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Comparative studies of the leachate of an industrial landfill by gas chromatography–mass spectrometry, liquid chromatography–nuclear magnetic resonance and liquid chromatography–mass spectrometry

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Abstract

Nowadays, the need to have a realistic characterization of industrial effluents in the environment has become more and more recognized. A palette of different analytical methods both for sample extraction and instrumental analysis are available today, some older, others introduced more recently. The aim of this research is to compare a number of these techniques. To do this we studied a real leachate from an industrial landfill and carried out chemical analyses for organic pollutants, using different extraction methods based on solid-phase extraction and solid-phase microextraction and different instrumental techniques such as GC–MS, LC–MS, NMR and LC–NMR. Results show the performances of the different techniques, which are complementary.

Keywords: Environmental analysis; Industrial chemicals; Water leachates

1. Introduction

The emissions of industrial pollutants in liquid effluents, are regulated in the EU by several directives and guidelines in which chemicals are listed which should not exceed a given concentration (European Union EU, directive). On the other hand, a chemical company may release a high number of chemicals which are not considered by this directive, and in many cases are unknown. Indeed, regulation tends to follow scientific achievements and there is a need to better understand the chemical nature of the large number of compounds present in many industrial effluents. This is why the number of parameters to be considered for assessing water quality has dramatically increased in recent decades, with most of these newly introduced parameters being organic chemicals [1].

Effluents of industrial origin may frequently contain a wide mixture of different chemicals. These compounds may be the final products, precursors or intermediates of the process, or else impurities and by-products obtained in a way that often is difficult to predict and, as a consequence, difficult to control. Moreover, the treatment of the effluents performed in most cases dramatically changes the composition of

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the chemicals typically present at the end of the production cycle [2–5]. The same is true in the case of leachate from industrial effluents [6]. The leachate may contain pollutants originally contained in the waste; furthermore, transformation occurs during the aging of the waste and, as a consequence, the leachate may collect contaminants produced inside the landfill [7–10]. Transformation products are often more polar than precursors.

Identification and quantification of these compounds may in most cases require more than a single analytical procedure, since a wide distribution of chemicals is expected, belonging to various compound classes and differing in their chemical properties, in particular their volatility and their polarity. As a consequence, a series of techniques has to be used to study such complex mixtures of the contaminants, with specific techniques being used successively to monitor specific pollutants.

So far, there hardly exists any published examples of these methods applied simultaneously for the characterization of organic compounds to the same industrial effluent, due to the complexity of such work. The literature reports examples of studies where complementarity of GC–MS and LC–MS have been used, instead [11–14].

The main goal of the present study is to identify as many compounds as possible using different techniques and to illustrate the potential and the complementary nature of the different techniques. We used a battery of chemical analyses on the same materials. Solid-phase extraction (SPE) and solid-phase microextraction (SPME) have been applied to the whole leachate; the extract has been analyzed by GC–MS. To gain a more detailed view of the polar acidic compounds, LC–MS, NMR and LC–NMR were employed. The results obtained with the different techniques are presented and discussed.

2. Experimental

2.1. Sample

The leachate considered comes from an industrial landfill which received industrial toxic and hazardous wastes from different sources. The leachate is collected in closed tanks. Its pH value is 8.5.

2.2. Materials

Carbopack B extractive phase and SPME fiber (PDMS, 100 μm) was purchased from Supelco (Bellefonte, PA, USA). Isolute C_{18} cartridges were obtained from International Sorbent Technology, (Hengoed, Mid Glamorgan, UK). LiChrolut EN cartridges were purchased from Merck (Darmstadt, Germany).

2.2.1. Chromatographic materials

GC capillary columns were purchased from Chrompack (Middelburg, The Netherlands). The LC column was from Merck (see below).

2.3. GC–MS analysis

For GC–MS analysis, the leachate was extracted by SPE or by SPME and then analyzed.

2.3.1. SPE extraction

Three different SPE methods were used; they are depicted in Table 1. Extracts were concentrated to 500 μl.

2.3.2. SPME procedures

A 10-ml volume of leachate was introduced into a vial and the extractive fiber exposed in the head space for 20 min, with magnetic stirring, at room temperature.

2.3.3. Instrumental methods

A HP 5971 (Hewlett-Packard) gas chromatograph–mass spectrometer (GC–MS) was used. We used different GC–MS conditions for SPE and SPME.

2.3.4. Analysis of SPE extracts

A CPSil8CB capillary column (25 m×0.25 mm× 0.25 μm) was used. Injector temperature: 280°C; detector temperature: 172°C; head pressure: 40 kPa; solvent delay: 3 min; oven temperature programme: initial temperature: 50°C (3 min), first ramp: 7°C/min to 100°C (0 min), second ramp: 10°C/min to 280°C (2 min).

Table 1
SPE methods

	Method		
	1	2	3
Solid phase	Carbopack B (400 mg)	Isolute C_{18} (500 mg)	LiChrolut EN (200 mg)
Washing	CH_2Cl_2–MeOH (80:20) (10 ml)	AcOEt (10 ml)	MeCN (5 ml)
Activation	(a) MeOH (5 ml) (b) HCl 0.01 *M* (20 ml) +ascorbic acid (200 mg) (c) Water (20 ml)	MeCN (10 ml)	Water (5 ml)
Sample	50 ml	50 ml	50 ml
Elution	(a) CH_2Cl_2–MeOH (80:20) (10 ml) (b) CH_2Cl_2–MeOH (80:20); (10 ml)+ CF_3COOH (0.02 ml)	AcOEt (10 ml)	MeCN (2×3 ml)

2.3.5. SPME analysis

A CPSil8CB capillary column (25 m×0.25 mm× 1.2 μm) was used. Injector temperature: 150°C; detector temperature: 172°C; head pressure: 40 kPa; solvent delay: 0 min; oven temperature programme: initial temperature: 40°C (0 min), first ramp: 10°C/min to 80°C (0 min), second ramp: 5°C/min to 180°C (3 min).

2.3.6. Mass spectrometry

Electron energy: 70 eV; scan range from 30 to 550 amu, for the SPE extract; from 30 to 400 for the SPME. Identification of mass spectra was performed with the instrument library (NBS75k).

2.4. Thermospray LC–MS analyses

2.4.1. Extraction and sample preparation

NaOH was added to 200 ml of the leachate sample to adjust the pH to a defined value of 9 (the original pH value was 8.4). Three preextractions with methylene chloride (20 ml) were performed to remove excess neutral and basic analytes; then the aqueous fraction was acidified with HCl (pH 1). Enrichment of compounds from the aqueous phase was performed by SPE on a LiChrolut EN cartridge. After the cartridge was dried with a stream of nitrogen, the analytes were eluted twice with 3 ml acetonitrile.

For the investigations by LC or LC–MS or LC–NMR aliquots of the extract were dissolved in the mobile phase after the solvent was blown off with nitrogen. For the LC–NMR investigations, a standard was prepared in addition which contained the compounds listed in Table 2, chosen on the basis of preliminary studies on the leachate (with the exception of *o*-hydroxybenzoic acid). The concentrations of the compounds were between 0.4 and 1.2 mg/ml.

Table 2
List of reference compounds

No.	Compound	Purity (%)	Origin
1	*p*-Chlorobenzenesulfonic acid	90	Aldrich[a]
2	Phthalic acid	99.5	Fluka[b]
3	Terephthalic acid	>99	Fluka
4	Isophthalic acid	99	Fluka
5	Phenylacetic acid	99	Aldrich
6	Benzoic acid	99.9	Merck[c]
7	*o*-Chlorobenzoic acid	>98	Fluka
8	*o*-Hydroxybenzoic acid	>99	Fluka
9	3-Phenylpropionic acid	99	Aldrich
10	*m*-Chlorobenzoic acid	>99	Fluka
11	*p*-Chlorobenzoic acid	>97	Fluka

[a] Aldrich, Steinheim, Germany.
[b] Fluka, Buchs, Switzerland.
[c] Merck, Darmstadt, Germany.

2.4.2. Chromatography

Analytes were investigated by liquid chromatography–diode array detection (LC–DAD) and thermospray LC–MS using a chromatographic system consisting of a liquid chromatograph from Varian (model 5000) and a Waters 990 diode array detector. The separation of the acidic components was carried out using a LiChrospher 100 RP-18 column, 250×4.6 mm, 5 μm, (Merck). The eluent was methanol (A)–0.2% HCOOH in water (B). An initial composition of A–B (48:52, v/v) was maintained for the first 15 min and then changed to 10% B within the following 45 min. The flow-rate for the LC–DAD investigations was 0.4 ml/min.

For the thermospray LC–MS experiments, the same LC conditions were used, but for buffer-assisted ionization an ammonium formate solution (0.17 mol) was added post-column at a flow-rate of 0.6 ml/min.

The LC–NMR on-flow experiments were carried out on a Merck LiChrolut EN column (customized packing), 75×4.0 mm, 7 μm. Isocratic chromatographic conditions with an eluent composition of acetonitrile–0.1% trifluoroacetic acid in $^{2}H_2O$ (60:40, v/v) at a flow-rate of 0.017 ml/min were used. The injection volume of the extract was 100 μl. The chromatographic system consisted of an LC gradient mixer from Bischoff (model 1155), a Bischoff LC pump (model 2250) equipped with micro-pump heads and a Bischoff UV detector (model Lambda 1000).

2.4.3. Mass spectrometry

A mass spectrometer from Finnigan (model 4500) equipped with a thermospray ion source from Vestec was employed. The ion source was operated with discharge at a vaporizer temperature of 250°C. Mass spectra were acquired both in the positive and negative ion mode.

2.5. NMR

The ^{1}H-NMR spectrum of the extract was recorded in acetonitrile-d_3 on a Bruker DPX 300 spectrometer operating at 300.13 mHz. Acquisition parameters used were as follows: 90° pulse angle, 6172 Hz sweep width, 32 000 data points, 1 s relaxation delay, 64 scans.

The chemical shift values of the reference compounds (Table 3) were extracted from the NMR chromatogram of the standard or determined from the spectra of reference compounds separately recorded on a Bruker DRX spectrometer at 600.13 mHz. In the latter case, the compounds were likewise dissolved in the mobile phase and measured under the following conditions: 90° pulse angle, 12 376 Hz sweep width, 32 000 data points and 1.8 s relaxation

Table 3
^{1}H-NMR chemical shift values[a] of reference compounds

No.	Compound	H2	H3	H4	H5	H6	–CH_2–
1	*p*-Chlorobenzenesulfonic acid	7.45 (pd)[b]	7.72 (pd)		7.72 (pd)	7.45 (pd)	
2	Phthalic acid		7.74 (m)	7.61 (m)	7.61 (m)	7.74 (m)	
3	Terephthalic acid	8.06 (s)	8.06 (s)		8.06 (s)	8.06 (s)	
4	Isophthalic acid	8.54 (d)		8.19 (dd)	8.60 (t)	8.19 (dd)	
5	Phenylacetic acid	7.22 (pd)	7.27 (pt)	7.20 (pt)	7.27 (pt)	7.22 (pd)	3.60 (s)
6	Benzoic acid	7.97 (pd)	7.47 (pt)	7.60 (pt)	7.47 (pt)	7.98 (pd)	
7	*o*-Chlorobenzoic acid		7.52 (d)	7.41 (t)[c]	7.40 (t)[c]	7.82 (d)	
8	*o*-Hydroxybenzoic acid		6.94 (dd)	7.50 (dt)	6.92 (dt)	7.84 (dd)	
9	3-Phenylpropionic acid	7.22 (d)	7.27 (t)	7.20 (t)	7.27 (t)	7.22 (d)	2.60 (t), 2.87 (t)
10	*m*-Chlorobenzoic acid	7.95 (s)		7.60 (d)	7.46 (t)	7.90 (d)	
11	*p*-Chlorobenzoic acid	7.97 (pd)	7.50 (pd)		7.50 (pd)	7.97 (pd)	

[a] Referenced to the solvent peak of acetonitrile (=2.00 ppm).
[b] Multiplicities of the signals: s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet; pd, pseudo doublet; pt, pseudo triplet.
[c] Assignment may be interchanged.

delay. Solvent suppression was achieved by using the pulse sequence mentioned below.

2.6. LC–NMR

The pseudo two-dimensional (2D) NMR chromatograms of the standard and the extract were recorded on a Bruker AMX 600 spectrometer at 600.13 mHz with a $^{1}H-^{13}C$ inverse probe (4 mm I.D. of measuring cell with a detection volume of 120 μl). Solvent suppression was achieved using a one-dimensional version of the Noesyprtp pulse sequence (Bruker) with presaturation during relaxation delay and mixing time on two frequencies simultaneously. The pseudo 2D NMR chromatogram was recorded within 64 rows, each row consisting of 128 free induction decays (FIDs) (sweep width: 14 706 Hz) collected into 32 000 data points with a relaxation delay of 15 s and a flip angle of 90°. This leads to a time resolution of 16 min per row. Data were multiplied with an exponential function in f1 (LB=1 Hz) and processed with the XWINNMR software.

3. Results

3.1. GC–MS

The gas chromatogram of the leachate extract is shown in Fig. 1. It illustrates the complexity of such a sample. GC–MS analyses allowed tens of com-

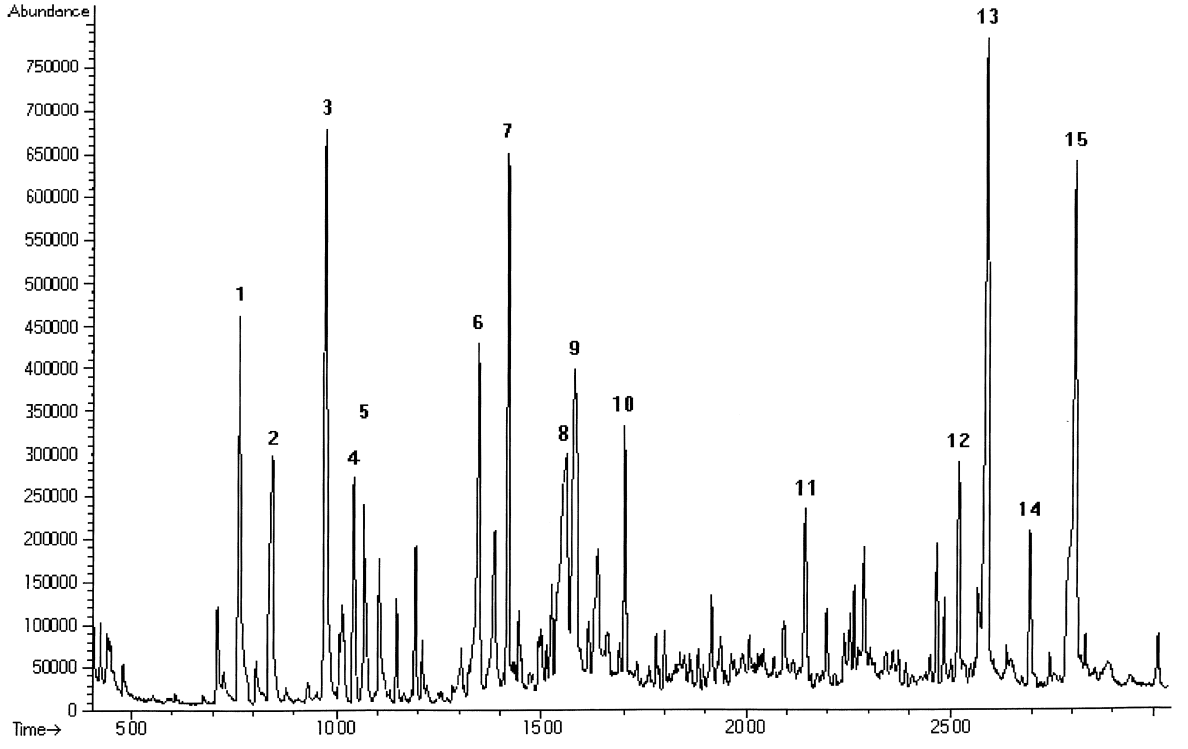

Fig. 1. Chromatogram of LiCrolut EN extraction of leachate (January 1996). Peaks: 1=ethanol, 2-butoxy-; 2=1,3-propanediol, 2,2-dimethyl-; 3=phenol; 4=2-propanol, 1-(2-methoxypropoxy)-; 5=2,2′-azobis(2-methylpropanenitrile); 6=1,3-pentanediol, 2,2,4-trimethyl-; 7=ethanol, -(2-butoxyethoxy)-; 8=caprolactam; 9=1,3-propanediol, 2-ethyl-2-(hydroxymethyl)-; 10=hydrocarbon; 11=benzenesulfonamide, 4-methyl-; 12=phenol, 2,2′-methylenebis-; 13=phenol, 4,4′-methylenebis-; 14=phenol, 4,4′-(1-methylethylidene)bis-; 15=not identified. Time scale in min.

pounds to be detected both with SPE and SPME methods; some of the identified chemicals, chosen on the basis of abundance and toxicity, are shown in Table 4, where the SPE/SPME phases capable of extracting them are also indicated. As it appears from this table, the results from the different extractive columns are not superimposible. As expected, C_{18} is able to extract a good number of non-polar compounds. LiChrolut can extract polar compounds, such as benzoic acids. However, these polar compounds are better detected under other instrumental conditions (see below). SPME is an interesting extractive procedure, because it extracts many compounds, and presents convenient characteristics, such as quickness and elimination of solvent [15].

The number of peaks counted in a gas chromatogram is not a sufficient parameter; in the case of qualitative analysis, another useful parameter is the number of chemicals identified [16]. The number of detected and identified compounds can vary with the extractive method. Table 5 summarizes the fraction of compounds identified (%) with the different extraction methods.

In Fig. 2 the number of identified substances extracted by the different phases was plotted depending on their functional group; the histogram of this figure gives a general overview on the compound classes identified in the leachate sample found in the leachate sample.

3.2. LC–MS

3.2.1. LC–DAD

In Fig. 3, typical LC chromatograms of the acidic components of the effluent sample at different detection wavelength are shown. From these chromatograms it became obvious that the separation efficiency of the LC method was insufficient for this type of application. Furthermore, UV-inactive compounds such as aliphatic carboxylic acids or sulfates cannot be detected. Therefore, the LC–DAD method is not suitable for the analysis of such complex mixtures. Nevertheless, for the confirmation of compounds which were identified or proposed by other methods (LC–MS, NMR or LC–NMR), reference compounds were run under the same conditions and their UV spectra compared with the tentatively identified compounds. (The UV spectra are available upon request).

3.2.2. Thermospray LC–MS

The leachate sample extracted under acidic conditions as described above was also analyzed by LC–MS using thermospray ionization (TSP). With this approach, 11 organic acids could be identified in the sample, as summarized in Table 6. The identification is corroborated by comparison with reference compounds and by LC–NMR. In this table, all ions observed in the negative and positive ion mode with an abundance of $>20\%$ (relative to the base peak) as well as their structures are summarized. In addition, pK_a values of these acids are listed.

In general, with these acidic compounds negative ions are preferentially formed, with the exception of phenylacetic and phenylpropionic acid, where positive ions are more abundant than negative ones by a factor of ten. This reflects the relatively high pK_a values of these compounds (p$K_a>4$).

As expected, the TSP mass spectra show abundant quasi-molecular ions and cluster ions in both ionization modes. Under negative ion conditions, $[M-H]^-$ and cluster ions formed with the buffer, ammonium formate, i.e. $[M+COOH]^-$, are predominantly formed. With most compounds, little fragmentation is observed. Intense fragments are only found with phthalic acid and *p*-chlorobenzene sulfonic acid. With the former compound loss of a water molecule leads to ionized phthalic acid anhydride (*m*/*z* 148) which is not observed with the other isomers (*ortho* effect). In the case of *p*-chlorobenzene sulfonic acid, loss of chlorine leads to the base peak. The weak acids phenylacetic acid and phenylpropionic acid show more abundant positive than negative ions under TSP conditions, where the $[M+NH_4]^+$ ion dominates the spectrum. These ions are also intense in the spectra of the isomeric phthalic acids and benzoic acid, although with these compounds more negative than positive ions are formed.

The results demonstrate that the LC–MS method is suited to the identification of polar, acidic compounds in leachate samples from industrial waste disposal sites. The identification is based on the abundant $[M-H]^-$ and $[M-COOH]^-$ ions under negative ion and $[M+NH_4]^+$ ions under positive ion conditions and the retention time. If chloro sub-

Table 4
Selected compounds retrieved in the leachate with the different extractive phases

Identified compounds	Carbopack	C_{18}	LiChrolut	PDMS 100 μm
1-Hexanol, 3,5,5-trimethyl-				●
1,3-Pentanediol, 2,2,4-trimethyl-		●	●	
1,3-Propanediol, 2,2-dimethyl-		●	●	
1-Propanol, 2-methyl-				●
Ethanol, 1-(2-butoxyetoxy)-		●	●	
2-Propanol, 1-ethoxy-		●	●	
Ethanol, 2-(2-butoxyethoxy)-	●			
Ethanol, 2-butoxy-		●	●	
2-Hexen-1-ol		●	●	
2,4-Pentanediol, 2-methyl-		●	●	
2-Propanol, 1-(2-metoxypropoxy)-		●		
Benzenemethanol,α,α-dimethyl			●	
Phenol, 2,2′-(methylene)bis-		●	●	
Phenol, 2,3-dimethyl-		●		
Phenol, 2,5-dimethyl-	●			
Phenol, 2,6-bis(1,1-dimethylethyl)-	●			
Phenol, 2,6-dimethyl-		●	●	
Phenol, 2,4,6-trimethyl-				●
Phenol, 3,4,5-trimethyl-				●
Phenol, 2-(1-methylethyl)-	●	●	●	●
Phenol, 2-ethyl-	●	●	●	●
Phenol, 2-methyl-	●	●	●	
Phenol, 2-[(4-hydroxyphenyl)methyl]-	●			
Phenol, 4,4′-(1-methylethylidene)bis-	●	●		
Phenol, 4,4′-(methylene)bis-	●	●		
Phenol, 4-chloro-			●	
Phenol		●	●	●
o-Hydroxybiphenyl	●			
Phenol, 4-(1,1-dimethylethyl)-	●			
2H-Indol-2-one, 1,3-dihydro-		●	●	
2H-Indol-2-one, 1,3-dihydro-1-methyl-	●			
Acridine		●		
Aniline			●	
Caprolactam		●	●	
2-Pyrrolidinone, 1-methyl-		●	●	
Benzenamine, 3-methyl-		●		
Formamide, N,N-dimethyl-		●	●	
Tributylamine	●			
Benzensulfonamide, N-butyl-		●	●	
Methane, tris(methylthio)-				●
Benzensulfonamide, 4-methyl-			●	
Benzensulfonamide, 2-methyl-			●	
2(3H)-Benzothiazolone	●	●		
Benzothiazole, 2-(methylthio)-	●	●	●	
Benzene, 1,2,3-trimethyl-				●
Benzene, 1,2-dimethyl-				●
Benzene, 1,4-dimethyl-				●
Ethylbenzene				●
Toluene			●	●
Pentadecane		●		
Tridecane				●
Naphthalene				●
Naphthalene, 1-methyl-				●
2-Cyclohexen-1-one, 3,5,5-trimethyl-		●		
Cyclohexanone		●	●	
2-Butanone				●
2-Hexanone				●
Camphor				●
Cyclohexanone, 3,3,5-trimethyl-				●

Table 5
Extraction and identification results with different extraction procedures

Extraction phase	Peak number	Identified peaks	Identification (%)
Carbopack B	98	44	45
Isolute C_{18}	101	60	60
LiChrolut EN	90	58	64
PDMS 100 μm	65	26	40

stituents are present, they facilitate the structure assignment. For an unambiguous identification, characteristic fragments are desirable. With thermospray ionization mass spectrometry such fragments could be produced by collision-induced fragmentation using the MS–MS technique which, unfortunately, was not available for this study. Very important structure information may also be obtained from LC–NMR, as discussed in Section 3.3.

3.3. NMR

The NMR spectrum (Fig. 4) gives a good overview of the complete organic pollution of the extract. In the high-field shift region, aliphatic compounds with straight and branched chains are indicated, whereas the aromatic part of the spectrum is dominated by the strong signals (7.62 and 7.75 ppm) of an *ortho*-disubstituted aromatic compound.

3.3.1. LC–NMR

The contour plot of the on-flow NMR chromatogram of the extract is shown in Fig. 5. In the aliphatic part, the resolution of the NMR information is relatively poor because the protons of many acidic aliphatic compounds, for instance carboxylic acids or sulfates (which have of course different retention times), resonate at nearly the same chemical shift values (0.9, 1.1, 1.3, 1.5 and 2.3 ppm). As a consequence, broad tails are observed along the chromatographic axis. Furthermore, the residual signals of the solvent acetonitrile and its ^{13}C satellites as well as the signals of propionitrile (an impurity of acetonitrile) make the analysis of this part of the NMR chromatogram more difficult.

On the other hand, the aromatic part of the NMR chromatogram is better resolved both in the NMR chemical shift and the chromatographic axis.

As can be seen from the time slices of the NMR chromatogram (Fig. 6) the spectra are rather simple and can be analyzed without use of further techniques. Eight organic acids could be identified in the NMR chromatogram on the basis of their retention times and by comparison with the chemical shift values of the reference compounds (Table 3). It is interesting that, at the beginning of the NMR chromatogram, besides the aromatic carboxylic acids (*p*-chlorobenzene sulfonic acid, isomeric phthalic acids, benzoic acid), some acidic aliphatic compounds also elute which, however, could not be identified up to now.

4. Discussion and conclusion

Leachate samples from industrial waste disposal sites may contain a large variety of anthropogenic compounds and their transformation products covering a wide range of polarities. Thus the extraction methods have to be adapted to the chemical character of the samples. We tested some SPE and SPME techniques. The analyses performed with different extraction methods allowed the identification of many compounds and demonstrated that these techniques often provide complementary information. These results might be expected in the case of complex mixtures, when different procedures can give usually different results. Divinylbenzene columns presented the advantage to extract a good number of compounds of different chemical nature, polar and non-polar. They proved to be useful for successive GC–MS, LC–MS and LC–NMR analyses.

Different instrumental techniques have to be applied for the exhaustive identification of the compounds. In the present study, chemical instrumental analyses with different advanced methods have been used to obtain the maximum information, resulting in

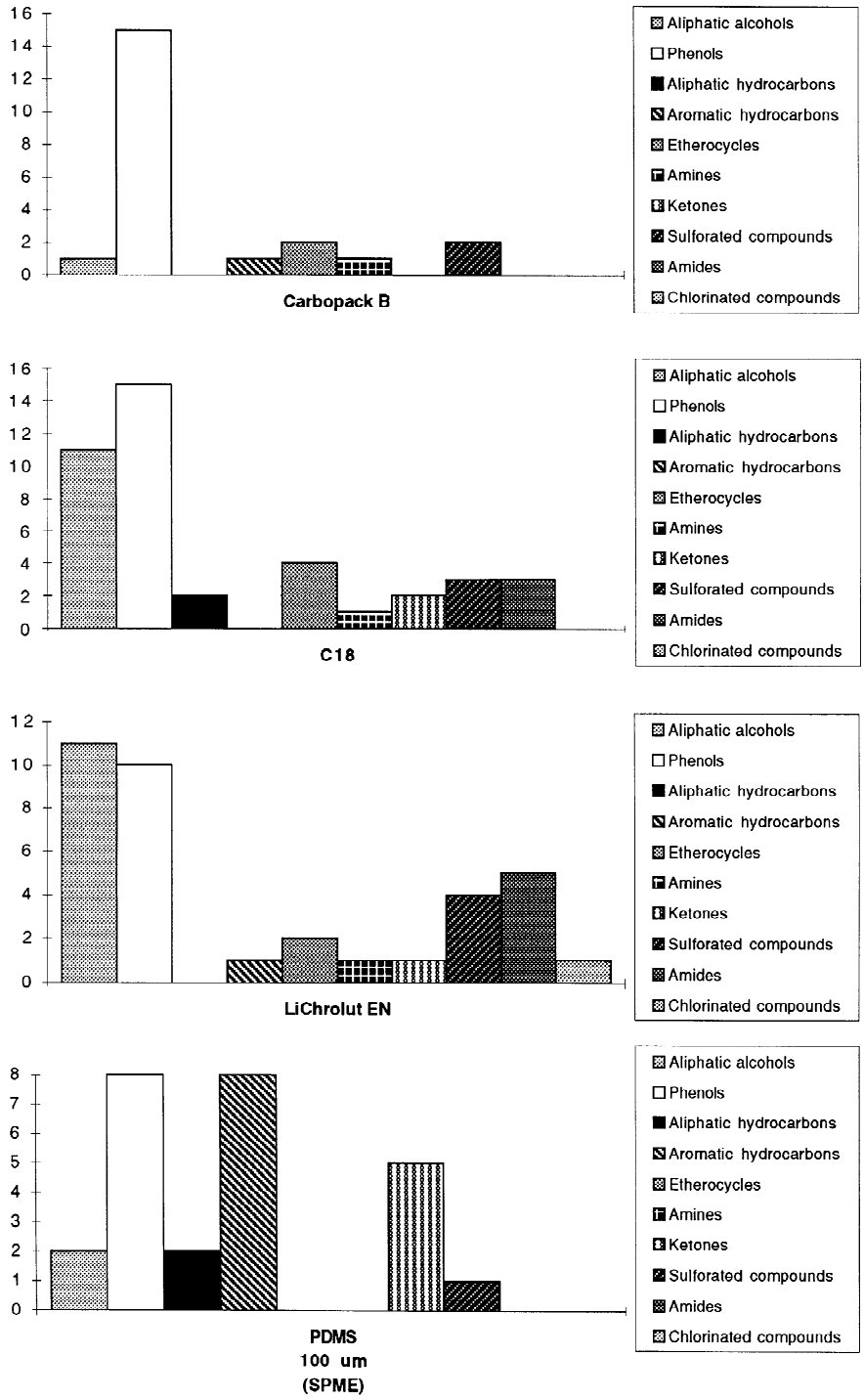

Fig. 2. Retention capacity of extractive phases for different chemical classes.

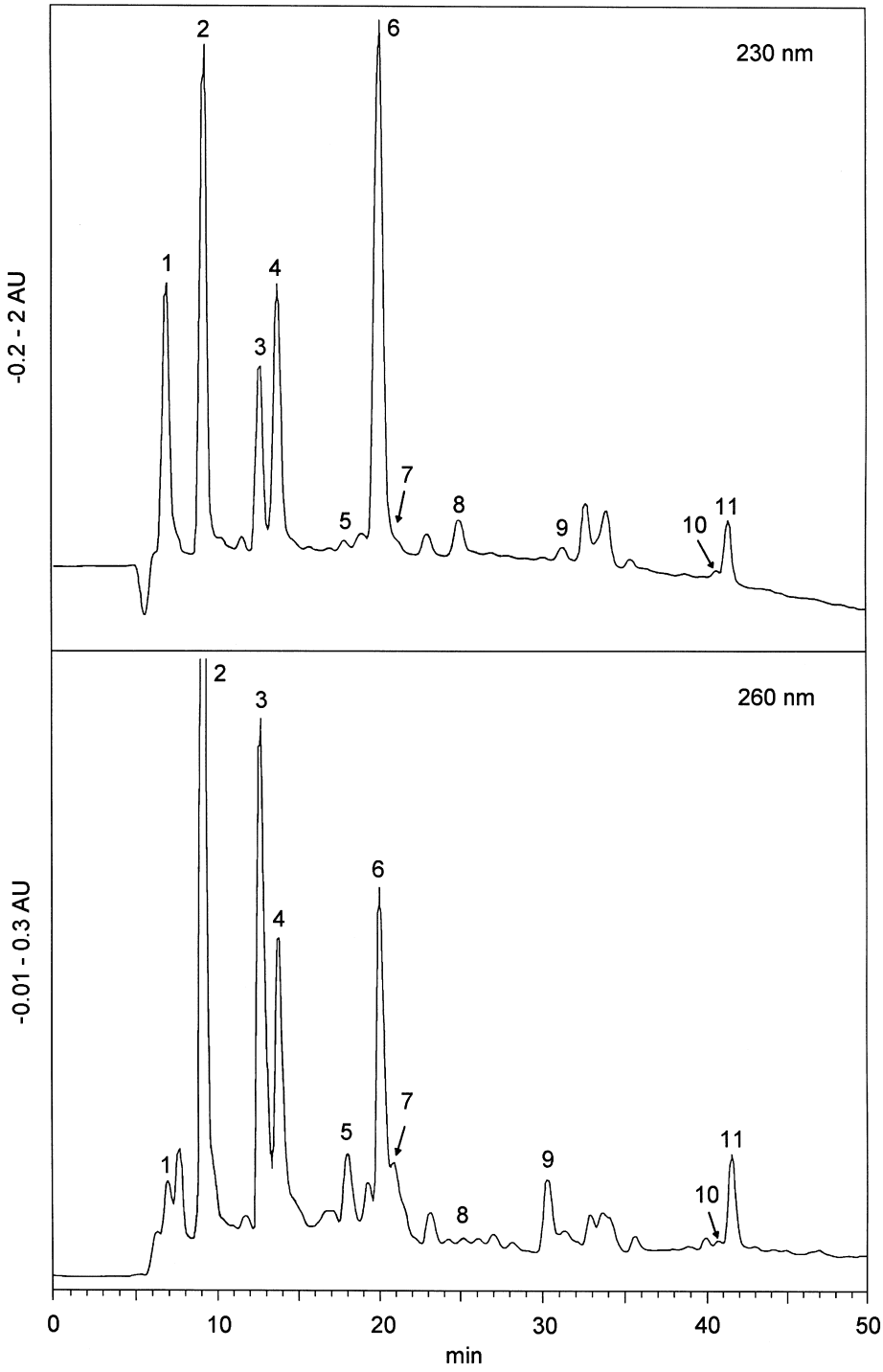

Fig. 3. LC chromatogram with photodiode array detection of the leachate sample (for peak assignment see also Table 3).

Table 6
Aromatic carboxylic acids identified in a leachate sample by LC–MS with thermospray ionization

No.	Compound	M_r	t_R (min)	Relative abundance (I)				pK_a
				Negative ions		Positive ions		
				100%	20%<I<100%	100%	20%<I<100%	
1	*p*-Chlorobenzenesulfonic acid	192	5.8	156 $[M-Cl-H]^-$	191 $[M-H]^-$ 50%			0.7[a]
2	Phthalic acid	166	8.7	165 $[M-H]^-$	148 $[M-H_2O]^-$ 20%	184 $[M+NH_4]^+$	167 $[M+H]^+$ 80%	2.89
3	Terephthalic acid	166	12.5	165 $[M-H]$	211 $[M+COOH]^-$ 80%	184 $[M+NH_4]^+$		3.51
4	Isophthalic acid	166	14.0	211 $[M+COOH]^-$	165 $[M-H]^-$ 30%	184 $[M+NH_4]^+$		3.54
5	Phenylacetic acid	136	17.3	181 $[M+COOH]^-$		154 $[M+NH_4]^+$		4.28
6	Benzoic acid	122	20.3	167 $[M+COOH]^-$		140 $[M+NH_4]^+$		4.19
7	*o*-Chlorobenzoic acid	156	21.6	201 $[M+COOH]^-$	155 $[M-H]^-$ 30%			2.92
8	*o*-Hydroxybenzoic acid	138	25.0	183 $[M+COOH]^-$				2.97
9	3-Phenylpropionic acid	150	30.7	195 $[M+COOH]^-$		168 $[M+NH_4]^+$		4.17
10	*m*-Chlorobenzoic acid	156	41.0	201 $[M+COOH]^-$	155 $[M-H]^-$ 30%			3.82
11	*p*-Chlorobenzoic acid	156	41.5	201 $[M+COOH]^-$	155 $[M-H]^-$ 30%			3.98

[a] pK_a of benzenesulfonic acid=0.7.

complementary data. Furthermore, several compounds have been detected using two different techniques, affording a more reliable identification.

For volatile thermally stable compounds, GC–MS is the method of choice due to its high separation efficiency, its specificity, sensitivity and the availa-

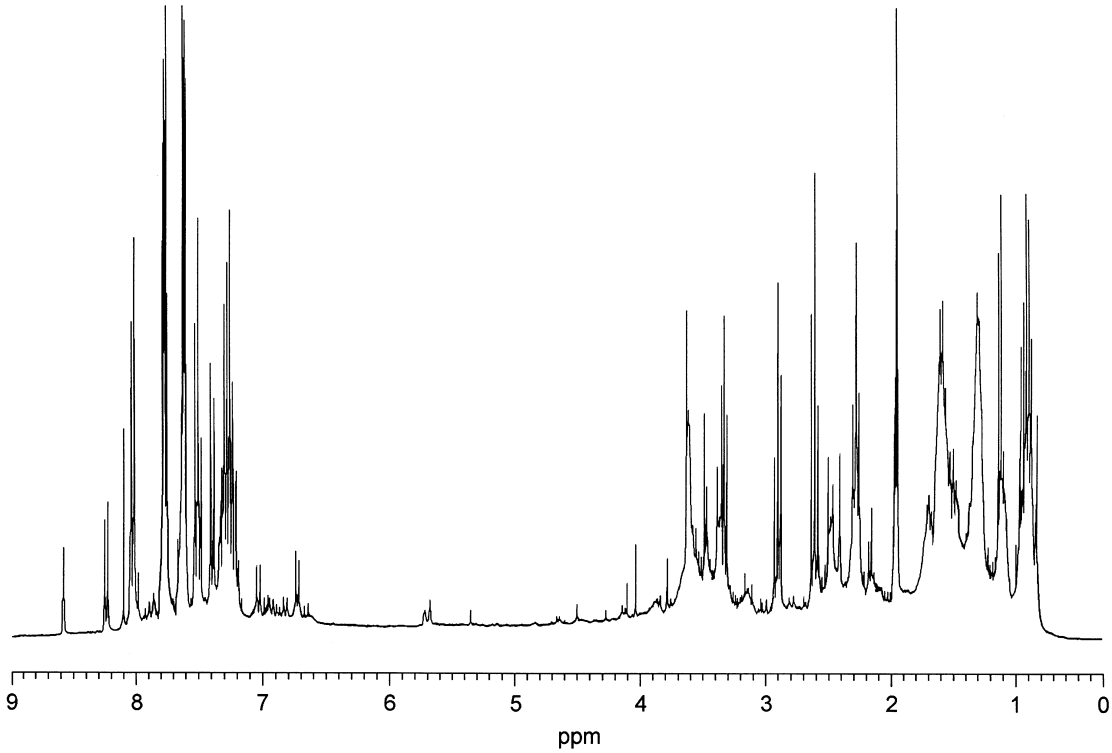

Fig. 4. 300 mHz ^{1}H-NMR spectrum of the leachate sample.

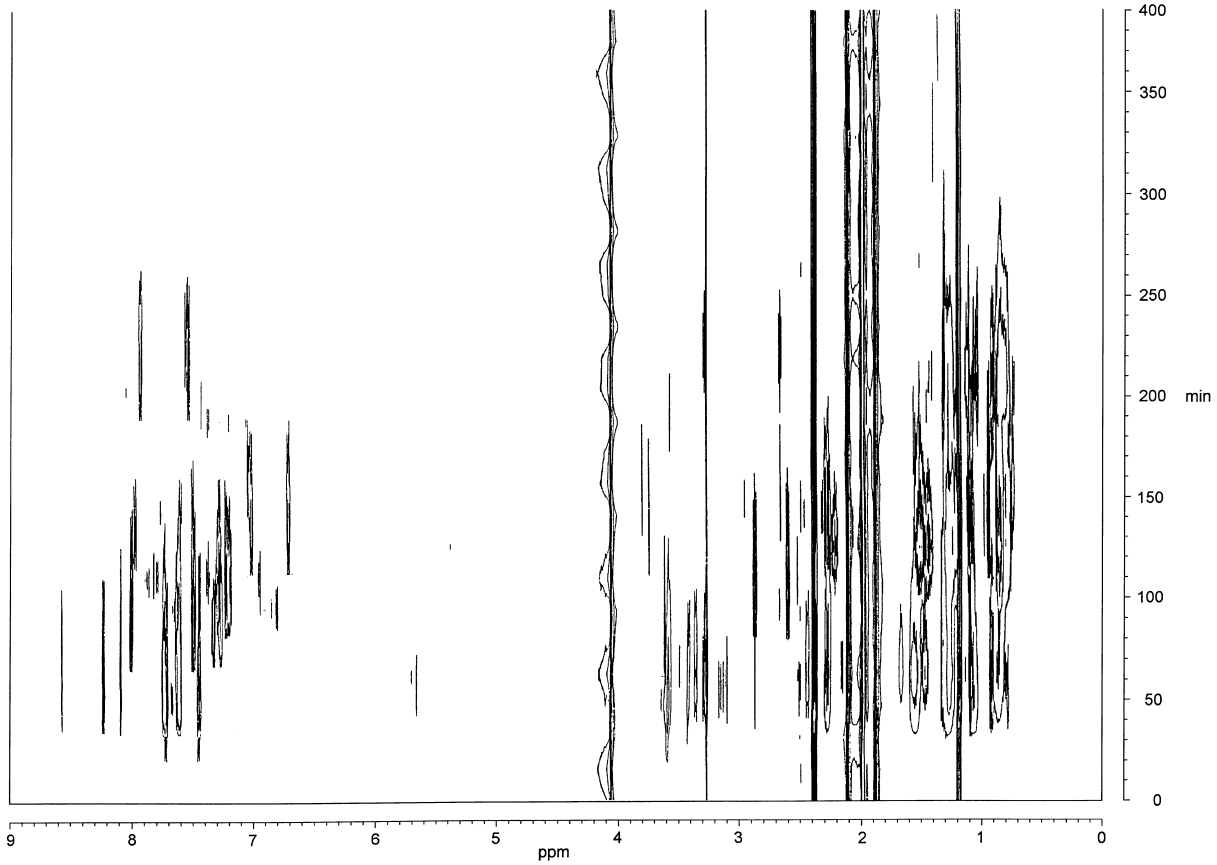

Fig. 5. Contour plot of the on-flow NMR chromatogram of the leachate sample.

bility of libraries containing hundreds of thousands of mass spectra.

SPME may represent an interesting technique to be coupled to GC–MS for identification of pollutants.

However, with GC–MS many polar pollutants can escape detection. In this study, we also devoted particular attention to water soluble compounds, whose extraction and instrumental analysis is more difficult, and, as a consequence, their chemical characterization requires more research. Indeed these substances commonly correspond to the major amount of the total organic carbon (TOC) present in the leachate samples [17]. In the literature there are more and more numerous indications that some of these pollutants are of concern on an environmental and toxicological point of view; for example surfactants, aromatic sulfonates, dyes etc. [18–20].

For polar compounds, both LC–MS and LC–NMR, which provide complementary analytical information, may be successfully employed. While the former technique gives information on the molecular mass, and eventually on structural moieties, considering diagnostic ions, the NMR method gives more structural information.

However, in complex mixtures this information is not always resolved. In this case, the necessary resolution of information can be achieved by coupling LC with NMR.

To facilitate the identification, we preferred to clean the extract using preliminary extraction of excess neutral and basic compounds.

Unfortunately, a library of mass spectra for LC–MS is not yet available, and each laboratory has to build up its own library.

LC–NMR is a recent technique which has been

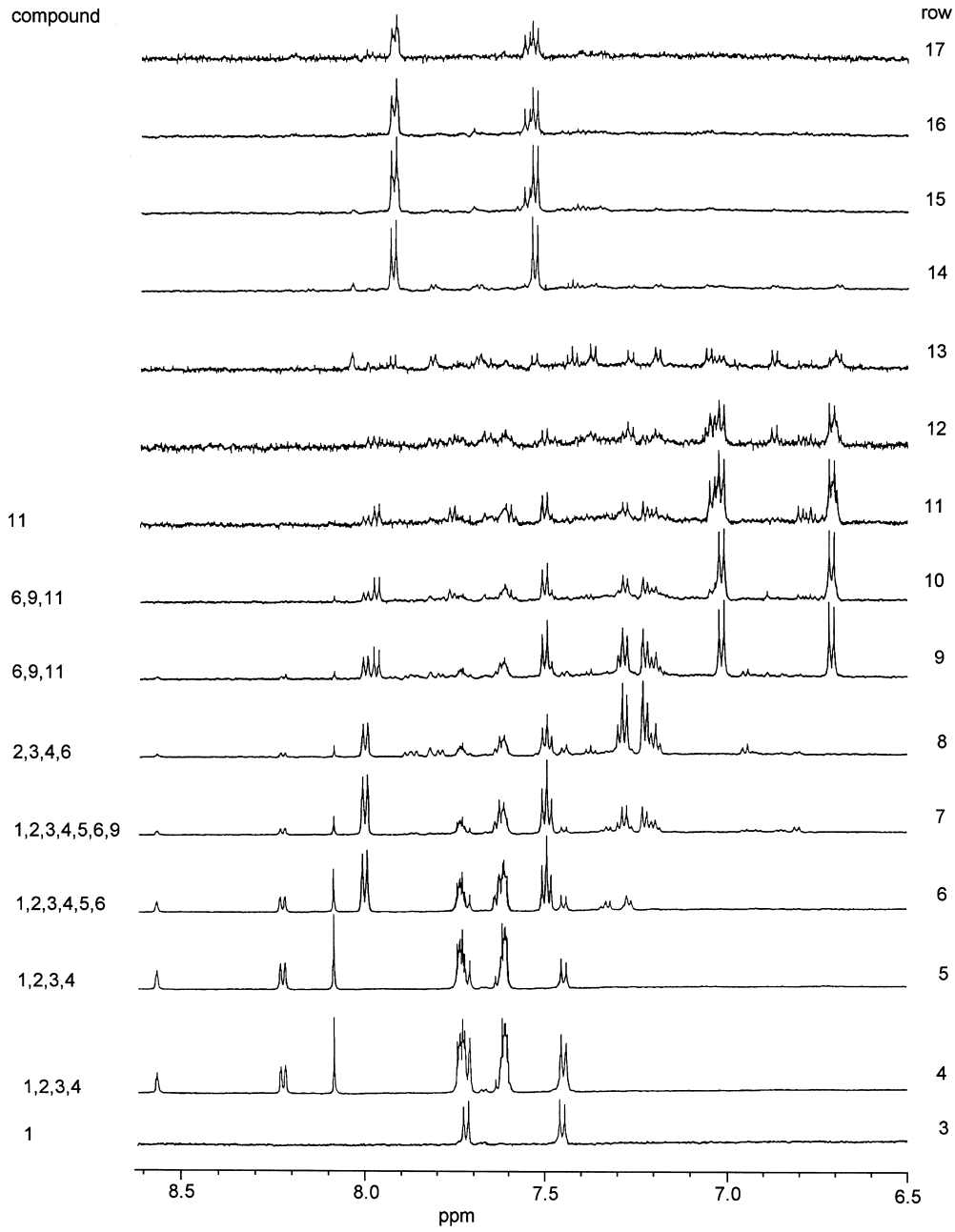

Fig. 6. Time slices of the NMR chromatogram of the leachate sample (chemical shift region of the aromatic protons).

used in a very limited number of cases for environmental analysis [21–24]. This technique is not yet a routine method, because it requires expert scientists and is expensive. In this study, it proved to be informative and useful for the identification of pollutants. Reference spectra are available. Although ultratrace analysis is not possible with this hyphenated technique, it is well suited for waste analysis where rather high concentrations of pollutants are present.

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