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Thermoanalytical methods for characterizing hydrocarbon–sludge–soil mixtures

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Abstract

Hydrocarbon sludges from petrochemical plants and soils contaminated with these sludges were characterized by applying thermoanalytical methods such as pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetry/mass spectrometry (TG-MS). In combination with conventional and supercritical fluid extraction (SFE) followed by GC/MS analysis, more than 100 constituents were identified. The Py-GC/MS technique is suitable for a qualitative rather than a quantitative analysis of organic pollutants in sludge–soil mixtures. The TG-MS method was used for describing interactions between pollutants and solid matrices (sludges and soils). It was found that a mild thermal treatment of samples (thermodesorption) did not release other compounds or higher quantities than those obtained by solvent extraction. Consequently, these organic pollutants must be fixed on soil organic matter (SOM) by sorption rather than by covalent binding. The TG-MS results permit us to distinguish between the release of a component by thermodesorption and by pyrolysis.

Keywords: Hydrocarbon sludge; Contaminated soil; Thermoanalytical technique; Fixation of pollutants

1. Introduction

In comparison with the environmental matrices of air and water, sediments and soils are known to be of a more complex nature; their analytical investigation creates a host of difficulties. In the specialist literature, a multitude of analytical techniques have been scrutinized to describe analytical features of sediments, soils and other solid matrices [1–5]. Besides, more recent methods, including primarily GC-MS, positive-ion bombard-

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ment MS and laser desorption/ionisation MS, the established thermo-analytical methods among them thermogravimetry (TG-TGA) and pyrolysis-gas chromatography/mass spectrometry (PY-GC/MS) possess a high potential for characterizing quantitatively and qualitatively both soil organic matter (SOM) and pollutants fixed therein [6–7].

The TGA-MS technique, which allows the detection of released organic compounds when heated in a time-resolved manner [8,9], has been capable of revealing interactions between SOM and organic pollutants, with the question of how the pollutants are attached to the solid matrix (covalently or sorptively) being a major topic. Conclusions drawn from these investigations are especially valuable for validating and remediating highly contaminated soils.

In the framework of investigations devoted to the disposal by biodegradation of oily sludges originating from petrochemical plants in a field experiment over 2 years [10], carried out at the University of La Plata (Argentina), we characterized these samples by applying thermoanalytical methods. We investigated: soil with fresh sludge (S + FS); soil with old sludge, with the latter having been deposited about 20 years ago (S + OS); old sludge (OS); fresh sludge (FS); non-contaminated soil, which served as a blank (soil control, SC).

2. Experimental

2.1. Sample preparation

The soil samples SC, S + FS and S + OS to be investigated were dried over $CaCl_2$ in a desiccator. The water containing sludges FS and OS was roughly dehydrated by means of a glass fibre filter and than sonicated with a benzene–acetone mixture (1:1) for extraction purposes (10 mg of sludge with 1 ml of extraction solvent). The roughly dewatered sludges were desiccated overnight to be accessible for TGA, TGA-MS and tube-furnace mass spectrometry (TF-MS) investigations. All the pretreatment procedures were carried out as simply and in as short a time as possible to minimize the loss of highly volatile compounds.

2.2. Supercritical fluid extraction (SFE)

A pre-dried soil sample (1.9 g) mixed with internal standard (100 ppm n-hexadecane) was weighed into an extraction chamber (2.5 ml, ISCO 2200®) and extracted by a two-stage procedure ((A) pure CO_2, 90°C, 37.5 MPa; (B) 5% methanol modifier addition, 120°C, 50 MPa). The acetone trapped extract was purified by SPE (Bakerbond C_{18}). Afterwards, the concentrated extract was subjected to GC or GC-MS analysis (for conditions see below).

2.3. PY-GC and GC-MS conditions

Sludge and sludge-soil mixtures deposited in a quartz tube were heated by means of a flash pyrolyzer (Pyroprobe 1000®, CDS, $T_{\text{interface}} = 250°C$, $T_{\text{set}} = 350°C$ and 700°C, heating rate = 0.5 K ms^{-1}, time of pyrolysis = 10 s). The thermodesorption and pyrolysis products released from the solid matrix were analysed by GC (DANI 86.10®, 50 m capillary column NB 54 coated with 5% phenyl- and 1% vinylsilicone gum, 0.32 mm i.d., film thickness 0.25 μm). The oven temperature was programmed from 60 (initial time 4 min) to 280°C (final time 10 min) at a rate of 10 K min^{-1}. In both cases the detector and injector block was set to 280°C. For data handling an APEX®-chromatography workstation was used.

GC-MS analyses were performed on an Shimadzu GC-instrument (GC 14A) linked to a mass spectrometer QP-1100EX (see also Fig. 1). The separation was accomplished on a fused silica capillary (25 m × 0.25 mm, Permabond OV-1-DF-0.25) in a splitless injection mode. GC-conditions were identical to those used in Py-GC-mode. The temperature of the transfer line was 250°C. Mass spectrometric detection was carried out by using 70 eV EI-ionisation, the ion-source temperature being 250°C, cycle time 1 s and mass range 10–300 amu. Data acquisition and handling was performed in a computer assisted way (Shimadzu software Newpac® and Class5000®).

2.4. *Thermogravimetry conditions*

The standard heating rate of the thermobalance (TGA 50, Shimadzu) employed in these studies was 10 K·min^{-1} up to 600 or 700°C. The initial sample mass was kept between 2 and 5 mg for FS and OS and 20 and 30 mg for SC, S + FS and S + OS. A helium atmosphere with a gas flow rate of 20 ml·min^{-1} was used. At the final temperature the burn-offs were realized with air. To evaluate the obtained thermograms we used the Shimadzu TA-workstation, version 1.01.

2.5. *Simultaneous thermoanalytical measurements*

The experimental device consisted of either a Shimadzu thermobalance (TGA-50) or a Raytest tube furnace (TF) connected to a Shimadzu mass spectrometer QP 1100EX via a heated transfer line and a split system. A schematic representation of the apparatus is depicted below and outlined comprehensively in Ref. [11].

All devices located after the TG or TF were set to a value of 250°C. The standard heating rate employed in these studies was 10 K min^{-1} up to the final value of 600 or 700°C. A helium atmosphere was used with a gas flow rate of 23 ml min^{-1} (split ratio 1:5). The total ion current (TIC) were recorded with a scan rate of 1 s^{-1}, a mass range of 10–300 amu and an EI-ionization energy of 70 eV were applied. For data acquisition and handling, see TGA and GC-MS conditions.

3. Results and discussion

The investigation of our soils and sludges has been a difficult job, due to some complications, among them the extraordinary multitude of organic pollutants fixed therein, the high variability of the water content in the kind of sample and both the chemical and geometrical inhomogeneity.

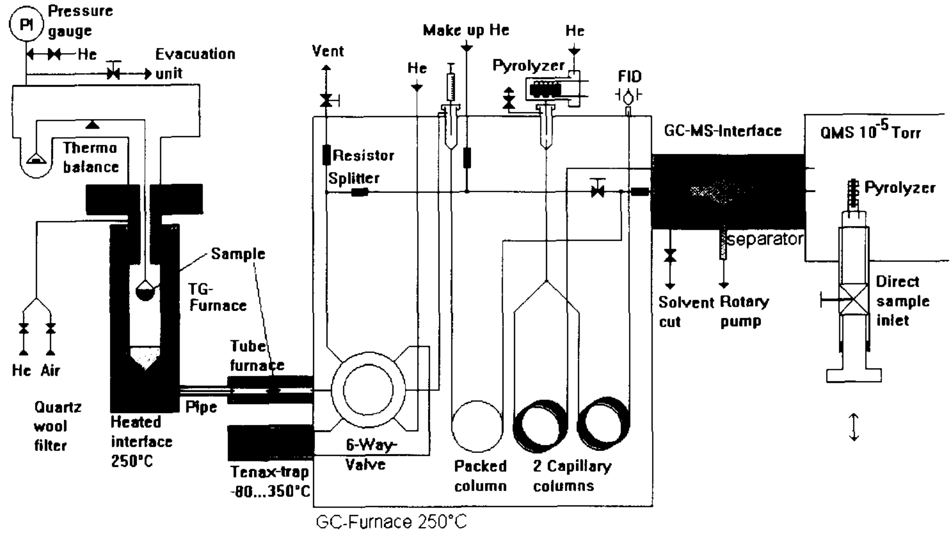

Fig. 1. A schematic presentation of the apparatus taken from Ref. [11].

The TGA experiments were aimed at establishing a mass balance (volatile compounds + coke + ash) and giving a rough description of the reactivity of organic constituents.

In the DTG curves, there are two maxima with soil samples and only one maximum with the sludge samples in the temperature range between 30 and 600°C. The pronounced maxima at 85 and 180°C can be attributed to the vaporization of physically bound water in soils and to the vaporization of hydrocarbons from sludges, respectively. The maximum at 420°C can be explained by the thermal decomposition of SOM. A re-

Table 1

Thermogravimetry of sludge and soil samples (30 up to 600°C, $T = 10$ K min^{-1}, values as wt%)

Sample	Volatile components[b]	Burn-off	Σ Weight loss	T_{DTGmax}/°C	$m_{\max}$/(% min^{-1})[c]
SC (11.7%)[a]	5.58 (incl. H_2O, 1.2% < 150°C)	1.55	7.13	85, 420	2.4
S + FS (11.8%)	6.82 (incl. H_2O, 1.3% < 150°C)	1.96	8.78	85, 420	2.3
S + OS (12.1%)	6.59 (incl. H_2O, 1.4% < 150°C)	2.81	9.40	85, 420	2.2
FS	50.50	11.05	61.55	180	–
OS	71.65	12.70	84.35	180	–

[a] Weight loss when drying the soil samples over $CaCl_2$.

[b] Weight loss up to 600°C.

[c] % weight loss related to the total content of organic matter.

markable finding is the fact that the DTG curves of the contaminated soils (S + FS, S + OS) show no significant maximum at the vaporization temperature of hydrocarbons in contrast to the sludge samples. This leads to the conclusion that the samples S + FS and S + OS contain only minor amounts of volatile hydrocarbons in relation to the total amount of SOM.

In the temperature range between 150 and 600°C the soil samples show the same maximum rates of decomposition of $2.3 \pm 0.1\% \cdot \mathrm{min}^{-1}$ (% weight loss per minute, normalized to the sum of SOM) as those exhibited by comparable materials such as sediments [11]. Comparing the blank soil with contaminated soils as regards the quantity of both volatile compounds and burn-off, we estimated the content of abiotic carbon introduced by the sludges to be in the range of 2–2.5 wt%.

In addition to volatile constituents, the sludges FS and OS contain heavy compounds, non-volatile components and ash. Assuming that the thermal decomposition of hydrocarbons begins at a temperature of some 350°C, the sum of volatile compounds (referred to the moisture free weight) amounts to 60 wt% and 40 wt% for OS and FS, respectively. The FS sample is distinguished from the OS sample by a higher ash content (40 wt% in contrast to 15 wt%), which is mainly due to a high content of carbonate (10 wt%).

To study organic compounds released by thermodesorption (up to 350°C) and pyrolysis (700°C), the soils S + FS, S + OS and sludge samples were subjected to a sequential thermal treatment, and these compounds are analyzed by GC and GC/MS. Surprisingly, during thermodesorption only 5% of their total GC-detectable carbon (the sum of the peak areas at both 350°C and 700°C treatment temperature) are released from the soils, this value being 85–90% with the two sludges under study.

Hence, there is strong evidence that the majority of organic pollutants are strongly attached to the soil matrix, or a slow, diffusion controlled transport of these pollutants inside this matrix prevails.

Although the qualitative and quantitative determination of pollutants by means of Py-GC and Py-GC/MS should be possible in principle, we decided to take advantage of classical methods (liquid-solid extraction as well as SFE in combination with GC and GC/MS). Both thermodesorption and pyrolysis did not give sufficiently reproducible results reflecting the real content of pollutants, because of the detection limit of the thermodesorption method. This holds especially true with soil samples having a low FID detectable content. Using the method of adding internal standard (100 ppm n-hexadecane), we found that the pollutants detected after thermodesorption were considerably lower in concentration (about 50%) than those obtained from the SFE-procedure. The reason for this finding may be the following: In contrast to the thermodesorption experiments with freshly spiked samples carried out previously [12], where high recovery rates of surrogates were obtained, thermodesorption does not give rise to their rapid release. These insufficient recovery rates of organic pollutants by thermodesorption, in contrast to SFE or solvent extraction, may be caused by the deep penetration of pollutants into the solid matrix (SOM) and/or extensive penetration times (diffusion controlled release). A careful inspection of the data presented previously by de Leeuw et al. (screening of pollutants in sediments and soils by evaporation) [13] reveals that the authors did not investigate quantitatively pollutants concentrations on the basis of Ev-GC/MS results. Instead, they used conventional solvent extraction followed by the GC

Table 2

Compilation of compounds in an extract from FS by GC-MS identification

Number	Compound	Number	Compound
1	Toluene	53	Methylacenaphthene
2	Dimethylcyclopentadiene	54	Methylacenaphthylene
3	*p*- and *m*-xylene	55	*m/z* = 170, 168, 167, 152
4	Styrene	56, 57	Methylacenaphthylenes
5	*o*-Xylene	58	Vinyldiphenyl
6	C_8H_{10}	59	n-$C_{17}H_{36}$
7	C_9H_{12} (non-aromatic)	60	Methylfluorene
9	Indane and α-/β-methylstyrene	61, 62	Dihydromethylfluorene
10	α-/β-methylstyrene	63	Methylfluorene
11	Ring-methylstyrene	64	Dihydromethylfluorene
12	Dicyclopentadiene	65	n-$C_{18}H_{38}$
13	Ring-methylstyrene	66	*m/z* = 180, 57
14	Indene	67	Phenanthrene
15	$C_{10}H_{12}$ (e.g. dimethylstyrene)	68	Anthracene
16	Methyldicyclopentadiene	69–73	*m/z* = 194, 192, 57 (dihydromethyl-phenanthrenes and -anthracenes)
17–19	Dimethyldicyclopentadienes	74	n-$C_{19}H_{40}$
20	Dihydronaphthalene	75	Phenylnaphthalene or vinylanthracene (-phenanthrene)
21	n-$C_{12}H_{26}$ and dihydronaphthalene	76	*m/z* = 192, 191, 57
22–24	Methylindenes	77, 78	Methylphenanthrenes and -anthracenes
25	Naphthalene	79	Methanophenanthrene
26	n-$C_{13}H_{28}$	80, 81	Methylphenanthrenes and -anthracenes
27–29	Dimethylindenes	82	$C_{15}H_{10}$
30, 31	Vinylindenes	83	n-$C_{20}H_{42}$
32	2-Methylnaphthalene	84	$C_{16}H_{12}$
33	1-Methylnaphthalene	85, 86	Dimethylphenanthrenes and -anthracenes
34	$C_{11}H_{10}$	87	Hexadecanoic acid
35	n-$C_{14}H_{30}$ and $C_{12}H_{12}$	88–91	Dimethylphenanthrenes and -anthracenes
36	Diphenyl	92	n-$C_{21}H_{44}$ and fluoranthene
37	$C_{12}H_{12}$	93	$C_{16}H_{12}$
38	$C_{12}H_8O$ (dibenzofurane ?)	94	Pyrene
39, 40	Dimethylnaphthalenes	95	$C_{16}H_{14}$
41	Ethylnaphthalenes	96	n-$C_{22}H_{46}$
42	n-$C_{15}H_{32}$	97–100	Methylfluoranthene and benzofluorene
43	Acenaphthylene	101	Methylpyrene
44	Dimethylnaphthalene	102	n-$C_{23}H_{48}$
45	Acenaphthene	103	Methylpyrene
46	*m/z* = 168,167	104	n-$C_{24}H_{50}$
47	i-$C_{16}H_{34}$	105	*m/z* = 226, 225
48	*m/z* = 170, 155	106	Benzo[*g*,*h*,*i*]fluoranthene
49	n-$C_{16}H_{34}$	107	Benzo[*a*]anthracene
50	Phenalene	108	Chrysene
51	Methylacenaphthylene	109	n-$C_{25}H_{52}$
52	Fluorene	110–114	5-ring PAHs with *m/z* = 252

analysis of the extract similar to the procedure described here. Obviously, the thermodesorption method is not convenient for strictly quantitative measurements.

After the pretreatment of the sludge samples FS and OS (see Section 2) we succeeded in identifying more than 100 constituents by using the combined application of mass spectra identification and the comparison of retention times on the basis of standards (see Table 2).

As can be taken from Table 2, the overwhelming majority of compounds we identified includes common hydrocarbons and only a minority of oxygen containing products. Both sludge samples reveal a completely identical pattern in their qualitative composition. The quantitative composition as regards the distribution in percent among the individual compounds we detected is similar between FS and OS (see Table 3). This finding points to their identical technological origin and a production process which has been modified only slightly during the past 20 years. The multitude of the hydrocarbons identified are typical products of steam cracking, in particular derivatives of cylcopentadienes which are known to be typical markers of thermal processes [14].

The OS and the FS samples were shown to have 25 wt% and 9 wt% , respectively, of compounds accessible to GC after extraction referred to the dry weight. These values correspond to 40 wt% and 25 wt%, respectively, related to the sum of compounds released from the samples during the TGA procedure up to 350°C. Those compounds which are not accessible to GC primarily include heavy, tar-like compounds (e.g. >5-ring-membered PAHs), the detailed identification of which is outside the scope of this paper.

Table 3

Content of substances and classes of compounds in sludge samples (GC analysis of benzene–acetone extracts)

Compound	FS in g kg^{-1}	OS in g kg^{-1}	OS/FS
Styrene	3.12	7.65	2.45
Indene	4.95	12.28	2.48
Methylindenes	4.50	13.46	2.99
Naphthalene	17.43	49.41	2.83
Methylnaphthalenes	7.43	23.74	3.19
Diphenyl	1.90	6.80	3.57
Acenaphthylene	4.07	12.13	5.85
Acenaphthene	1.05	3.38	3.21
Fluorene	1.88	6.60	3.51
Phenanthrene	6.34	15.64	2.46
Anthracene	1.67	3.86	2.31
Fluoranthene	1.37	2.22	1.67
Pyrene	2.00	4.13	2.01
Benzo[*a*]anthracene	0.15	0.48	3.20
Chrysene	0.16	0.53	3.30
Σn-alkanes	8.93	14.72	1.64
ΣOther compounds	26.36	74.26	2.81
Sum	93.31	251.29	2.72

Table 4

Content of substances and classes of compounds in soil samples (GC analysis of SFE extracts)

Compound	S + FS in mg kg^{-1}	S + OS in mg kg^{-1}
Naphthalene	12	13
Methylnaphthalenes	8	5
Diphenyl	2	-
Acenaphthylene	**188**	**201**
Acenaphthene	**5**	**3**
Fluorene	13	7
Phenanthrene	235	42
Anthracene	101	31
Fluoranthene	263	78
Pyrene	580	180
Benzo[*a*]anthracene	132	48
Chrysene	137	58
ΣOther compounds	(3100)	(1900)
Sum	~4800	~2600

A survey of concentrations of some selected PAHs (naphthalene to chrysene) in the soil-sludge mixtures extracted by using SFE is given in Table 4.

For reasons of comparison, investigations devoted to the blank sample (SC) mentioned above were carried out. We could not find any of the more than 100 compounds identified in sludges in concentrations above 1 ppm (see Table 2).

Attention should be focused on the concentration ratio of acenaththene and acenaphthylene in the polluted soils. It is equal to 0.02 (see Table 4). This ratio is reduced by a factor of about 20 in comparison with the sludges (0.4). This result indicates a special behaviour of acenaphthylene which may be due to specific interactions with SOM, the other PAHs being presumably incapable of entering into these interactions [15]. A stronger binding of acenaphthylene to SOM gives rise to a lower vapour pressure as well as to lower bioavailability. As a consequence, it is enriched in the remaining SOM. Beyond this, the concentration of PAHs in sludge–soil mixtures is reduced in strong correlation with decreasing boiling points. Additionally, the K_{ow} values (octanol/water partition coefficient) as a measure of the hydrophobia of PAHs also correlate with their boiling points, that means volatility and solubility (bioavailability) of PAHs point in the same direction [16,17]. There is some evidence in the literature that the loss of PAHs by evaporation out of soils is significant at least up to 3-ring-membered PAHs [18]. Therefore, a quantitative distinction between the loss of pollutants by evaporation and by biodegradation is difficult to accomplish (see Table 5).

To describe the interactions between pollutants and solid matrices (sludge and soils) we used the TG-MS and the tube-furnace (TF)-MS device. These hyphenated techniques allow the time-resolved tracing of processes occurring with the continuous heating of the sample. The total ion current (TIC) thermogram obtained contains information on products resulting from vaporization and pyrolysis. In contrast to the DTG-curve, the TIC-curve can be partitioned into individual curves for each selected ion. By using characteristic fragments or molecular ions which can be assigned to defined molecules (see Table

Table 5

Relative concentrations of selected PAHs in soils and sludges (data as wt% normalized to 100% of selected PAHs)

Compound	OS	S + OS	OS/S + OS	FS	S + FS	FS/S + FS
Naphthalene	37.4	1.8	20.7	38.3	0.7	54.7
Methylnaphthalenes	18.0	0.9	20.0	16.4	0.5	32.8
Diphenyl	5.1	–	–	4.3	0.1	41.0
Acenaphthylene	**9.2**	**27.1**	**0.3**	**9.0**	**11.2**	**0.8**
Acenaphthene	**2.6**	**0.5**	**5.2**	**2.3**	**0.3**	**7.7**
Fluorene	7.2	1.1	6.5	4.1	0.8	5.1
Phenanthrene	11.8	9.5	1.2	13.9	14.0	1.0
Anthracene	2.9	6.0	0.5	3.6	6.0	0.6
Fluoranthene	1.7	11.0	0.14	3.0	15.6	0.19
Pyrene	3.3	26.8	0.12	4.4	34.6	0.12
Benzo[*a*]anthracene	0.4	6.9	0.06	0.3	7.8	0.05
Chrysene	0.4	8.4	0.05	0.4	8.2	0.05

5) and classes of substances (e.g. $m/z = 57$ for alkanes), it is now possible to draw conclusions about the bonding behaviour of pollutants to the solid matrix.

The results are exemplified by experiments with the samples FS, S + FS, S + FS (extracted with hexane under both sonication and reflux) and S + FS (extracted with benzene/acetone 1:1 under both sonication and reflux).

In our opinion, coupling TG with MS brings about some experimental artefacts, which are mainly due to a secondary cracking of heavy tars deposited on the walls of the thermobalance. To circumvent this artefact, the samples were heated in a temperature programmed tube furnace (see Fig. 1) with a more appropriate temperature profile and flow characteristic. In thus, a comparison of TG and MS curves (mass loss rate versus temperature and TIC versus temperature, respectively) is more reasonable. However, the

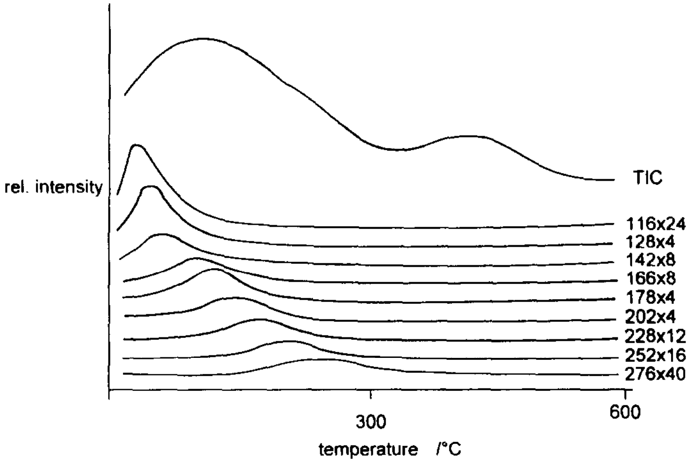

Fig. 2. Desorption maxima of selected PAHs from FS.

Table 6

TF-MS of FS and S + FS (desorption maxima of selected PAHs)

Compound	*m/z* (molecular weight)	FS ($T_{\mathrm{des.max}}$/°C)	S + FS ($T_{\mathrm{des.max}}$/°C)
Indene	116	35	n.d.[a]
Naphthalene	128	50	n.d.
Methylnaphthalenes	142	70	175
Acenaphthylene	152	85	195
Acenaphthene	154	85	195
Fluorene	166	105	220
Phenanthrene/anthracene	178	120	240
Fluoranthene/pyrene	202	150	(200)
Chrysene/benzo[*a*]anthracene	228	180	245
5-Ring PAHs	252	205	260
6-Ring PAHs	276	235	285

[a] Not detectable.

MS-thermogram does not include the contribution of the heavy tar fraction that cannot be transferred into the ion source under atmospheric pressure.

In all TICs recorded by us there are two maxima of each of the single ions (see Figs. 2 and 3). The first maximum occurs at different temperatures, whereas the second maximum (not shown on the scale of Fig. 2) is close to 460°C, where the thermal decomposition of SOM is known to take place. Therefore, we are able to distinguish between vaporization or desorption processes, on the one hand, and the pyrolysis-induced formation of defined hydrocarbons we had paid attention to on the other. Table 6 surveys the desorption maxima measured for both the sludge and soil samples (see also Fig. 2).

The different desorption maxima of PAHs obtained with sludges, on the one hand, and soils, on the other, points to a stronger sorptive interaction of PAHs to the soil matrix as

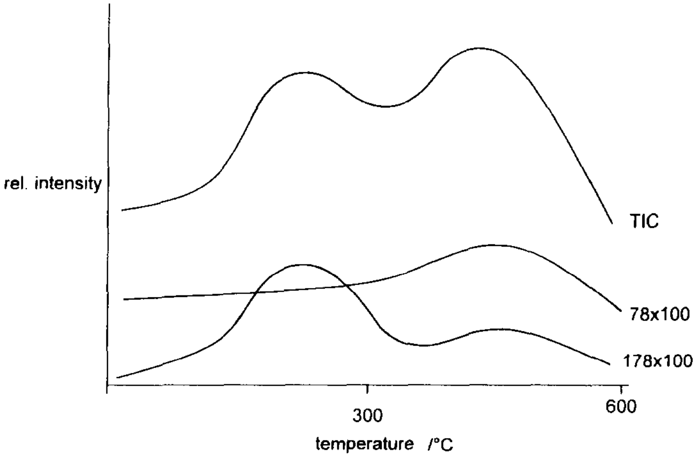

Fig. 3. Comparison of selected mass numbers typical for desorption and pyrolysis.

opposed to the sludge matrix. All desorbed components appear at temperatures which are below those characteristic of a pyrolytical formation [11] (see Fig. 3).

Additional information may be obtained by means of extraction with different solvents. n-Hexane as a solvent removes 0.55 wt% of organic compounds from S + FS, whereas the benzene–actone mixture can accomplish a deeper extraction (1.2 wt%). In comparison, the GC-detectable portion of the extract of S + FS amounts to 0.48 wt% (see Table 4). Consequently, the majority of GC accessible compounds can be extracted by hexane. The more polar solvent mixture, however, additionally extracts a lot of heavy compounds, not accessible to GC analysis. The extraction degree of PAHs after the solvent extraction procedure by n-hexane was verified by TF-MS analysis. By monitoring the ion trace $m/z = 178$ it confirmed a reduction of the phenanthrene/anthracene content in the extracted sample to less than 5% of the original value.

Finally, we can conclude that all pollutants released by thermodesorption can also be extracted by organic solvents, i.e. these organic components must be fixed on SOM by sorption rather than covalent binding. Low molecular weight compounds released from the solid matrix above temperatures of about 300°C are only formed by pyrolysis due to their strong fixation via covalent binding.

4. Conclusion

The usefulness of the various thermoanalytical techniques alongside standard methods (GC and GC-MS after SFE or solvent extraction of soils) for describing interactions between pollutants and soil organic matter has been demonstrated, and the advantages and limitations of the different methods discussed. A reason for the insufficient recovery rate of organic pollutants by thermodesorption in contrast to SFE or solvent extraction may be the deep penetration of "old" pollutants into the solid matrix and their rather slow diffusion controlled release. The concentration of PAHs in sludge–soil mixtures is reduced in strong correlation with decreasing boiling points which, in turn, correlate with the corresponding K_{OW} values. This makes it difficult to distinguish between the loss of pollutants by evaporation or by biodegradation. As a result of the TG-MS experiments, we found that all the pollutants that are thermo-desorbable up to 300°C are also extractable by solvents. Low molecular weight compounds formed by pyrolysis above temperatures of about 300°C are strongly bound to the solid matrix via covalent bonds.

The aim of the field experiment in Argentina was the biological disposal of an industrial waste product. On the basis of a balance of the hydrocarbons brought into the soil, it can be concluded that after the relatively short period of 2 years, the main portion had been lost, but no statement on how it was removed is possible.

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