packard Model 5880 gas chromatograph with flame ionization detector interfaced to the Hewlett-Packard 3357 Laboratory Automation System (LAS); or a Hewlett-Packard 5985 GC/MS system with an RTE-VI operating system. Both analytical systems used J&W wide-bore (0.32 mm) 30 m fused-silica capillary columns with DB-5 bonded phase (0.25  $\mu\text{m}$  film thickness). The centrifuge was a DuPont-Sorvall model RC-5B.

All organic solvents were Burdick and Jackson high purity. The standards included Supelco base-neutral and phenol mixtures, polychlorinated biphenyl (PCB) mixtures prepared from isomers supplied by Ultra Scientific, and deuterated surrogate standards from MSD Isotopes. Metal salts were obtained from Fisher Scientific and Scientific Products. The Kovats standard was prepared from alkanes  $\text{C}_7$  to  $\text{C}_{34}$  from Supelco, Inc. Sequential rinsing by concentrated sulfuric acid, methanol and methylene chloride, followed by air drying was used to clean centrifuge tubes. Other glassware was cleaned by typical sequential washing procedures, followed by heating to 450°C for 4 h.

A typical precipitation procedure involved spiking analyte and surrogate standards into a 1-l aqueous sample. Magnesium sulfate (3.0 g) was dissolved in the sample and ammonium hydroxide (10 ml of 25%) was pipetted into the sample and mixed thoroughly. Aliquots of the sample were centrifuged at 2800 rpm for 8 min, with supernatant being used to rinse the precipitate from the bottle into the centrifuge tubes. After collecting the precipitate from a sample in one centrifuge tube and decanting as much of the supernatant liquid as possible without loss of precipitate, ammonium chloride (0.7 g) and sulfuric acid (*ca.* 700  $\mu\text{l}$ ) were added to dissolve the precipitate and the solution was extracted with three 10-ml portions of methylene chloride. The combined extract was reduced to 1.0 ml under nitrogen in a 60°C sand bath and transferred to a 1.5-ml autosampler vial with PTFE-faced septum for analysis.

The gas chromatographic (GC) sample analysis, in the case of the gas chromatograph-flame ionization detection system, was completely automated. The injections of blanks, standards, samples, etc., were controlled by Sequences and Methods input to the LAS. Specially written methods automatically calculated the Kovats retention index for each peak, based on externally run Kovats standards, and then named and quantified those peaks which matched the Kovats indices of the reference materials. Further information on the details of this analysis procedure can be found in refs. 2 and 3.

## RESULTS AND DISCUSSION

### *Selectivity*

To assess the extraction selectivity of magnesium hydroxide for organic compounds, the precipitation was conducted with three mixtures: a 45-component base-neutral mixture, a 24-component PCB mixture, and an 11-component phenol

mixture. The mixtures along with surrogate compounds ( $[^2\text{H}_5]$ pyridine, 1,2-dichloro- $[^2\text{H}_4]$ benzene, and  $[^2\text{H}_{10}]$ pyrene) were added to 1 l of distilled water at levels close to 10 ppb. Since the final volume for GC analysis was 1.0 ml, the analyte concentration would have been 10 ppm for 100% recovery.

No phenols were found in the extract from the phenol mixture. Analytes identified from the base-neutral and PCB mixtures were those of greater GC retention times, which correspond in most instances to compounds of higher molecular weight, as seen in Table I. Higher molecular weight PAHs were selectively concentrated relative to the ethers and phthalates, until octyl phthalate was reached. In the range between acenaphthylene and fluorene, the nitroaromatics, 2,4- and 2,6-dinitrotoluene, were not found.

The lack of recovery of the amines, N-nitrosodiphenylamine, 1,2-diphenylhydrazine, benzidine, and 3,3'-dichlorobenzidine, indicates discrimination against amines, but our GC system had some tendency to discriminate against the benzidines, so the magnitude of the effect may not be accurate. No deuterated surrogates were recovered other than  $[^2\text{H}_{10}]$ pyrene, which as found at an expected level.

Analysis of the PCB mixtures, with individual analyte concentrations in the 2 ppb range in the water (2 ppm after concentration), also displayed higher recoveries for congeners with longer retention times, as seen in Table II. The trichlorobiphenyls were the lowest molecular weight isomers to be identified. Recovery was relatively constant for the pentachlorobiphenyls through decachlorobiphenyl.

### *Repeatability*

To obtain some idea of the repeatability of analyses by this technique, several 1-l samples were prepared simultaneously using distilled water, and concentrated by magnesium hydroxide precipitation. Four were prepared for the base-neutral mixture, and three for the PCBs, with results shown in Tables I and II. All identifications and quantifications of the analytes were done automatically by the LAS system, as described previously, using an internal standard method based on  $[^2\text{H}_{10}]$ anthracene. Further studies should be conducted on both pure and contaminated water samples to substantiate that the relative standard deviations (R.S.D.s) are comparable with other low level environmental analyses.

Base-neutral R.S.D.s between 13 and 20% and PCB R.S.D.s between 5 and 20% were observed.

### *Other metal hydroxides*

Since all but the alkali metal ions form insoluble metal hydroxides, it was of interest to examine a few common cations other than magnesium. Chosen were aluminium chloride ( $\text{AlCl}_3$ ), zinc sulphate ( $\text{ZnSO}_4$ ), and iron(II) chloride ( $\text{FeCl}_2$ ). These metal salts all gave useable precipitates and the systems were studied using the base-neutral mixture. Owing to instrumental difficulties at the time of analysis, the results were not quantitative in nature; however the trends of selectivity were clear. In the case of aluminium hydroxide, fluorene was recovered, and also the compounds of higher molecular weight starting with hexachlorobenzene. The results with zinc hydroxide were similar, except that it appeared that possibly the phthalates might be concentrated more efficiently. Iron(II) hydroxide gave similar results to those of aluminium hydroxide.

TABLE I

## PERCENT RECOVERIES OF BASE-NEUTRAL COMPONENTS FROM REPLICATE MAGNESIUM HYDROXIDE PRECIPITATIONS

A blank indicates that the compound was not detected. All values were calculated by an internal standard method; see text. The average and standard deviation were calculated only when the analyte was detected in all four samples.

Compound name	Recovery (%)				Average	S.D.
	Analysis Number					
	MGR006	MGR007	MGR008	MGR009		
Bis(2-chloroethyl) ether						
1,3-Dichlorobenzene	1.7		2.4	1.4		
1,4-Dichlorobenzene						
1,2-Dichlorobenzene						
Bis(2-chloroisopropyl) ether						
Hexachloroethane						
N-nitroso-di- <i>n</i> -propylamine						
Nitrobenzene						
Isophorone						
Bis(2-chloroethoxy)methane						
1,2,4-Trichlorobenzene						
Naphthalene						
Hexachlorobutadiene						
Hexachlorocyclopentadiene						
2-Chloronaphthalene						
Acenaphthylene	2.9	1.4	2.1	1.9	2.1	0.6
Dimethyl phthalate						
2,6-Dinitrotoluene						
Acenaphthene	1.4					
2,4-Dinitrotoluene						
Fluorene	10.3	6.7	7.8	6.7	7.9	1.7
4-Chlorophenyl phenyl ether						
Diethyl phthalate						
N-Nitrosodiphenylamine						
1,2-Diphenylhydrazine	1.4					
4-Bromophenyl phenyl ether	3.3	2.4	1.4			
Hexachlorobenzene	55.4	44.0	42.0	37.8	44.8	7.5
Phenanthrene	52.3	39.2	41.6	35.5	42.2	7.2
Anthracene	60.0	45.1	48.8	41.7	48.5	7.9
Di- <i>n</i> -butyl phthalate	4.3	2.7	5.4	2.8	3.8	1.3
Fluoranthene	86.2	69.4	74.5	62.8	73.2	9.9
Benzidine						
Pyrene	85.8	72.2	73.4	62.2	73.4	9.7
Butyl benzyl phthalate	4.7	3.0	3.1			
Benzo[ <i>a</i> ]anthracene	84.8	66.2	70.0	57.0	69.5	11.6
Chrysene	93.8	69.4	67.0	63.8	73.5	13.7
3,3'-Dichlorobenzidine			0.6			
Bis(2-ethylhexyl) phthalate	85.2	65.8	68.1	56.1	68.8	12.1
Di- <i>n</i> -octyl phthalate	82.3	62.6	63.7	51.5	65.0	12.8
Benzo[ <i>b</i> ]fluoranthene	86.3	68.8	72.0	57.6	71.2	11.8
Benzo[ <i>k</i> ]fluoranthene	85.8	67.7	70.1	59.0	70.7	11.2
Benzo[ <i>a</i> ]pyrene	80.1	60.1	67.7	52.4	65.1	11.8
Ideno[1,2,3- <i>cd</i> ]pyrene	87.0	70.1	72.0	55.8	71.2	12.8
Dibenzo[ <i>a,h</i> ]anthracene	84.8	67.0	67.5	52.8	68.0	13.1
Benzo[ <i>g,h,i</i> ]perylene	88.3	71.0	72.8	56.9	72.2	12.9
<i>Surrogate standards</i>						
[ <sup>2</sup> H <sub>5</sub> ]Pyridine						
[ <sup>2</sup> H <sub>6</sub> ]Phenol						
1,2-Dichloro[ <sup>2</sup> H <sub>4</sub> ]benzene						
[ <sup>2</sup> H <sub>10</sub> ]Pyrene	83.6	68.5	76.9	63.3	73.1	9.0

TABLE II

## PERCENT RECOVERIES OF PCB ISOMERS FROM REPLICATE MAGNESIUM HYDROXIDE PRECIPITATIONS

A blank indicates that the compound was not detected. All values were calculated by an internal standard method: see text.

Compound name	Recovery (%)				
	Analysis Number			Average	S.D.
	MGR016	MGR014	MGR013		
2-Chlorobiphenyl					
3-Chlorobiphenyl					
4-Chlorobiphenyl					
2,2'-Dichlorobiphenyl					
2,5-Dichlorobiphenyl					
2,4'-Dichlorobiphenyl					
2,4,6-Trichlorobiphenyl	10.6	15.2	15.0	13.6	2.6
4,4'-Dichlorobiphenyl					
2,4,4-Trichlorobiphenyl	25.1	25.8	27.2	26.0	1.1
2,3,4-Trichlorobiphenyl	24.0	23.6	24.6	24.1	0.5
2,3',4,6-Tetrachlorobiphenyl	36.9	36.6	41.3	38.3	2.6
2,2',4,4'-Tetrachlorobiphenyl	41.5	42.5	50.9	45.0	5.2
2,3,5,6-Tetrachlorobiphenyl	38.8	35.4	40.4	38.2	2.5
2,2',4,5,5'-Pentachlorobiphenyl	58.6	56.3	62.8	59.2	3.3
2,2',3,4,5'-Pentachlorobiphenyl	59.4	58.2	69.0	62.2	5.9
2,2',3,4,5-Pentachlorobiphenyl	59.5	58.6	68.8	62.3	5.7
2,2',3,3',6,6'-Hexachlorobiphenyl	61.7	60.0	71.6	64.4	6.3
2,2',3,4,4',5'-Hexachlorobiphenyl	69.6	64.9	79.0	71.2	7.2
2,2',3,4,4',5',6-Heptachlorobiphenyl	67.8	63.5	70.1	67.1	3.4
2,2',3,3',4,4'-Hexachlorobiphenyl	67.3	65.2	77.6	70.0	6.6
2,2',3,3',4,4',6-Heptachlorobiphenyl	68.6	64.8	80.4	71.3	8.1
2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	59.1	28.2	80.8	56.0	26.5
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	69.7	66.8	81.0	72.5	7.5
Decachlorobiphenyl	66.6	51.8	77.9	65.4	13.1
<i>Surrogate standards</i>					
[ <sup>2</sup> H <sub>5</sub> ]Pyridine					
[ <sup>2</sup> H <sub>6</sub> ]Phenol					
1,2-Dichloro[ <sup>2</sup> H <sub>4</sub> ]benzene					
[ <sup>2</sup> H <sub>10</sub> ]Pyrene	35.4	25.4	17.7	26.2	8.9

It appears that any of a large number of metal hydroxides might give results similar to those of magnesium, but there are some practical advantages to magnesium. Aluminum, being amphoteric, was very sensitive to the pH, requiring particular care to maximize the amount of precipitate. Zinc hydroxide was more difficult to dissolve than the magnesium and more difficult to centrifuge because the particles did not readily cohere. The iron(II) hydroxide (which was dissolved using a sodium oxalate-sulfuric acid mixture) was highly resistant to compaction by centrifugation, so it was never possible to remove the supernatant liquid without also removing variable amounts of the precipitate. Because of the difficulties encountered in the use of other metal hydroxides, it was concluded that magnesium was the preferred ion

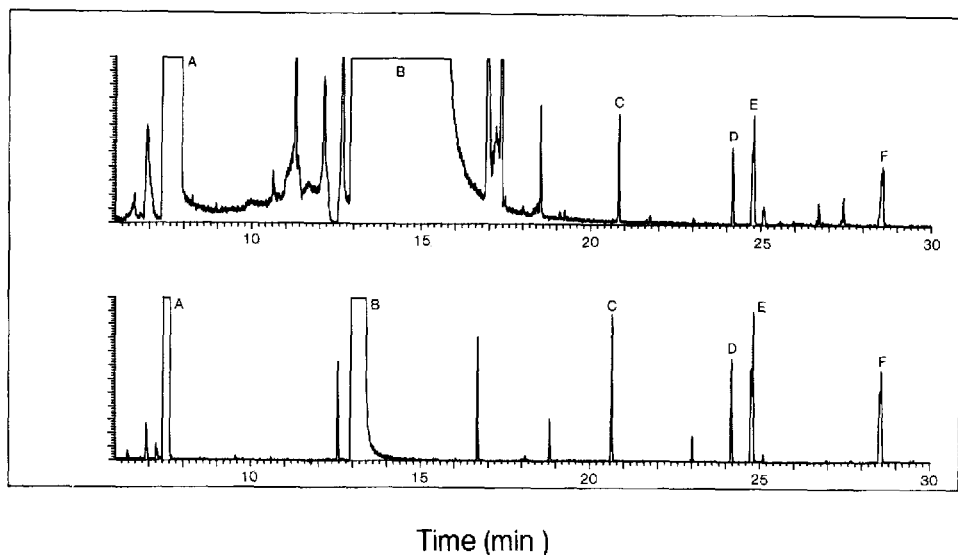


Fig. 1. Analysis of highly contaminated sample by two methods: methylene chloride extraction (upper) and magnesium hydroxide precipitation (lower). The unidentified peaks are impurities from the two major components. Peaks: A = dichlorobenzene, B = *p-tert.*butylphenol, C = [ $^2\text{H}_{10}$ ]anthracene, D = fluoranthene, E = pyrene and [ $^2\text{H}_{10}$ ]pyrene, F = [ $^2\text{H}_{11}$ ]chrysene and benzo[*a*]anthracene.

among those tested. A brief check on the analyte recovery when the magnesium ion concentration in the water was varied from 0.02 *M* to 0.50 *M*, yielded no difference in recovery as a function of  $\text{Mg}^{2+}$  concentration. The larger amounts of precipitate produced in the procedure at higher magnesium concentrations were cumbersome to work with, so a concentration close to that originally used by Faltusz was chosen for this work.

#### Complex matrices

Some preliminary attempts were made to assess the applicability of the magnesium hydroxide precipitation to the analytes contained in complex matrices.

Water from four test wells was analyzed by the hydroxide precipitation technique and by a methylene chloride extraction procedure similar to EPA Method 625<sup>4</sup>. Two of the wells proved to have very clean water, and two contained significant levels of phenols and camphor-related compounds, which were determined by GC-MS analyses. None contained PAHs or PCBs according to either extraction procedure. Thus the magnesium hydroxide precipitation yielded only surrogate recovery. The [ $^2\text{H}_{10}$ ]pyrene recovery was much lower than with distilled water samples, as expected; but recovery averaged only 12% for the well samples. [ $^2\text{H}_{12}$ ]Chrysene, which had been added as an additional surrogate for these samples, was recovered in higher, but widely varying percentages, ranging from 33% to 84%. The percent recovery was unrelated to the total concentration of organics observed in the samples. Further study of this recovery problem must be conducted.

A more encouraging result was obtained by analyzing a deliberately contam-

inated sample. A 2-l sample of distilled water was saturated with *o*-dichlorobenzene and *p*-*tert.*-butylphenol, then spiked with surrogate standards at 10 ppb each, and fluoranthene, pyrene and benzo[*a*]-anthracene at 4 ppb each. This would correspond to a real-world situation of monitoring water samples for PAHs if an uncontrolled spill occurred just prior to sampling. A 1-l volume of this contaminated water sample was concentrated by methylene chloride extraction and a second 1-l volume by magnesium hydroxide precipitation. The chromatograms obtained from these two procedures are shown in Fig. 1. The important point of comparison is the major reduction in the dichlorobenzene and *p*-*tert.*-butylphenol components without appreciable reduction in the PAHs when using the precipitation technique. The percent reduction in the two major components by the magnesium hydroxide precipitation (Fig. 1, lower trace) as compared with the methylene chloride extraction (Fig. 1, upper trace) cannot be calculated, owing to saturation of the MS detector by the large quantities of material, but the extent of the reduction is visually apparent. The percent recovery of the PAHs averaged 72% for the methylene chloride extraction and 67% for the precipitation technique. We intend to extend this study to the cases in which major contaminants coelute with PAHs, where the advantage of the precipitation technique could be demonstrated.

## CONCLUSION

Faltusz's method of selective concentration of analytes from aqueous solutions appears to be a viable approach for analyzing environmental samples when one is interested in higher molecular weight PAHs and PCBs. Further work must be done to delineate the situations of maximum utility of this method.

## REFERENCES

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