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Screening of Anthropogenic Compounds in Polluted Sediments and Soils by Flash Evaporation/Pyrolysis Gas Chromatography–Mass Spectrometry

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The use of flash evaporation and pyrolysis gas chromatography–mass spectrometry as a fast screening procedure for anthropogenic substances in environmental samples is demonstrated by the analysis of polluted soil and sediment samples. Polycyclic aromatic hydrocarbons, haloorganics, aliphatic hydrocarbons, heteroaromatics, elemental sulfur, cyanides, and pyrolysis products of synthetic polymers are among the anthropogenic substances that can be readily detected by this method in one analysis. Elimination of wet chemical sample preparation enables a complete analysis to be performed and data to be quickly analyzed. The detection limits are in the low part-per-million range using mass spectrometric detection. Alternatively, detection of compounds can be achieved by all common gas chromatography detectors (flame ionization detector, electron capture detector, and flame photometric detector), and detection limits are determined by the method of detection employed.

Qualitative and quantitative analysis of pollutants in soils and sediments is an expensive and time-consuming task. Moreover, each suite of pollutants normally requires other analytical methods and techniques, so a large number of separate analyses have to be performed before a more or less complete picture of the pollution pattern is obtained.

Recently two different fast screening procedures to monitor organic contaminants in the environment have been reported (*1*, *2*). Hunt et al. (*1*) used a triple quadrupole mass spectrometer configuration to analyze various series of contaminants with few wet chemical and chromatographic separation steps. McMurtrey et al. (*2*) reported a fast procedure that also omits the usual extraction and cleanup steps to monitor the presence of polychlorinated biphenyl contaminants in a sediment using a pyrolysis gas chromatography–mass spectrometric technique.

Over the last years we have used similar pyrolysis techniques, in particular Curie point flash pyrolysis mass spectrometry (Py MS) and Curie point flash pyrolysis gas chromatography–mass spectrometry (Py GC–MS), to chemically characterize biopolymers such as lignins, polysaccharides, peptides, and "geopolymers" like humic substances, peats, kerogens, and coal (*3–10*). During these studies it became clear that nonpolymeric compounds which are reasonably volatile at elevated temperatures do not fragment on the pyrolysis wire but simply evaporate from it (*10–12*). Therefore, it appeared possible that the organic matter present in sediments and soils can be characterized and identified very rapidly without any pretreatment by direct evaporation/pyrolysis (Ev/Py) of whole samples. This flash evaporation/pyrolysis method followed by on-line separation and identification techniques is thought to be applicable to monitor the volatile and nonvolatile (polymeric) contaminants in environmental samples such as soils, sediments, and tissues.

In this paper we demonstrate the usefulness of Ev/Py GC–MS as a screening technique for anthropogenic substances in two polluted environmental samples without pretreatment. The samples were also extracted, and some compounds present in the extract were quantitated to establish the limits of detection of the screening approach.

EXPERIMENTAL SECTION

Samples. Polluted soil (1 m^2) was removed with a spade from the top 10 cm from a site in the northwestern part of the Netherlands and thoroughly mixed. Approximately 2 kg of this wet soil was placed in a stainless-steel jar and brought to the lab. Samples were further homogenized by grinding before analysis.

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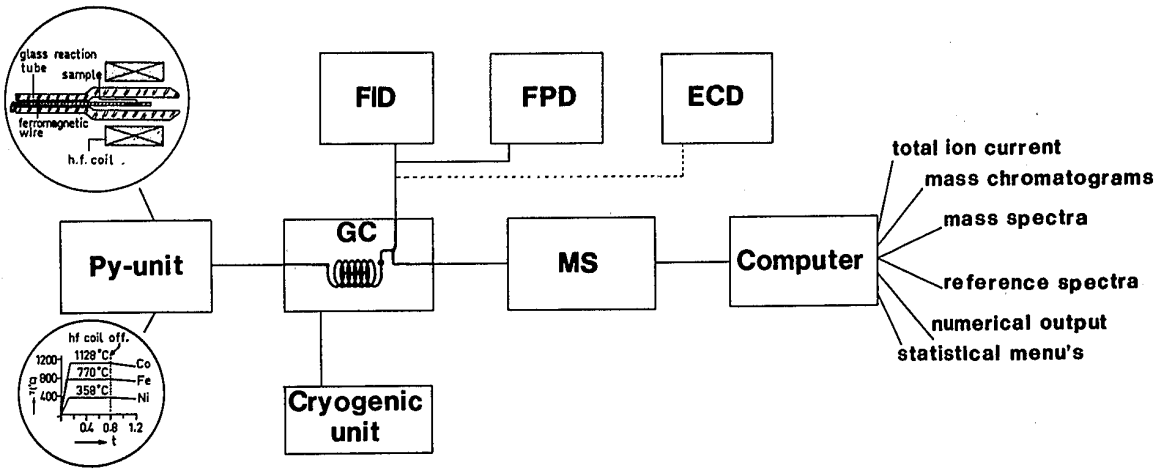

Figure 1. Instrumental setup for screening analysis by evaporation/pyrolysis gas chromatography.

A surface sediment (500 g wet weight; water depth ca. 4.5 m) from a polluted harbor in the southwestern part of the Netherlands was taken by use of a Hydrobios sludge sampler (Ekman-Birge). The upper 10 cm was collected and stored in polyethene containers. An aliquot of 50 g of wet sludge was homogenized by sonication.

Evaporation/Pyrolysis Gas Chromatography–Mass Spectrometry. Aliquots of the homogenized samples were suspended in methanol (5 mg/mL). One or two drops, corresponding to approximately 200 μg of sample, were applied to the pyrolysis wire. The Curie temperature of the pyrolysis wire was 510 °C. Ev/Py GC–MS analyses were performed on a Varian MAT 44 S intrument connected with a PDP 11/45 computer. The pyrolysis reactor, previously described by van de Meent et al. (*5*), was directly mounted on the detector block of the Varian 3700 gas chromatograph. The temperature of the detector block was 300 °C. Separation was performed on a fused silica capillary column coated with CP-SIL 5 (25 m, 0.22 mm i.d.) using helium as a carrier gas. The temperature was programmed from 0 °C, by using a cryogenic unit, to 275 °C at a rate of 3 °C/min. Mass spectrometric detection was carried out with 80-eV EI ionization, ion source temperature 250 °C, cycle time 1.5 s, and mass range 50–550 amu. Data handling was carried out on a PDP 11/45 computer with software developed at Delft University of Technology. Blank determinations are routinely carried out by using unloaded pyrolysis wires. Replicate Py GC analyses indicated a reproducibility of 5–10%, a reproducibility common for this method as reported previously (*11*).

Quantitation Studies. The soil sample (13.5 g) was ultrasonically extracted 11 times with 10 mL of CH_2Cl_2/MeOH (1:1). After addition of 35 mL of distilled water the CH_2Cl_2 layer was obtained and concentrated to 1 mL. Isolation of the polycyclic aromatic hydrocarbons (PAH) from this extract was performed according to Giger and Schaffner (*13*). The PAH fraction was further chromatographed on a silica column using 25 mL of toluene as an eluent. After addition of 75 mL of methanol, the purified PAH fraction was concentrated by means of a rotatory evaporator.

The wet sediment sample (4.74 g) was serially extracted with 25 mL of MeOH/CH_2Cl_2 (3:1), 25 mL of MeOH/CH_2Cl_2 (1:1), 25 mL of MeOH/CH_2Cl_2 (1:3), and two additional times with 25 mL of CH_2Cl_2 using ultrasonication and centrifugation. The CH_2Cl_2 used was spiked with 1-chlorododecane (806 μg/L). All supernatants were combined in a separatory funnel, and sufficient distilled water was added to achieve phase separation. The CH_2Cl_2 layer was separated, washed with distilled water, dried with $MgSO_4$, and, after filtration, concentrated to a small volume.

Gas chromatography of the PAH fraction isolated from the soil sample was carried out on a Carlo Erba 4160 instrument equipped with a flame ionization detector and an on-column injector (*14*, *15*) provided with a special cooling system (*16*). A glass capillary column (20 m, 0.32 mm i.d.) coated with SE-52 was used, and helium was used as a carrier gas (p_i = 0.5 atm). Samples were injected at 80 °C. The oven temperature was programmed from 130 °C to 330 °C at 4 °C/min after elution of the solvent.

Gas chromatography of the sediment extract was carried out on a Varian 3700 instrument equipped with a flame ionization detector and a fused silica capillary column (25 m, 0.25 mm i.d.) coated with CP-SIL 5. Samples were injected spitlessly, and nitrogen was used as a carrier gas. The oven temperature was programmed from 40 °C (5 min) to 300 °C at 5 °C/min.

Both GC instruments were connected with a PDP 11/45 computer via an analog-to-digital converter. The peak areas were calculated from the digitalized chromatographic data by means of software developed at Delft University of Technology.

The PAH in the soil sample were quantitated by using an external standard of anthracene. Pentadecane in the sediment sample was quantitated by using the internal standard 1-chlorododecane.

Analytical Approach. The instrumental setup for the screening analysis is shown in a very schematic way in Figure 1. A ferromagnetic wire with a selected Curie temperature (see insert) is coated with a methanol suspension of the soil or sediment sample to be analyzed and allowed to dry in the air. The coated wire is inserted into a Pyrex tube and positioned in the pyrolysis unit between the high-frequency coils. Powering of this high-frequency coil causes a rapid temperature rise of the wire containing the sample to the Curie temperature within 0.1–0.2 s (see Figure 1). The compounds generated, either by pyrolysis or evaporation, are fed to a capillary column (*4*) that is cooled by means of a cryogenic device where they are trapped on the liquid phase of the capillary column. These compounds are then separated on the capillary column, and the individual compounds can be monitored by common flame ionization detectors (FID), flame photometric detectors (FPD), or electron capture detectors (ECD), or they can be monitored and identified by a mass spectrometer (GC–MS mode). The choice of detector(s) is based on the screening requirements. The FID and the mass spectrometer have a very broad application. The ECD can be used in the selective screening of organohalogens and nitrated compounds, while the FPD is applicable for selective screening of sulfur and phosphorus compounds.

It is clear that the sensitivity of the method is partially based on the characteristics of the detector used. The GC–MS mode adds another dimension to the data that can be readily exploited by data handling techniques such as mass chromatography with which patterns of many groups of pollutants can be recognized even if these are present in trace amounts within a very complex mixture.

RESULTS

Soil Sample. Figure 2 shows the total ion current trace and a number of appropriate mass chromatograms obtained from the Ev/Py GC–MS analysis of the polluted soil sample. The upper trace represents a part of the total ion current (TIC) magnified 8 times. The peak numbers correspond with the numbers mentioned in Table I and refer to the identified compounds. The identification was based on manual comparison of mass spectra and relative GC retention times with

Table I. Identified Evaporation and Pyrolysis Products of the Soil Sample

peak no.	compd	peak no.	compd	peak no.	compd
1	H_2S, CO_2, CO	28	biphenyl	51	methylbenzofuran
2	dicyanogen	29	unknown organic sulfur compound (m/z 67, 100, 164)	52	methylbenzofuran
3	hydrogen cyanide			53	methylbenzofuran
4	ethylbenzene	30	1-ethylnaphthalene + dimethylbenzo[*b*]thiophene	54	α-1-phenyl ethyl ether (tentative)
5	styrene				
6	α-methylstyrene	31	2,6- and/or 2,7-dimethylnaphthalene	55	2-methylfluorene
7	3-methylstyrene	32	1,3-dimethylnaphthalene	56	1-methylfluorene
8	4-methylstyrene	33	1,7- and/or 1,6-dimethylnaphthalene	57	C_2-benzofuran
9	indene	34	2,3- and/or 1,4-dimethylnaphthalene	58	9-fluorenone
10	α,3-dimethylstyrene	35	acenaphthalene	59	C_2-benzofuran
11	3-ethylstyrene	36	1,2-dimethylnaphthalene	60	C_2-benzofuran
12	α,4-dimethylstyrene	37	(C_1-phenyl)ethyl *tert*-butyl ether (tentative)	61	dibenzothiophene
13	3,5-dimethylstyrene			62	C_2-benzofuran
14	α,2- or 2,5- or 2,4-dimethylstyrene	38	(C_1-phenyl)ethyl *tert*-butyl ether (tentative)	63	phenanthrene
				64	anthracene
15	phenyl ethyl ether	39	acenaphthene + 4-methylbiphenyl	65	bis(1-phenylethyl) thioether (tentative)
16	2,3-dimethylstyrene	40	3-methylbiphenyl		
17	3,4-dimethylstyrene	41	dibenzofuran	66	elemental sulfur
18	methylidene	42	C_3-naphthalene	67	fluoranthene
19	isomeric methylidenes	43	C_3-naphthalene	68	pyrene
20	napthalene	44	C_3-naphthalene	69	isomeric naphthobenzofurans
21	benzo[*b*]thiophene	45	C_3-naphthalene	70	benzo[*c*]phenanthrene
22	methylbenzo[*b*]thiophene	46	C_3-naphthalene	71	benzo[*a*]anthracene
23	2-methylnaphthalene	47	fluorene	72	chrysene + triphenylene
24	methylbenzo[*b*]thiophene	48	C_3-naphthalene + dimethylbiphenyl	73	benzo[*a*]pyrene + benzo[*e*]pyrene
25	methylbenzo[*b*]thiophene	49	dimethylbiphenyl		
26	1-methylnaphthalene	50	unknown organic sulfur compound (m/z 67, 100, 196)		
27	1-phenylethyl *tert*-butyl ether (tentative)				

Table II. Identified Evaporation and Pyrolysis Products of the Sediment Sample

peak no.	compd	peak no.	compd
1	styrene	15	phenanthrene
2	*n*-undecane	16	anthracene
3	methylidene	17	*n*-octadecane
4	naphthalene	18	2,6,10,14-tetramethylhexadecane (phytane)
5	*n*-dodecane		
6	2-methylnaphthalene	19	*n*-nonadecane
		20	*n*-hexadecanoic acid
7	*n*-tridecane	21	*n*-eicosane
8	*n*-tetradecane	22	*n*-heneicosane
9	2,6,10-trimethyltridecane	23	*n*-docosane
		24	*n*-tricosane
10	*n*-pentadecane	25	*n*-tetracosane
11	*n*-hexadecane	26	*n*-pentacosane
12	2,6,10-trimethylpentadecane (norpristane)	27	*n*-hexacosane
		28	*n*-heptacosane
		29	*n*-octacosane
13	*n*-heptadecane	30	*n*-nonacosane
14	2,6,10,14-tetramethylpentadecane (pristane)		

Table III. Concentration[a] of Several Contaminants in the Soil and Sediment Samples

compd	concn, ppm
soil	
phenanthrene	506
anthracene	144
fluoranthene	340
pyrene	208
benz[*a*]anthracene	79
chrysene/triphenylene	103
benzo[*e*]pyrene	35
benzo[*a*]pyrene	38
perylene	12
sediment	
pentadecane	300

[a] Based on wet weight.

literature data (*17*, *18*) and with data of standards available. In some cases unknown compounds were tentatively identified on the basis of a priori interpretation of their mass spectra (labeled "tentative" in Table I).

Because no pretreatment of the samples was carried out, the peaks present in the TIC trace reflect components generated by pyrolysis of primary sample compounds ("real pyrolysis products") and components that are present as such in the sample and simply evaporate ("free products"). If desired these two types of products may be differentiated by using wires with a Curie temperature of 358 °C (*12*). It was demonstrated in separate analyses (not shown here) that most compounds were not generated by pyrolysis but were present as such in the sample and "thermally extracted". Compounds 1–8 and 10–17, 27, 37, 38, 54, and 65 were only present in Py GC analyses carried out with wires having a Curie point of 510 °C and therefore are considered to be real pyrolysis products.

Sediment Sample. Figure 3 shows the total ion current trace and some mass chromatograms obtained by Ev/Py GC–MS analysis of the polluted sediment sample. All compounds present in this complex mixture were not listed. A selection was made to exemplify several aspects of the screening approach. The peak numbers correspond with the numbers in Table II. Identifications were based on the same criteria as mentioned above. Although several components were shown to be real pyrolysis products, all the compounds we will discuss hereafter are present as such in the sample and resulted from simple thermal extraction from the wire. This was shown in separate analyses using ferromagnetic wires with a Curie temperature of 358 °C.

Quantitative Aspects. To obtain some insight into the sensitivity of this screening method, additional analyses were carried out. The amounts of 10 polycyclic aromatic hydrocarbons in the soil sample were determined according to Giger and Schaffner (*13*). Table III lists the PAH selected and their quantities in the soil sample and also mentions the quantity of pentadecane present in the sediment sample.

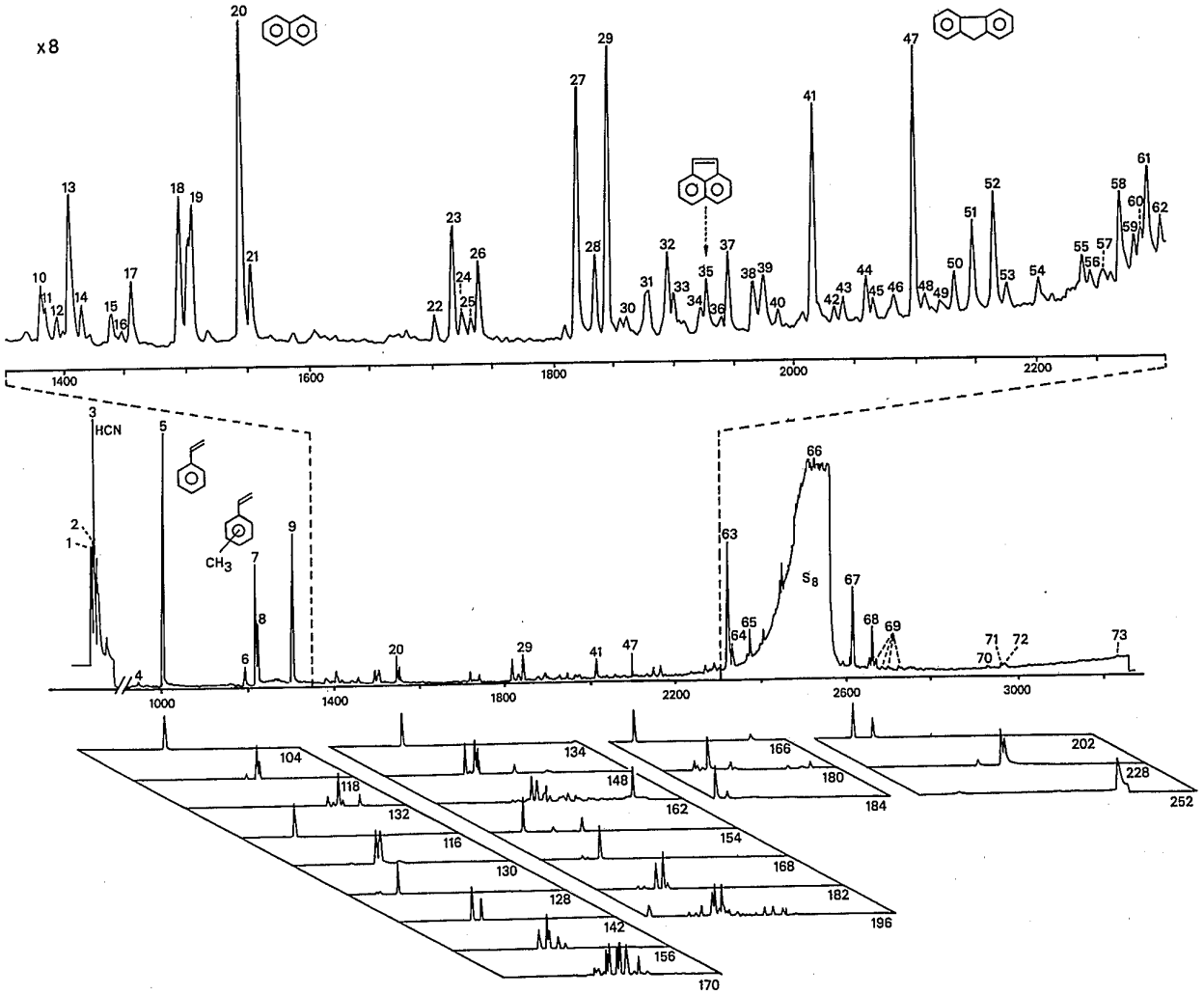

Figure 2. TIC of Ev/Py GC–MS analysis of the polluted soil sample. The upper trace represents a part of the TIC magnified 8 times. The number in the mass chromatograms represent the m/z values indicative of the following classes of compounds: m/z 104, 118, 132 (C_0–C_2 styrenes); m/z 116, 130 (C_0–C_1 indenes); m/z 128, 142, 156, 170 (C_0–C_3 naphthalenes); m/z 134, 148, 162 (C_0–C_2 benzo[*b*]thiophenes), m/z 154 (biphenyl m/z 116, 130 (C_0–C_1 indenes); m/z 128, 142, 156, 170 (C_0–C_3 naphthalenes); m/z 134, 148, 162 (C_0–C_2 benzo[*b*]thiophenes), m/z 154 (biphenyl and acenaphtene); m/z 168, 182, 196 (C_1–C_2 biphenyls and C_0–C_2 dibenzofurans); m/z 166, 180 (C_0–C_1 fluorenes and 9-fluorenone); m/z 184 (dibenzothiophene); m/z 202 (fluoranthene and pyrene); m/z 228 (benzo[*c*]phenanthrene, benz[*a*]anthracene, chrysene, and triphenylene); m/z 252 (benzo[*e*]pyrene and benzo[*a*]pyrene). The *x* axes of the mass chromatograms correspond exactly with the appropriate parts of the TIC *x* axis directly above them (e.g., the major peak in the mass chromatogram of m/z 168 corresponds with peak 41 in the total ion current trace).

No attempts were made to determine the error in the numbers mentioned in Table III. In our view this is not necessary at this stage, since our quantitative goal was only to roughly indicate the limits of detection using this screening approach.

DISCUSSION

Soil Sample. Four different suites of anthropogenic compounds were discriminated by Ev/Py GC–MS: HCN and dicyanogen (pyrolysis products), elemental sulfur (present as such), PAH (mainly unsubstituted, present as such), and styrenes and phenyl ethers (pyrolysis products).

The co-occurrence of cyanides, sulfur, and mainly unsubstituted PAH lead us to the conclusion that this soil sample is polluted with compounds generated as byproducts in a coal gasification plant (*19*), which was previously located near the sample site. HCN and $(CN)_2$ are thought to be pyrolysis products of complex cyanides such as Prussian blue that were produced during HCN fixation from the coal-produced gas (*19*). Elemental sulfur was produced via a desulfurization step, and the PAH probably represent remnants of the coal tar.

The styrenes encountered are well-known characteristic products of polystyrenes, which did not originate at the coal gasification plant. Styrenes are formed easily upon pyrolysis from polystyrenes via the "unzipping" mechanism (*20*). The phenethyl ethers are likely generated from phenethyl ether moieties present in the polystyrenes and indicate the sort of radical initiation species orginally used during the polystyrene synthesis. In summary we can conclude from this Ev/Py GC–MS analysis that the soil sample is polluted with byproducts of a coal gasification plant and with a more recent type of pollution: polystyrenes.

Diphenethyl thioether (compound 65, Table I) is thought to be a secondary product as a consequence of the relative high amounts of sulfur and styrene present during the flash pyrolysis. Benzothiophenes and dibenzothiophenes (compounds 21, 22, 24, 25, 30, and 61 in Table I) are well-known constituents of coals and are therefore not considered to be reaction products generated during the heating of the sample (*3*).

In order to get some insight into the quantitative aspects of this screening method procedure, 10 polycyclic aromatic components were separately quantitated using more traditional methods. The amount of phenanthrene (peak 63) and benzo[*a*]pyrene (peak 73) was 506 and 38 ppm, respectively (Table III). As the sample load on the wire was approximately 200 μg it can be easily calculated that ca. 100 ng of phenanthrene and ca. 7.5 ng of benzo[*a*]pyrene have been applied to the wire. Based on the response of these compounds in the Py/GC–MS detection limit of about 2 ng/PAH component

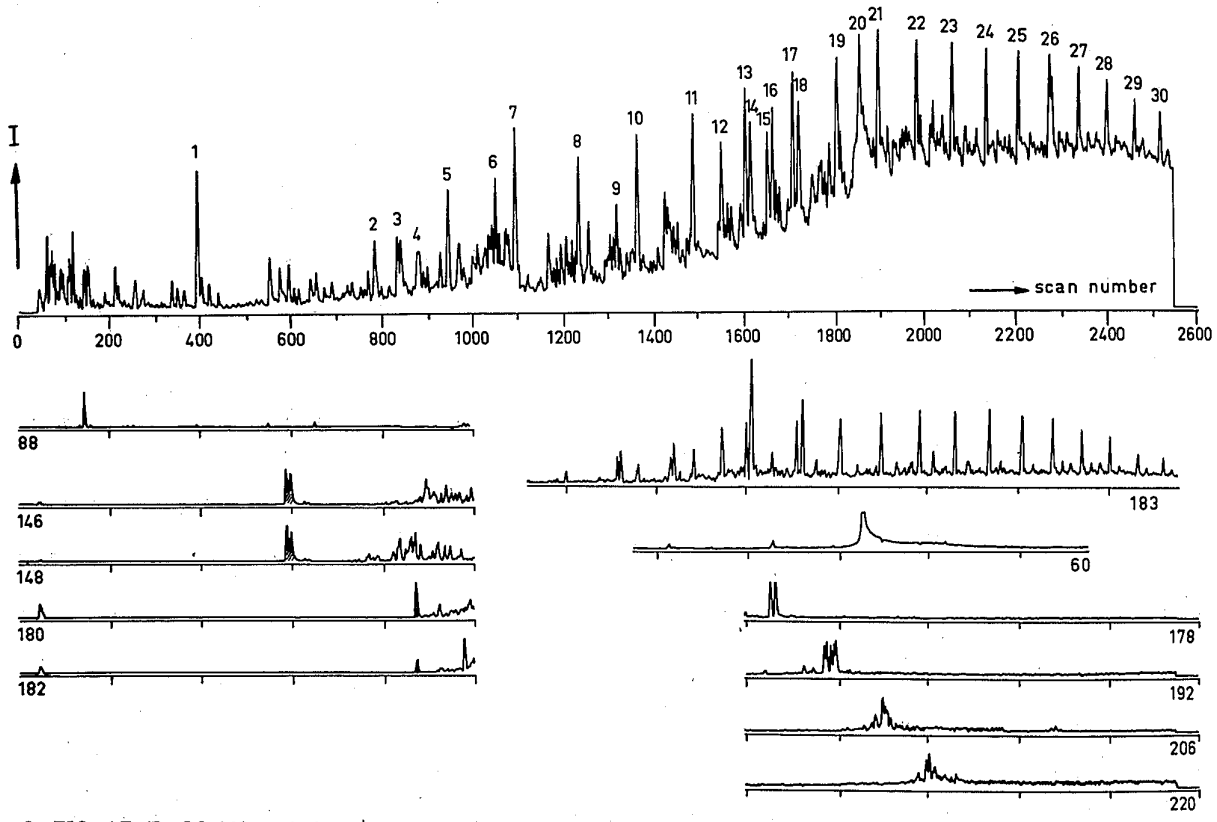

Figure 3. TIC of Ev/Py GC–MS analysis of the polluted sediment sample. The numbers in the mass chromatograms represent the m/z values indicative of the following compounds m/z 88 (dioxane); m/z 146, 148 (dichlorobenzene); m/z 180, 182 (trichlorobenzene); m/z 183 (alkanes from C_{14}); m/z 60 (hexadecanoic acid); m/z 178, 192, 206, 220 (C_0–C_3 anthracenes and phenanthrenes)

was estimated. This means that with a sample load of about 200 μg, 5 ppm of a PAH component can be monitored by this method.

Sediment Sample. The major contamination found in this sediment sample is derived from mineral oil fractions; a homologous series of *n*-alkanes with no odd-over-even predominance is abundantly present, and other even more specific markers for mineral oil such as the isoprenoid hydrocarbons norpristane, pristane, and phytane are also major components (peaks 12, 14, and 18 in Figure 3). To exemplify this oil pattern, a mass chromatogram of m/z 183 was generated, which almost exclusively reveals the alkane pattern. Phytane and pristane show relatively higher intensities in this mass chromatogram as m/z 183 is enhanced in the mass spectra of these isoprenoid compounds. Mass chromatographic data reduction was further used to visualize a number of other anthropogenic compounds.

The m/z 60 trace shows the presence of stearic acid. A series of mass chromatograms at m/z 178, 192, 206, and 220 selectively revealed the distribution pattern of the unsubstituted and C_1–C_3 substituted phenanthrenes and anthracenes.

Mass chromatography of m/z 146 and 148 and m/z 180 and 182 is shown to be highly selective for di- and trichlorobenzenes. These components are only present in relatively minor amounts. A mass chromatogram at m/z 88 showed the presence of the rather volatile compound dioxane. This sediment sample obviously is heavily polluted with nonbiodegraded mineral oil fractions and a number of other components (i.e., stearic acid, chlorinated benzenes), which point to spills of numerous bulk chemicals.

Based on the quantitative determination of pentadecane (see Table III) it was calculated that—with a sample load of about 200 μg—alkanes are detected by this screening method if their concentration is 5 ppm or more. It is obvious that highly volatile compounds when present as such (e.g., dioxane) cannot be measured quantitatively because considerable losses of such components occur during the evaporation of the suspension liquid from the pyrolysis wire when it is prepared. Quantities measured for such compounds must therefore be considered as minimum values.

Naturally occurring compounds in soils and sediments (lipids, polysaccharides, lignins, etc.) have also been determined by this method (*3–10*). The compounds generated from nonpolluted soils and sediments are completely different and easily discriminated from anthropogenic contributions.

CONCLUSIONS

The results reported here for a polluted soil and sediment sample indicate that this flash evaporation/pyrolysis technique combined with GC–MS is a valuable tool for rapidly screening polluted samples for virtually all types of anthropogenic contaminants except for heavy metals.

This method allows for the simultaneous detection of highly volatile (e.g., dioxane), volatile (e.g., PAH), and nonvolatile (e.g., polystyrene) substances. The sensitivity of the method depends of course on the detector(s) used. In the GC–MS mode reported here most compounds could be readily detected in the low part-per-million range.

At the moment this method is being used to monitor other polluted samples with a variety of detectors. Several analytical aspects are further investigated to obtain a more detailed insight into the scope and limitations of this screening technique.

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Registry No. H_2S, 7783-06-4; CO_2, 124-38-9; CO, 630-08-0; dicyanogen, 460-19-5; hydrogen cyanide, 74-90-8; ethylbenzene, 100-41-4; styrene, 100-42-5; α-methylstyrene, 98-83-9; 3-methylstyrene, 100-80-1; 4-methylstyrene, 622-97-9; indene, 95-13-6; α,3-dimethylstyrene, 1124-20-5; 3-ethylstyrene, 7525-62-4;

α,4-dimethylstyrene, 1195-32-0; 3,5-dimethylstyrene, 5379-20-4; phenyl ethyl ether, 103-73-1; 2,3-dimethylstyrene, 40243-75-2; 3,4-dimethylstyrene, 27831-13-6; methylindene, 29036-25-7; naphthalene, 91-20-3; benzo[b]thiophene, 95-15-8; methylbenzo[b]thiophene, 31393-23-4; 2-methylnaphthalene, 91-57-6; 1-methylnaphthalene, 90-12-0; 1-phenylethyl *tert*-butyl ether, 90367-83-2; biphenyl, 92-52-4; 1-ethylnaphthalene, 1127-76-0; dimethylbenzo[b]thiophene, 30027-44-2; 2,6-dimethylnaphthalene, 581-42-0; 2,7-dimethylnaphthalene, 582-16-1; 1,3-dimethylnaphthalene, 575-41-7; 1,7-dimethylnaphthalene, 575-37-1; 1,6-dimethylnaphthalene, 575-43-9; 2,3-dimethynaphthalene, 581-40-8; 1,4-dimethylnaphthalene, 571-58-4; acenaphthalene, 208-96-8; 1,2-dimethylnaphthalene, 573-98-8; acenaphthene, 83-32-9; 4-methylbiphenyl, 644-08-6; 3-methylbiphenyl, 643-93-6; dibenzofuran, 132-64-9; fluorene, 86-73-7; dimethylbiphenyl, 28013-11-8; methylbenzofuran, 25586-38-3; bis(phenylethyl) ether, 93-96-9; 2-methylfluorene, 1430-97-3; 1-methylfluorene, 1730-37-6; 9-fluorenone, 486-25-9; dibenzothiophene, 132-65-0; phenanthrene, 85-01-8; anthracene, 120-12-7; sulfur, 7704-34-9; fluoranthene, 206-44-0; pyrene, 129-00-0; benzo[c]phenanthrene, 195-19-7; benz[a]anthracene, 56-55-3; chrysene, 218-01-9; triphenylene, 217-59-4; benzo[a]pyrene, 50-32-8; benzo[e]pyrene, 192-97-2; *n*-undecane, 1120-21-4; *n*-dodecane, 112-40-3; *n*-tridecane, 629-50-5; *n*-tetradecane, 629-59-4; 2,6,10-trimethyltridecane, 3891-99-4; *n*-pentadecane, 629-62-9; *n*-hexadecane, 544-76-3; norpristane, 3892-00-0; *n*-heptadecane, 629-78-7; pristane, 1921-70-6; *n*-octadecane, 593-45-3; phytane, 638-36-8; *n*-nonadecane, 629-92-5; *n*-hexadecanoic acid, 57-10-3; *n*-eicosane, 112-95-8; *n*-heneicosane, 629-94-7; *n*-docosane, 629-97-0; *n*-tricosane, 638-67-5; *n*-tetracosane, 646-31-1; *n*-pentacosane, 629-99-2; *n*-hexacosane, 630-01-3; *n*-heptacosane, 593-49-7; *n*-octacosane, 630-02-4; *n*-nonacosane, 630-03-5; perylene, 198-55-0; dioxane, 123-91-1; dichlorobenzene, 25321-22-6; trichlorobenzene, 12002-48-1.

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Sampling and Determination of Gas-Phase Hydrogen Peroxide following Removal of Ozone by Gas-Phase Reaction with Nitric Oxide

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A method for the determination of hydrogen peroxide in the ambient atmosphere is described, using impinger or diffusion scrubber collection of H_2O_2 with aqueous-phase analysis by an enzyme-catalyzed fluorescence technique. Interference from ozone at ambient levels is removed by gas-phase reaction with excess nitric oxide. The impinger and diffusion scrubber collection techniques give equivalent results for atmospheric gas-phase H_2O_2 with limits of detection of 0.1 ppbv for approximately 60-min and 10-min sampling times, respectively.

The development of techniques for measuring gaseous and aqueous H_2O_2 and other hydroperoxy compounds has been the focus of substantial research effort following the recognition that H_2O_2 could rapidly oxidize dissolved S(IV) compounds to sulfuric acid throughout the normal pH range of rain, cloud, and fog waters (pH 2–7) (*1*, *2*). The high solubility of H_2O_2 in water (Henry's law constant $\sim 10^5$ M atm^{-1}) leads to significant aqueous concentration (1–100 μM) in, e.g., cloud water, even at low parts-per-billion by volume gaseous H_2O_2 concentrations in air entering clouds (*3–5*). Several methods for determining aqueous-phase H_2O_2 in atmospheric samples have been developed or improved recently based on luminol chemiluminescence (*6*), (*p*-hydroxyphenyl)acetic acid (POHPAA) dimer fluorescence (*5*, *7–9*), scopoletin fluorescence quenching (*10*), and peroxyoxalate chemiluminescence (*11*).

Measurements of gas-phase hydrogen peroxide have been attempted by collection of the peroxide in aqueous solution using impingers or condensation collection devices (*12*). However, these efforts have been shown to give unreliable results due to the in situ formation of hydrogen peroxide from low-solubility constituents of ambient air and/or compressed air during collection (*13–15*). It has been suggested that this

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