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INVESTIGATION OF A COMPREHENSIVE APPROACH FOR TRACE ANALYSIS OF DISSOLVED ORGANIC SUBSTANCES IN WATER

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SUMMARY

An isolation–fractionation scheme for the analysis of dissolved trace organic substances in natural and drinking waters was developed. The principle behind this scheme was to concentrate dissolved organic solutes and separate them into fractions by adsorption on different adsorbents (XAD-8 resin, AG-MP-50 cation-exchange resin and Carbopack B graphitized carbon black) under varying pH conditions. Test solutions containing 22 model organic substances and inorganic salts were used to monitor process performance. High-resolution gas chromatography was employed for the separation and quantitation of each model compound. Chemical derivatization procedures were established for several highly polar model compounds. Gas chromatography–mass spectrometry was used for the confirmation of compound identity in each separated fraction.

INTRODUCTION

During the past few years efforts to elucidate the specific nature of trace organic substances present in natural and drinking waters have spurred the development of analytical methods for the identification of hundreds or organic substances[1,2]. However, despite the success achieved and the great increase in our knowledge of water chemistry, it is widely recognized that only a small fraction of the organic constituents in water has so far been characterized. More precisely, the fraction that consists of soluble, polar and ionizable organic substances has not been analyzed as extensively as the purgeable and solvent-extractable fractions. The reasons for this lag in development are many, but some can be attributed to the inadequacy of the isolation methods and to the shortcomings of gas chromatography (GC) for separation and measurement. The traditional isolation methods used in analytical schemes are generally inefficient for trace levels of highly polar materials, and many of these materials are not directly amenable to separation by conventional

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GC techniques. Therefore, among the most recent advances in water analysis, one can recognize attempts to develop methods that permit the assessment of a broader range of trace organic substances. This implies that other isolation and concentration methods should be investigated for their performance towards several different classes of organic compounds. Moreover, as gas chromatography–mass spectrometry (GC–MS) still represents the most sensitive and reliable technique for the identification and quantitation of organic compounds in complex environmental mixtures, a continuing effort to develop chemical derivatization techniques for low-level organic compounds and of GC columns with greater inertness and temperature stability is warranted.

A "master analytical scheme" for trace organics in water has recently been proposed and is still under evaluation[3]. The isolation techniques investigated include the "purge-and-trap" (PT) method, batch liquid–liquid extraction (BLLE), ion-exchange adsorption and fractional or azeotropic distillation. High-resolution (HR) GC and HRGC–MS are recommended for final identification and quantitation. Junk and Richard[4] evaluated a modified Amberlite XAD-4 anion-exchange resin with macroreticular characteristics, and isolated and identified the anionic and the neutral constituents of different types of water using HRGC–MS. Derivatization, *e.g.*, with diazomethane, is required for the anionic compounds. Leenheer[5] proposed an analytical scheme whereby the dissolved organic carbon (DOC) compounds in natural and wastewaters can be separated into operationally defined fractions, based on their adsorption on different substrates (macroreticular and ion-exchange resins) under varying pH conditions. The recovery of input and size of the individual fraction have been evaluated in terms of total organic carbon (TOC) analysis. Recently, the fractionation scheme has been used to identify several polar organic solutes in oil-shale retort water[6]. In an attempt to analyze a large number of contaminants, XAD-4/8 columns, connected in series, together with an activated-carbon column, have been utilized for the isolation of organic solutes from 1000 l of tap water[7]. GC–MS analysis of the solvent eluent fractions has made possible the identification of several organic compounds at the ng/l level.

The need for a comprehensive approach towards the analysis of trace organic substances in water has led to the development of an isolation–fractionation scheme in which organic compounds with different functionalities and sorption parameters are first separated and concentrated in fractions with similar behavior, which permits subsequent instrumental analysis. Test solutions containing 22 model organic substances, which represent a wide range of chemical classes, functional group contents and molecular weights, were selected as the basis for evaluating the isolation–fractionation scheme. The use of glass capillary columns allows the direct analysis of 15 out of the 22 model substances, whereas chemical derivatization procedures have been investigated for the remainder of the compounds that are highly polar.

EXPERIMENTAL

Resin and carbon adsorbents

Amberlite XAD-8 was obtained from Rohm & Haas (Philadelphia, PA, U.S.A.) as an industrial-grade preparation in 20–50-mesh beads. The cation exchanger AG MP-50, 20–50 mesh, was suplied by Bio-Rad Labs. (Richmond, CA, U.S.A.). Clean-up, preparation procedures and storage of both resin types followed

the recommendations of Leenheer[5], except for XAD-8, which was Soxhlet-extracted an additional time with dichloromethane after acetone and hexane extractions. Glass columns (200 × 13 mm I.D.) with PTFE stopcocks were packed with approximately 15 ml of the resins. GCB Carbopack B, 100–120-mesh, was purchased from Supelco (Bellefonte, PA, U.S.A.). Acetone, dichloromethane and "organic-free" water (OFW) were used to wash the carbon, 200 mg of which were packed into a glass column (200 × 5 mm I.D.), as recommended by Bacaloni *et al.*[8].

Reagents

All of the model compounds were purchased from Aldrich (Milwaukee, WI, U.S.A.), Alfa Products (Danvers, MA, U.S.A.), Fluka (Hauppauge, NY, U.S.A.), and Analabs (North Haven, CT, U.S.A.), in purities ranging between 96% and 99%, as specified in the manufacturer's literature. Inorganic salts, hydrogen peroxide (50% solution) and mineral acids and bases were obtained from Fisher (Fair Lawn, NJ, U.S.A.). The organic solvents were all of "distilled-in-glass" grade, as supplied by Burdick & Jackson Labs. (Muskegon, MI, U.S.A.). Heptafluorobutyric anhydride and trifluoroacetic anhydride were obtained from PCR Research Chemicals (Gainesville, FL, U.S.A.); acetyl chloride was supplied by Mallinckrodt (Paris, KY, U.S.A.), Diazald by Aldrich and N-methylbistrifluoroacetamide and N,O-bis(trimethylsilyl)trifluoroacetamide by Pierce (Rockford, IL, U.S.A.). Humic acid was provided by the Health Effects Research Laboratory of the U.S. Environmental Protection Agency (Cincinnati, OH, U.S.A.), and had been prepared from a commercial-grade humic acid (Fluka). OFW was prepared by passing tap water through a series of treatment steps according to the following sequence: (i) Millipore 360 activated carbon cartridge (Continental Water Systems, El Paso, TX, U.S.A.); (ii) Millipore 300 deionizer cartridge; (iii) glass column (60 × 3 cm I.D.), packed with 50 g of 16–30-mesh virgin activated carbon Filtrasorb F-400 (Calgon, Pittsburgh, PA, U.S.A.); and (iv) two modified ultraviolet disinfection modules (Model H-50, Ultraviolet Technology, San Diego, CA, U.S.A.) in the presence of hydrogen peroxide. The finished water had an average TOC content of 27 ± 15 ppb* and a hydrogen peroxide residue of < 100 ppb[9].

Instrumentation

A Hewlett-Packard 5830-A gas chromatograph equipped with a split–splitless capillary injection system and a flame-ionization detector was employed for the quantitation of each model compound. A Shimadzu GDM-1 glass-drawing machine was used to draw glass capillaries (*ca.* 100 m × 0.3 mm I.D.) from soft-glass tubing (121 × 0.6 cm I.D.; Kimble, Toledo, OH, U.S.A.), which had been washed with a detergent solution and rinsed with OFW and acetone. The glass capillaries were subsequently leached and deactivated, according to the procedure proposed by Grob[10]. These capillaries (*ca.* 30 m) were then coated by the static method[11] with SE-54 or SE-52 silicone gum phases (*ca.* film thickness 0.2 μm). The GC conditions were as follows: injection volume, 1 μl; injection mode, splitless; oven temperature, 40°C (2 min), then increased to 290°C at 4 or 15°C/min. Hexamethylbenzene (HMB) was used as an internal standard for the evaluation of both relative retention time and quantitative data.

* Throughout this article, the American billion (10^9) is meant.

Analytical confirmation of the model compounds and tentative identification of organic impurities introduced during the handling of the test solution through the fractionation scheme were accomplished by means of a Finnigan 4023 mass spectrometer interfaced with a Hewlett-Packard 5830-A gas chromatograph, as described elsewhere[12]. Fused-silica tubing served as the sample transfer line between the column effluent and the ionization source. The MS conditions were as follows: ionization mode, electron impact; electron multiplier, 1500 V; electron energy, 70 eV; emission current, 0.5 mA; mass range, 45–450 a.m.u.; and scan rate, 0.95 sec/decade. The GC conditions were identical with those employed in the GC analysis. The mass spectrometer was tuned with perfluorotributylamine, and a solution of decafluorotriphenylphosphine (1 μl) was subsequently injected on to the chromatograph to verify the tuning thus obtained. 5-Chlorouracil was analyzed on a Perkin-Elmer Series 3 high-pressure liquid chromatograph equipped with a Rheodyne injection system, an LC65-T variable-wavelength UV–visible detector and a LiChrosorb C_{18} reversed-phase column (Altex, Berkeley, CA, U.S.A.). The HPLC conditions were as follows: eluent, 10% aqueone methanol, isocratic; flow-rate, 1 ml/min; detection, UV (254 nm).

Fractionation scheme and analytical procedures

Stock solutions of quinaldic acid, glycine and glucose (500 mg/l) were prepared with OFW, 5-chlorouracil with 2 *N* ammonia solution and all of the other compounds with methanol. Humic acid was first dissolved in dilute sodium hydroxide solution (0.02 *N*). The test solution (Table I) was prepared by adding salts and by diluting the required volumes of stock solutions with OFW.

TABLE I

MODEL SUBSTANCES AND COMPOSITION OF TEST SOLUTIONS

Compound	*Concentration*	*Compound*	*Concentration*
Trimesic acid	100 μg/l	1-Chlorododecane	10 μg/l
Stearic acid	100 μg/l	Biphenyl	100 μg/l
Quinaldic acid	100 μg/l	Phenanthrene	2 μg/l
Humic acid	2000 μg/l	Isophorone	100 μg/l
Glycine	100 μg/l	Anthraquinone	100 μg/l
Furfural	100 μg/l	Methyl isobutyl ketone (MIBK)	100 μg/l
Quinoline	100 μg/l	2,4-Dichlorophenol	100 μg/l
Caffeine	100 μg/l	2,6-Di-*tert.*-butyl-4-methylphenol (butylated hydroxytoluene, BHT)	100 μg/l
5-Chlorouracil	100 μg/l	Chloroform	100 μg/l
Glucose	100 μg/l	$CaSO_4$	210 mg/l
2,4′-Dichlorobiphenyl	100 μg/l	$CaCl_2 \cdot 2H_2O$	47 mg/l
2,2′,5,5′-Tetrachlorobiphenyl	10 μg/l	$NaHCO_3$	70 mg/l
Bis(2-ethylhexyl)phthalate	100 μg/l		

Solvents of increasing polarity (hexane → acetone → OFW) were spiked with phenanthrene, 1-chlorododecane, 2,4′-dichlorobiphenyl and 2,2′,5,5′-tetrachlorobiphenyl by gradual exposure to them and intermediate drying with nitrogen and sonication. The test solution (500 ml) was acidified to pH 2 and passed through an XAD-8

column at a flow-rate of <30 column volumes per hour. The "hydrophobic acid" fraction of the proposed isolation fractionation scheme (see Fig. 1) was desorbed with a total volume of 20 ml of 0.1 and 0.01 *N* sodium hydroxide solution. The XAD-8 effluent was adjusted to pH 10 and processed through the same XAD-8 column at an identical flow-rate. The "hydrophobic base" fraction was eluted with a total volume of 20 ml of 0.1 and 0.01 *N* hydrochloric acid. The XAD-8 resin was then removed from the column and the "hydrophobic neutral" fraction was desorbed with 100 ml of dichloromethane in a separating funnel. The effluent from the XAD-8 column was again adjusted to pH 2 and passed through an AG MP-50 column at the same flow-rate. A total volume of 20 ml of ammonia solution was used to elute the "hydrophilic base" fraction. A test solution with the following composition was used to evaluate Carbopack B GCB: inorganic salts (70 ppm of $NaHCO_3$, 210 ppm of $CaSO_4$, 47 ppm of $CaCl_2 \cdot 2H_2O$); organic compounds (quinoline, 2,4-dichlorophenol, isophorone, 1-chlorododecane, 2,4′-dichlorobiphenyl, anthraquinone, 2,2′,5,5′-tetrachlorobiphenyl, bis(2-ethylhexyl)phthalate, phenanthrene, caffeine, furfural, methyl isobutyl ketone) at the 100 ppb level. The flow-rate was maintained at 4 ml/min by means of a metering pump. The adsorbed organic compounds were eluted directly from the column with 50 ml of dichloromethane. The "hydrophobic neutral" fraction was concentrated to approximately 5 ml in a Kuderna–Danish apparatus and adjusted to 1 ml under a stream of nitrogen. After addition of the internal standard (HMB), it

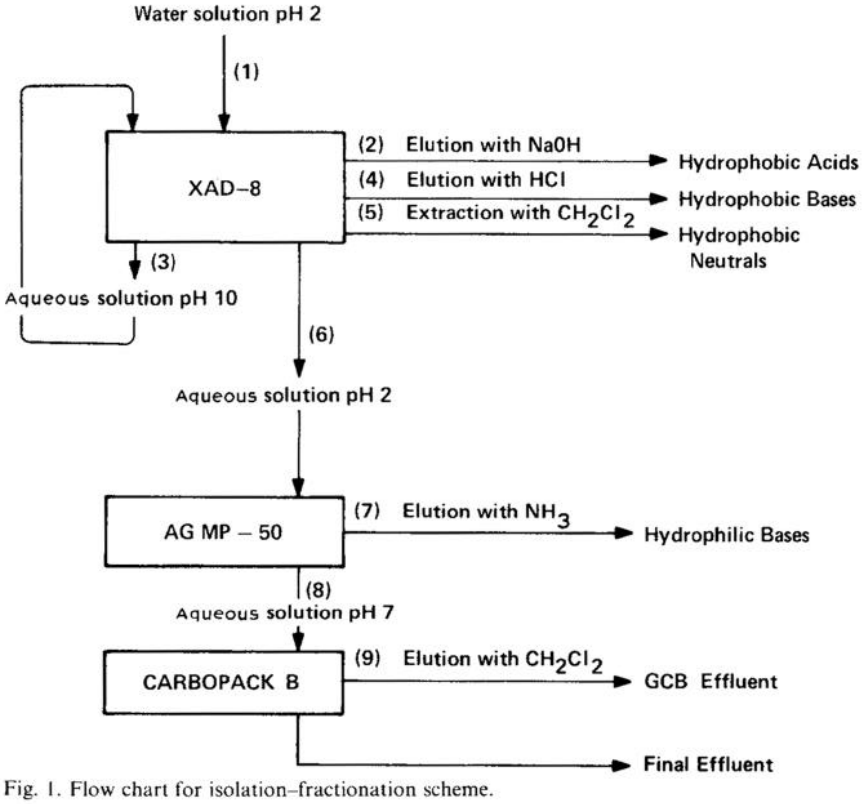

Fig. 1. Flow chart for isolation–fractionation scheme.

was submitted to instrumental analysis. A 1–2-ml volume of the "hydrophobic acid" fraction was spiked with surrogates (undecanoic acid, 3-quinolinecarboxylic acid), dried under a gentle stream of nitrogen, adjusted to pH 2, dried again and redissolved in 1 ml of diethyl ether. The solution was then methylated with gaseous diazomethane[13]. Finally, the solution was adjusted to 100 μl, spiked with HMB and analyzed by GC. The "hydrophobic base" fraction was solvent extracted with three aliquots of dichloromethane (100:50:50) after adjusting the solution pH to 10. The extract was concentrated in a Kuderna–Danish apparatus and under a stream of nitrogen and then analyzed by GC. A 1–2-ml volume of "hydrophilic base" fraction was first spiked with a surrogate (L-alanine), dried under a stream of nitrogen, acidified with hydrochloric acid and derivatized according to the procedures described elsewhere[14]. The final solution was adjusted to 100 μl with addition of HMB and analyzed by GC. The dichloromethane extract from the carbon column was adjusted to 1 ml and analyzed by GC. Humic acid was quantitated in the "hydrophobic acid" fraction by spectrophotometric analysis at 430 nm at the same pH as the standard solutions used for instrument calibration.

RESULTS AND DISCUSSION

Attempts were made to perform qualitative and quantitative analyses by GC and GC–MS. Therefore, much emphasis was placed on the selection of GC columns that would allow the direct analysis of the majority of the model organic substances (see Table I). For those which could not be analyzed by GC, the investigation of methods for the preparation of "volatile" derivatives at trace levels was pursued. Following recent developments in glass capillary technology, the "persilylation" deactivation method[10] was adopted to prepare non-polar glass capillary columns (SE-54 and SE-52 silicone gum phases). A mixture of HMDS + DPTMDS in pentane (1:1:2) was used for the "persilylation" treatment. Fourteen out of the 22 model substances appeared to be satisfactorily eluted, as shown in Fig. 2. Chloroform, which was eluted with the solvent front (dichloromethane), was analyzed separately on the same column together with the purgeable priority pollutants by the purge-and-trap method[12].

Trimesic acid, stearic acid, quinaldic acid and glycine required chemical derivatization. Gaseous diazomethane[13] was found to be satisfactory for the methylation of acids, as shown in Fig. 3. Treatment with diazomethane until the solution was yellow did not appear to improve the yield of esters. On the contrary, it actually contributed to a drastic increase in the amount of contaminants. An optimum "bubbling period" of 10–20 sec with a nirogen flow-rate of *ca.* 40–60 ml/min was established for solutions containing up to 200 μg/ml of acids. Glycine was converted into the N(O)-heptafluorobutyric isoamyl ester derivative[14]. However, our attempts to derivatize glucose and 5-chlorouracil failed to result in adequate reproducibility. A high-performance liquid chromatographic method was preferred for 5-chlorouracil, and glucose was not monitored in this study.

Previous investigations by Leenheer[5] and Leenheer and Huffman[15] were closely followed for the evaluation of the isolation scheme. A 500-ml volume of test solution (see Table I) was used throughout. The presence of inorganic salts caused precipitates to occur when the pH of the test solution was increased to 10. In order to

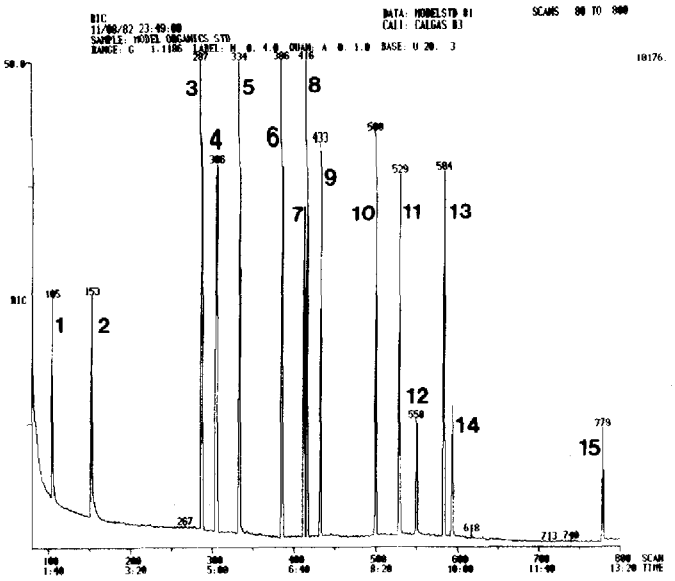

Fig. 2. Reconstructed ion chromatogram (RIC) of selected model compounds. Approximately 20 ng/μl (1 μl splitless); temperature, 40°C (3 min), increased to 290°C at 15°C/min. Peaks: 1 = methyl isobutyl ketone; 2 = furfural; 3 = isophorone; 4 = 2,4-dichlorophenol; 5 = quinoline; 6 = biphenyl; 7 = 1-chlorododecane; 8 = hexamethylbenzene (I.S.); 9 = 2,6-di-*tert*.-butyl-4-methylphenol (BHT); 10 = phenanthrene; 11 = 2,4′-dichlorobiphenyl; 12 = caffeine; 13 = 2,2′,5,5′-tetrachlorobiphenyl; 14 = anthraquinone; 15 = bis(2-ethylhexyl)phthalate.

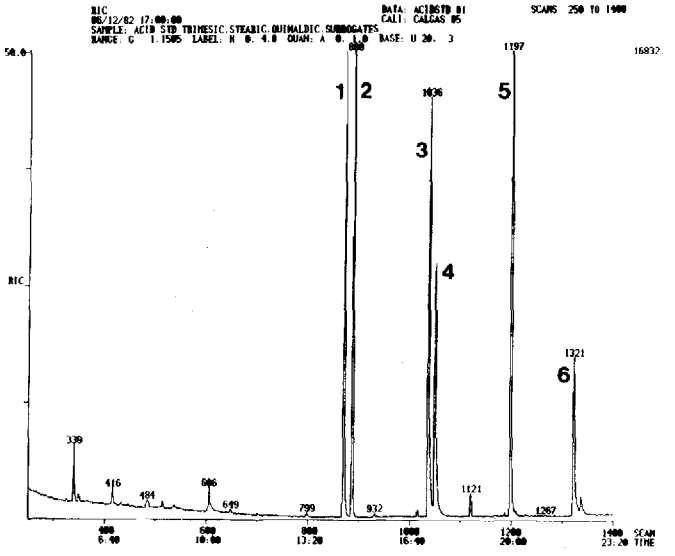

Fig. 3. RIC of model organic acid methyl esters. Approximately 20 ng/μl (1 μl splitless); temperature, 40°C (2 min), increased to 290°C at 10°C/min. Peaks: 1 = undecanoic acid (surrogate); 2 = hexamethylbenzene (I.S.); 3 = 3-quinolinecarboxylic acid (surrogate); 4 = quinaldic acid; 5 = trimesic acid; 6 = stearic acid.

overcome this problem, the sequence of adsorption on XAD-8 was reversed so that the test solution was first adjusted to pH 2 to adsorb the hydrophobic acids and "neutrals" and then increased to pH 10 to adsorb the "hydrophobic bases" (see Fig. 1). The test solution eluent was then adjusted to pH 2 and processed through a AG MP-50 column to isolate the "hydrophilic" base fraction (see Fig. 1). Six repetitive experiments were conducted under these conditions. The results, expressed as mean recoveries, are given in Table II. A mass balance determination was attempted for the "solvent-extractable" model substances.

TABLE II

AVERAGE RECOVERY OF MODEL COMPOUNDS FROM RESIN

OA = hydrophobic acid (XAD-8); OB = hydrophobic base (XAD-8); ON = hydrophobic neutral (XAD-8); IB = hydrophilic base (AG-MP-50); EF = final effluent (solvent extraction). $n = 6$.

Compound	*Mean recovery ± S.D. (%)*				
	OA	*OB*	*ON*	*IB*	*EF*
Stearic acid	32.4*				
Trimesic acid	41.8**				
2,4-Dichlorophenol				13.8 ± 11.1	23.6 ± 8.9
Quinaldic acid				NQ§	
Isophorone			80.8 ± 18.5		
Biphenyl			82.7 ± 5.8		
1-Chlorododecane			33.8 ± 6.8		
BHT			50.2 ± 8.6		
2,4′-Dichlorobiphenyl			74.2 ± 5.3		
2,2′,5,5-Tetrachloro-biphenyl			44.4 ± 22.1		
Anthraquinone			58.0 ± 13.3		
Phenanthrene			77.8 ± 13.3		
Bis(2-ethylhexyl)-phthalate	1.8*** ± 1.5		37.6 ± 7.9	2.3**	9.2 ± 4.2
Furfural					38.3 ± 38.1
Quinoline		22.1 ± 10.6	5.2 ± 1.9		
5-Chlorouracil				NQ	
Caffeine			16.4 ± 5.4	3.7**	25.2 ± 6.2
Glycine				56.5*** ± 19.6	
Humic acids	88.1 ± 6.5				
Chloroform	–				
MIBK			NQ		

* 3 values.
** 2 values.
*** 4 values.
§ NQ = Found but not quantitated.

Malcolm *et al.*[16] and Thurman *et al.*[17] observed that the adsorption of solutes on XAD-8 macroreticular resins could be predicted by means of a linear correlation between log (capacity factor) and the inverse of log (water solubility) of each solute. This correlation was confirmed under our experimental conditions, except with 2,4-dichlorophenol, which was expected in the "hydrophobic acid" fraction. The relative-

ly poor recovery of 1-chlorododecane and tetrachlorobiphenyl may attributable to their poor solubilities in water and subsequent losses by adsorption on the reservoir and tube walls, although precautions were taken during the preparation of the test solutions (see Experimental). MIBK, and 5-chlorouracil and quinaldic acid were recovered in only very small amounts in the "hydrophobic neutral" and "hydrophilic base" fractions, respectively. Loss through volatilization is suspected to be the major reason why the detection of chloroform in the "hydrophobic neutral" fraction was prevented. Fourteen out of the 22 model substances were found to give average recoveries between 30 and 90%.

An examination of the flame-ionization traces revealed that the isolated fractions showed the presence of organics other than the selected spike compounds. The "hydrophobic neutral" fraction, in particular, appeared to contribute the most contaminants. However, except for the two or three major contaminants the abundance of which was comparable to that of the model compounds, the remainder was relatively small. At least one impurity was tentatively identified by GC–MS as the oxidation product of one of the selected model compounds (BHT).

The presence of appreciable amounts of several model substances in the final effluent led us to consider using a carbonaceous adsorbent in the fractionation scheme in an attempt to recover those model compounds retained either partially or not at all by the resins. Carbopack B GCB[8] was investigated with test solutions containing the salts and the selected model compounds under neutral pH conditions. The results are reported in Table III. Phenanthrene, quinoline, caffeine and 2,4-dichlorophenol, in particular, appeared to be efficiently recovered.

It is widely recognized that no single isolation–concentration method is suitable for the comprehensive characterization of trace organic compounds in natural and drinking water. The use of schemes in which several methods are arranged in a sequential and logical order is one of the alternatives. From consideration of the overall results of this study, the proposed isolation–fractionation scheme (Fig. 1) appears to allow the identification and quantitation of a wide range of organic sub-

TABLE III

RECOVERY OF MODEL COMPOUNDS ON CARBOPACK B

Compound	*Desorbed from GCB (%)*	*Extracted from water after GCB (%)*
2,4-Dichlorophenol	115.2	NF*
Quinoline	97.5	NF
Isophorone	16.3	92.4
1-Chlorododecane	51.2	NF
2,4′-Dichlorobiphenyl	48.6	9.9
2,2′,5,5′-Tetrachlorobiphenyl	54.1	3.7
Antrhraquinone	92.1	NF
Bis(2-ethylhexyl)phthalate	51.1	64.3
Phenanthrene	114.0	NF
Caffeine	92.1	NF
Furfural	NF	26.0
MIBK	6.7	65.5

* NF = Not found.

stances. However, as several other organic classes still cannot be efficiently recovered, the investigation of other isolation and concentration methods as an integral part of the scheme may be suggested. Purge-and-trap and/or closed-loop stripping[18] analyses may be used for the highly volatile compounds (*e.g.*, chloroform), whereas freeze-drying and/or reverse-osmosis methods may be utilized for the highly water-soluble compounds (*e.g.*, furfural, glucose).

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