

This is a draft manuscript to be presented at
the 20th Roland Frei Memorial Symposium on Environmental
Analytical Chemistry. Strasbourg, France,
April 17-20, 1990, and the contents are subject to change.

CHARACTERIZATION OF GROUNDWATER
CONTAMINANTS USING ON-LINE THERMAL
DESORPTION-GC-MS

by

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April 1990
NWRI Contribution #90-70

ABSTRACT

The analysis of groundwater contaminated by municipal or industrial leachates is very time consuming. It is not rare to find more than one hundred peaks in a chromatogram of a dichloromethane extract, yet, it often represents only a fraction of the dissolved organic carbon. The contaminants which constitute the greatest threat to aquifers are those which in addition to being toxic are highly soluble in water and are thus very mobile. It is those very contaminants that are the least well served by the routine extraction in solvents such as dichloromethane.

By adsorbing the groundwater sample on a quartz tube filled with graphitized charcoal (Carbotrap, Carbotrap C) and thermally desorbing it in a Envirochem Unacon 810 unit directly interfaced with a GC-MSD, it was possible to detect the major groundwater contaminants originating from several types of industrial landfills. Compounds such as aniline, dioxane, and phenols and were measured simultaneously without any sample preparation. The results were compared to those obtained by dynamic thermal stripping and by conventional solvent extraction followed by GC-MS. This method is much more cost effective since it requires only a few minutes of the analyst's time for the introduction of the sample. It is also superior for the analysis of water soluble compounds which are poorly extracted into solvents. The tentative identification of unknowns using computerized library searches is fully automated, and quantitation is also possible with the addition of an internal standard.

RÉSUMÉ

L'analyse des eaux souterraines contaminées par des lexiviats de déchets industriels et municipaux est longue et coûteuse. Il n'est pas rare de trouver plus d'une centaine de pics dans un chromatogramme d'un extrait au dichlorométhane, pourtant ceci ne représente qu'une fraction du carbone organique dissout. Les contaminants qui constituent le plus grand danger pour les aquifères sont ceux qui en plus d'être toxiques sont solubles dans l'eau et sont donc très mobiles. Ce sont ces derniers qui sont le moins bien servi par les méthodes d'extraction conventionnelles par les solvants tel que le dichlorométhane.

En absorbant un échantillon d'eau souterraine dans un tube de quartz rempli de charbon graphitisé (Carbotrap, Carbotrap C) et en le désorbant thermiquement dans une unité Envirochem Unacon 810 couplée directement à un CG-DMS, il a été possible de détecter les principaux contaminants provenant de divers types de sites d'enfouissement industriels. Des composés tels que l'aniline, la dioxane et les phénols ont été mesurés simultanément sans aucune préparation des échantillons. Les résultats ont été comparés à ceux obtenus par le dépouillement dynamique thermique et par l'extraction conventionnelle par les solvants suivi de CG-DMS. Cette méthode est plus économique puisqu'elle requiert seulement quelques minutes de la part de l'analyste pour l'introduction de l'échantillon. Elle est aussi supérieure pour l'analyse des composés peu extraits par les solvants. Les essais d'identification des inconnus utilisant les algorithmes de comparaison avec une bibliothèque informatisée de spectres est entièrement automatisée et la quantification est aussi possible grâce à l'ajout d'un étalon interne.

MANAGEMENT PERSPECTIVE

This paper describes a new method for the analysis of heavily contaminated groundwaters such as those found near industrial and municipal landfill site. The technique is less labor intensive than the commonly utilised methods and focusses on analytes that are commonly found in landfills. Results obtained with EPA priority pollutants are shown as a means of comparison with other analytical methods. The results obtained with several groundwater samples from a variety of site in Canada are also given: Sydney N.S., former coke oven site; Ville-Mercier Que., industrial dumpsite; Elmira Ont., former industrial waste lagoons; Guelph Ont., municipal landfill leachate.

PERSPECTIVE - GESTION

Ce rapport décrit une nouvelle méthode d'analyse des eaux souterraines fortement contaminées telles que rencontrées aux abords des sites d'enfouissement industriels et municipaux. Cette technique demande moins de main d'oeuvre que les méthodes utilisées couramment et ciblée sur les composés que l'on retrouve communément dans les sites d'enfouissement. Les résultats obtenus avec les composés prioritaires de l'APE américaine sont présentés pour fin de comparaison avec les techniques existantes. On présente aussi les résultats obtenus dans plusieurs sites canadiens: ville de Sydney, N.E., ancien four à coke; Ville-Mercier Qué., dépotier industriel; Elmira, Ontario, anciennes lagunes de déchets industriels; Guelph Ont., lexiviat de site d'enfouissement municipal.

INTRODUCTION

Characterization of groundwater contaminated with industrial wastes contained in landfills is a very difficult task, because usually, several hundred different chemicals which were either products or by products are co-disposed over a very long period of time. Most commonly, solvent extraction followed by GC-MS analysis is used in the initial characterization, where a tentative estimate is made of the identity and the approximate concentration of the chemicals dissolved in the groundwater [1]. Other broad monitoring parameters such as total phenols or dissolved organic carbon (DOC) are also measured. Less than ten percent of the DOC is usually accounted for by the total of chemicals found by the U.S. EPA methods 624 and 625 [2], the rest of the DOC must be composed of non-volatile or non-extractable compounds such as humic and fulvic acids. Techniques such as LC-MS have been employed to analyse poorly extractable compounds. Unfortunately this technique is not as widely available as GC-MS and thus another alternative was sought to characterize highly contaminated samples.

A method that would allow for rapid screening of samples would help reduce the astronomical costs of hazardous waste site assessment. Sample preparation is the most time consuming and labour intensive part of a typical GC-MS analysis. Volatile analysis is done by using either headspace or purge-and-trap techniques. Experiments were conducted to investigate the possibility of extending the range of contaminants amenable to this simpler technique. Aqueous samples were purged with nitrogen in an Envirochem Dynamic Thermal Stripper which is effectively a purge and trap system at elevated temperature. This method has its limitations especially for highly water soluble compounds. An alternate method whereby a small amount of aqueous sample was directly injected onto a solid sorbent and thermally desorbed

into a GC-MS was also investigated. The technique of adsorption-thermal desorption (ADS) has been applied to the analysis of organic contaminants in air [3] and in water, but for volatiles only [4]. Thermal desorption has also been used for solid samples [5]. This is an attempt to extend ADS to the analysis of semi-volatiles in aqueous samples.

METHODS

1. Dynamic Thermal Stripping (DTS).

Aqueous samples (10 mLs) were purged for 30 min. in an Envirochem Dynamic Thermal Stripper (Envirochem Inc. Route 896, Kemblesville PA 19347, USA). This unit is a purge and trap device which can be operated at elevated temperatures. The upper limit is the boiling point of the solvent. The oven was operated at 95°C, and the sorbent tube heater at 60°C. It is necessary to keep the sorbent tube heated to prevent the excessive condensation of water. The system is also equipped with make up gas to help entrain contaminant onto the sorbent and to evaporate the water. The sorbent tubes were 20 cm X 6mm diam. quartz tubes obtained from TR Associates filled with Carbotrap B (3 cm)and Carbotrap C (1.5 cm), (Supelco Canada, Oakville Ontario). After purging, the sorbent tube was dried with make-up gas only at 30 cc/min. for 10 min. The tube was then transferred to the tube desorber of the Unacon 810 and analysed as described below.

2. Adsorption on solid sorbent (ADS).

Alternately, the samples (100 uL) were injected directly onto the Carbotrap/Carbotrap C adsorbent in the sorbent tube described above. One uL of a 100 ug/mL solution of d-10-anthracene in

methanol was also added as an internal standard. The sample tube was dried by passing a nitrogen at 30 cc/min. for 5 min. while kept in a heated sleeve at 50°C.

3. Thermal desorption- GC-MS

The sorbent tube from step one or two was transferred to the thermal desorption chamber of the Unacon model 810 purge and trap (Envirochem Inc.) which was interfaced to a Hewlett-Packard model 5890-5970 GC-MS. The sample was desorbed by heating the tube rapidly to 350°C. The analytes were sequentially adsorbed and desorbed onto the Unacon internal traps packed with Tenax/Ambersorb/charcoal/glass beads, and then desorbed onto the analytical column (J&W DB-5, 30 m, 0.32 mm i.d., 1 µm film thickness). In one experiment, the Unacon internal trap packings were replaced with Carbosieve SIII, Carbotrap B and Carbotrap C (Supelco Canada Inc.) [6] and glass beads. The gas chromatograph was ramped from 35°C to 275°C at the rate of 10°/min. Mass spectral data were acquired from 45 to 450 a.m.u. at the rate of 1 scan/sec.

3. Standards

Priority pollutant base-neutral and acid standards were obtained from Bio-Scientific Lab Supplies (Mississauga, Ont.) as injection-ready mixtures. One µL of each mixture made in methanol was injected on the sorbent tube or in organic free water and then treated as described above for the samples.

RESULTS

DTS VS. ADS FOR EPA PRIORITY POLLUTANTS

Although priority pollutants are seldom the only major contaminants in a landfill, their analysis provides a good basis for comparison of analytical techniques. Chromatograms for standards spiked into water then purged using the DTS and standards injected directly onto sorbent tubes (ADS) are shown in figures 1 and 2 respectively. The range of molecular weights which could be determined using either technique is the same and comprises some of the volatiles and the more volatile fraction of the semi-volatiles as defined by the U.S. EPA. The polynuclear aromatic hydrocarbon (PAH) with a molecular weight of 202 was the last eluting compound in both chromatogram and its recovery was poor. The thermal limitation is mostly due to the numerous transfer lines within the system which cannot be heated beyond 250 °C, whereas the last PAH to be eluted using EPA method 625 requires a GC temperature of 295 °C.

There was a definite discrimination against the chlorinated phenols using the DTS. Acidification of the sample and addition of salt did not improve the recoveries. ADS allowed for the simultaneous recovery of nitrosamines and chlorinated phenols including pentachlorophenol. The reproducibility for both methods is listed in Table 1. ADS gave better recoveries for most of the analytes, and the results were also more consistent. More work will be necessary to improve the reproducibility of the method, although these results all fall within the U.S.EPA acceptance criteria [7]. It was found essential to ensure as complete as possible a removal of the water because although the DB-5 fused silica column is relatively unaffected by water, the ion source and the electron multiplier of the mass spectrometer are easily

damaged by large quantities of water vapour. The quantity of water left in the tube also seemed to have some effect on the efficiency of the thermal desorption.

It is also important to note that the total quantity of analyte was the same in both methods although the effective concentration range was lower for the DTS because the sample size is larger. It was found however that in most applications of severe groundwater contamination, detection limit was not important and most samples were diluted at least ten times when using the DTS.

ENVIRONMENTAL SAMPLES

The techniques of DTS and ADS-GC-MS were applied to various contaminated groundwater samples. Although the elution temperature range of the analytes amenable to those techniques was more limited than with solvent extraction, it was found that for groundwater contamination problems it would not be a serious disadvantage, because the contaminants which are of most concern are often the most water soluble, often the lower boiling ones, most of which were found to be amenable to this technique.

Samples were collected from groundwater monitoring wells at three industrial sites: Sydney (Nova-Scotia), Ville-Mercier (Quebec), Elmira (Ontario). These sites offer a wide range of contaminants, from coal tar and creosote, to chlorinated solvents and waste oils and finally wastes from pesticide and rubber antioxidant manufacturing. In addition, leachate collected from a municipal landfill (Guelph, Ontario) was also analysed.

Typical chromatograms from Sydney, Ville-Mercier and Elmira are shown in figures 3,4 and 5 respectively. The results for quantitative analysis for priority pollutants are listed in Tables 2,4,6 comparing the results obtained using DTS and ADS-GC-MS.

In general, DTS permitted the identification of a larger number of compounds than ADS, probably because of the larger sample size. However, the recoveries of the analytes were better using ADS, which gives a more accurate idea of the quantity of each contaminant present at the expense of the minor constituents which are masked by the larger peaks. Saturation of the analytical column was frequent using ADS. DTS effectively acts as a cleanup step, preventing the more soluble polar compounds from reaching the analytical column. However, if the more soluble components are the ones of greater interest, then ADS is definitely the technique of choice.

IDENTIFICATION OF UNKNOWNNS

As stated above, priority pollutants are seldom the major contaminants at a hazardous waste site. It is therefore important to have analytical techniques which can identify the largest number of contaminants with the minimal amount of effort. Both DTS and ADS offer such an alternative since they do not require any manual solvent extraction and the sample preparation is minimal. Because most samples are heavily contaminated, extracting large quantities is usually futile since it is necessary to dilute the extract in order not to overload the analytical column. Although an acid/base extraction could serve as a separation technique, experience has shown that in the case of heavily contaminated samples, the separation is usually incomplete, and thus of limited usefulness. In addition, it is more cost effective to recombine the fractions and do a single GC-MS analysis [7].

Also, in many groundwater monitoring wells, it is difficult to obtain enough sample to do all the required analyses. These techniques can be done from a single 25 mL vial. The total analytical time per sample is one hour. Computerized library searches can then be performed automatically. The results obtained then are independent of the sample introduction technique, and the reliability of the output strongly depends on the chemist's interpretation [1].

The data presented in tables 3, 5 and 7 was collated from computerized searches of the spectrum of an unknown against a 42,000 compounds NBS library. The samples were unknowns, therefore there was no true value to compare with. Within each table, the samples were collected from several monitoring wells on the same site. It was therefore not expected that 100% correlation be found between them. The percent purity obtained as a match with library spectra was showed as an indicator of the amount of confidence which can be placed in the library search. While a high number usually indicates that it is very likely that the compound was correctly identified, the converse is not always true as can be seen in the case of compounds for which standards were available (Table 7). One hundred percent indicates that the compound was in the correct retention time window as compared to a standard, the number below is the match that was obtained using comparison of spectra with the NBS library. This clearly demonstrates that a match of 70 % may be the correct identification. An arbitrary cut off point of 50% was used to indicate a relatively low confidence in the identification.

The spectrum is subtracted for background before searching, a procedure that allows the identification of partially resolved components. If the intensities of the two peaks are similar then this procedure can work well. However in the case where one component is a lot smaller, or if they have many mass spectral

peaks in common, the subtraction procedure does not work because some essential peaks are removed from the spectrum before searching. Low intensity peaks are in general not easily identified because the mass spectrum obtained is often partial, with some of the characteristic peaks, such as a low intensity molecular ion, absent.

Low resolution mass spectrometry is also relatively poor at distinguishing between isomers, regardless of the mode of introduction of the samples. Only with comparison with authentic standards is it then possible to arrive at a correct identification.

The correlation between the results obtained by DTS and ADS for selected samples are listed in table 9. In general, most of the compounds found using DTS were also found by ADS. The converse is not true mainly because of the fact that water soluble compounds such as phenols and acids cannot be purged even at higher temperature. It is interesting to note that some matrix effects may be very important. It was surprising to get relatively good recovery for phenol and dimethyl phenol using the DTS since the standards had not been recovered; this difference may be due to the very large concentration of phenol in the Sydney samples. For this sample, only 100 μ L was used for the DTS (and diluted to 10 mLs).

For Sydney, the results of the analysis of coal tar by ADS were also reported. Most of the compounds identified in the groundwater samples did seem to originate from the coal tar. However many more PAHs and aromatic heterocyclic compounds were found in the tar than in the samples. One of the reasons is that the aqueous solubility of PAHs is inversely proportional to their molecular weight. They are therefore less important as groundwater contaminants since they tend to adsorb to soils and not migrate very far [8,9]. It is a very important point to consider when looking at the applicability of the technique for

groundwater contamination: the inability to measure high m. wt. compounds is not crucial.

The Ville-Mercier dumpsite was known to have received waste oils and chlorinated compounds, typical of the petrochemical industry in the Montreal area in the early seventies. This analysis confirms these suspicions. Analysis of some non-aqueous phase liquid found in one of the monitoring wells also revealed the presence of polychlorinated biphenyls. The ADS techniques allowed the identification of up to pentachlorobiphenyls. None of the aqueous samples analysed contained measurable amounts of PCBs. Trace levels had however been identified at the site over the years. Again, their poor solubility in water accounts for the fact that they are not the major aqueous contaminants.

The results obtained from the Guelph municipal landfill leachate demonstrate the complementarity of the two methods. Indeed, ADS correctly identified the aliphatic carboxylic acids as the major contaminants of the landfill (total > 8,000 mg/L measured independently) [10]. This of course did tend to overload the analytical column and overshadow many of the other contaminants present. The chromatogram (fig 6) obtained by ADS was somewhat better resolved and allowed the identification of numerous naturally occurring compounds such as terpenes, as well as some aromatic hydrocarbons commonly found in petroleum products which have been identified in municipal landfills [2,11].

The samples from the Uniroyal site in Elmira revealed a series of chemicals which were very typical of the products of the plant which are rubber additives and pesticides. In this case, only ADS was used, but the results were compared with conventional solvent extraction followed by GC-MS. These results are discussed in detail elsewhere [12], but in general the correlation between the two analyses were good. ADS allowed for the identification of some water soluble compounds such as acetic acid, morpholine and

dithiane which were not extracted into dichloromethane, yet were major components in the groundwater.

CONCLUSIONS

The analysis of severely contaminated ground waters for organic contaminants can be done very efficiently by using adsorption followed by thermal desorption GC-MS. Alternately, dynamic thermal stripping can be used for less contaminated samples with the restriction on the recovery of water soluble components. Although the system is limited to compounds eluting below 250°C, this is not crucial for many groundwater contaminants since high molecular weight PAHs are not very water soluble and thus are very minor components in the mixture. Several different types of contaminated sites were examined and the results obtained were consistent with the expected. This type of analysis can be used for screening a large number of samples at a fraction of the time necessary for the currently used methodologies. There is room for improvement in the accuracy obtained with library searches, but this is independent of the sample introduction mode. In the future, databases of contaminants typically found at landfill could reduce this uncertainty.

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Table 1 Analysis of EPA Priority Pollutants by DTS and ADS.

COMPOUNDS	Mass	DTS (n=3)				ADS (n=5)			
		Design	AVG	SD _{DEV}	%RSD	Design	AVG	STD DEV	%RSD
		conc				conc			
		mg/L				mg/L			
N-Nitrosodimethyl amine	74	0.02	nd			2	2.65	1.73	65.3
Phenol	94	0.06	nd			6	6.06	1.66	27.3
Bis-2-chloroethyl ether	93	0.02	0.005	0.004	76.2	6	1.53	0.45	29.2
2-Chlorophenol	128	0.05	0.001	0.002	141.4	5	3.43	1.64	47.9
1,3-Dichlorobenzene	146	0.02	0.011	0.002	15.4	2	1.37	0.65	47.8
1,4-Dichlorobenzene	146	0.02	0.008	0.002	28.4	2	1.49	0.91	61.3
1,2-Dichlorobenzene	146	0.02	0.011	0.001	6.4	2	1.34	0.83	61.5
Bis-2-chloroisopropyl ether	121	0.02	0.010	0.006	57.1	2	1.32	0.46	34.8
N-nitrosodi-n-propylamine	70	0.02	0.055	0.030	53.6	2	12.33	9.33	75.7
Hexachloroethane	117	0.02	0.000	0.001	141.4	2	1.07	0.52	48.7
Nitrobenzene	123	0.02	0.009	0.006	71.3	2	1.70	0.70	40.9
Isophorone	82	0.02	0.004	0.005	130.0	2	1.98	0.78	39.2
2-Nitrophenol	139	0.05	nd			2	3.74	2.70	72.2
2,4-Dimethyl phenol	122	0.05	0.014	0.011	82.2	5	2.82	1.25	44.2
Bis-2-chloroethoxy methane	93	0.02	0.003	0.002	70.8	5	0.97	0.52	53.3
2,4-Dichlorophenol	162	0.05	0.002	0.002	141.4	5	3.68	1.05	28.5
1,2,4-Trichlorobenzene	180	0.02	0.007	0.002	22.5	2	1.45	0.58	40.1
Naphthalene	128	0.02	0.011	0.000	0.4	2	1.39	0.65	47.2
Hexachlorobutadiene	225	0.02	0.008	0.001	11.2	2	1.07	0.57	53.6
4-Chloro-3-methyl phenol	107	0.25	0.040	0.056	141.4	25	25.21	4.00	15.9
2,4,6-Trichlorophenol	196	0.05	0.001	0.002	141.4	5	2.87	1.41	49.2
2-Chloro-naphthalene	162	0.02	0.011	0.001	7.1	5	1.12	0.46	41.6
Dimethyl phthalate	163	0.02	0.001	0.001	122.3	2	1.02	0.56	54.8
Acenaphthylene	152	0.02	0.015	0.001	8.5	2	1.14	0.46	40.4
4-Nitrophenol	139	0.25	0.102	0.072	70.7	25	22.34	18.22	81.6
2,6-Dinitrotoluene	165	0.02	0.005	0.006	127.8	5	0.66	0.68	103.8
Acenaphthene	154	0.02	0.010	0.001	5.3	2	0.82	0.64	78.4
2,4-Dinitrotoluene	164	0.02	0.001	0.001	141.4	2	0.70	0.73	105.3
Diethyl phthalate	149	0.02	0.003	0.003	105.1	2	0.93	0.62	66.6
4-Chlorophenyl phenyl ether	204	0.02	0.007	0.001	13.7	2	0.92	0.56	60.5
Fluorene	166	0.02	0.008	0.006	71.7	2	0.92	0.62	67.3
N-nitrosodiphenylamine	169	0.02	0.015	0.003	21.6	2	1.15	0.61	53.3
4-Bromophenyl phenyl ether	248	0.02	0.008	0.001	9.3	2	0.81	0.64	79.1
Hexachlorobenzene	284	0.02	0.016	0.005	34.7	2	1.07	0.89	82.7
Pentachlorophenol	266	0.25	nd			25	9.01	11.15	123.7
Phenanthrene	178	0.02	0.014	0.001	5.3	2	1.13	0.80	70.9
Anthracene	178	0.02	0.014	0.002	12.3	2	0.94	0.67	71.2
Di-n-butyl phthalate	149	0.02	0.011	0.012	110.3	2	0.90	0.82	91.4
Fluoranthene	202	0.01	0.004	0.001	32.8	1	0.69	0.57	83.1
Pyrene	202	0.01	0.003	0.001	33.0	1	0.51	0.43	84.1

Table 2 Priority pollutants in groundwater from the former Sydney coke oven plant site. All results are expressed in mg/L.

SAMPLE COMPOUND	4a		4b		2a	
	DTS	ADS	DTS	ADS	DTS	ADS
Phenol			35.5	20.5	5.2	2.4
2,5-Dimethyl phenol			13	34	5.8	
Di-n-butyl phthalate					0.57	
Naphthalene			2.0	13	0.8	45
Acenaphthene	0.69		0.24	0.49	0.27	
Acenaphthylene	0.22		0.06	0.24	0.05	1.1
Fluorene	0.30	0.12	0.10		0.01	
Phenanthrene	0.41		0.06		0.04	
Anthracene	0.11		0.02		0.02	
Fluoranthene			1		0.01	
Pyrene			1		0.13	

Table 3 Results of library searches. Groundwater samples from the Sydney Coke Oven Site. Percent confidence of the library search.

Sample Compounds	RET. TIME	2A		4A		4B		Coal tar ADS
		ADS	DTS	ADS	DTS	ADS	DTS	
1 Acenaphthene	18.20							74
2 Acenaphthylene	17.80							60
3 Acetophenone	15.93	<50	60					
4 Aniline	9.75		<50				<50	
	10.64							
5 Anthracene	22.30							70
6 Benzene	4.46	93						
7 Benzeneacetoneitrile	11.88							<50
8 Benzo[a]fluorene	26.74							70
9 Benzo[b]thiophene	13.85±.15	96	<50	96	89			
10 Benzo[c]phenanthrene	28.68							<50
11 Benzofuran	10.35±.21	87	<50			83	87	
12 Biphenyl	16.00±.98		68					73
13 Biphenyl]-4-carbox-								
14 aldehyde [1,1	19.99		70					83
15 Bis-2-ethylhexyl phthalate	28.99							83
16 C-4 Alkyl benzene	17.38		81					
17 C-4 Alkyl phenol	15.80		80					
18 Carbazole	22.66							52
19 Chlorobenzene	7.65	52	52					
20 Chlorobenzofuran (5- ?)	12.92	<50						
21 Chlorooctane	11.41						71	
22 (2,4-Cyclopentadienyli- dene)ethyl benzene	19.47		60					
23 Dibenzofuran	18.33±.33		60		63	87	60	51
24 Dibenzothiophene	21.59							79
25 Diethyl phenol	16.03		79					
26 Dihydro-Indenol 2,3-	15.88					<50		
27 Dihydroindenone 2,3-	15.08					93		
28 Dihydroindene 2,3-	11.05	79	81			89		70
29 Dihydro-1-nitrosopyrrole 2,5-	11.89					<50		
30 Dihydro-5-methylindene 2,3-	12.89					73		
31 Dimethyl benzaldehyde	11.91						<50	
32 Dimethyl benzene (m+p xylene)	8.02±.06	97	86				54	
33 Dimethyl benzene (o-xylene)	8.53±.02	95	71				54	
34 Dimethyl benzeneamine (3,4- ?)	13.58		81					
35 Dimethyl dibenzofuran	21.38							<50
36 Dimethyl benzofuran	14.10							60

Table 3 Continued

Sample Compounds	RET. TIME	2A		4A		4B		Coal tar ADS
		ADS	DTS	ADS	DTS	ADS	DTS	
37 Dimethylethyl azulene	20.58							<50
38 Dimethyl isocyanobenzene	15.28		55					
39 Dimethyl naphthalene								
(1,6- ?)	15.49				96			
(1,8- ?)	15.87				99			
(1,2- ?)	15.94				95			
(1,4- ?)	16.33				89			
(1,7- ?)	16.92		97					
	17.00							89
	17.07					86		
(1,8- ?)	17.13		96					
(1,3- ?)	17.18						81	
	17.26							83
	17.49							83
(1,2- ?)	17.41		96					
40 Dimethyl pentene								
(4,4- ?)	10.80						65	
41 Dimethyl phenanthrene	24.34							66
42 Dimethylphenol								
(2,6- ?)	12.03					61		
(2,4- ?)	12.24		81				83	70
2,5-	13.28							86
2,3-	13.21±.21		92			97	87	94
43 Dimethyl pyridine								
(2,6- ?)	8.28						71	
(2,3- ?)	8.98					84	96	
(2,4- ?)	8.67					82	97	
44 Dimethyl thiophene								
(2,4- ?)	8.21		83					
(2,5- ?)	8.74		86					
45 Diphenyl-2,5-cyclo- hexanedione	28.27	<50						
46 Ethenyl anthracene	23.96							78
47 Ethenyl naphthalene								
(2- ?)	16.44					<50	64	
48 Ethoxybenzaldehyde (3-?)	15.73					<50		
49 Ethyl benzene	7.92±.02	76	76					67
50 Ethyldimethyl phenol	14.94		80					
51 Ethyl hexanol	11.00		<50					
52 Ethylmethyl phenol	13.76±.34		<50			95	52	
	14.59±.10		70				74	<50
53 Ethyl naphthalene	16.30±.95		60		86			592A
54 Ethyl phenol (2-)	12.58±.11		76			95	94	
(3-)	13.23		76					
55 Ethylphenyl ketone	12.36		<50					

Table 3 Continued

Sample Compounds	RET. TIME	2A		4A		4B		Coal tar ADS
		ADS	DTS	ADS	DTS	ADS	DTS	
56 Ethyl pyridine (2- ?)	8.68						55	
57 Ethyl pyridinone	11.52						<50	
58 Ethyl toluene	9.72					60		87
	10.87	87						
	13.37						<50	
59 Ethylidene indene	11.33				81			
	15.36±.07	81	81			93	81	
60 Fluoranthene	25.31							60
61 Fluorene	19.67							70
62 Furo[3,2-g][1]benzopyran- trione	23.73	<50						
63 Heptane	4.93	<50						
64 Heptanone (2- ?)	8.36	<50	76					
65 Hexane	3.56	<50						
66 Hexanone (2- ?)	6.50		78					
67 Indene	11.32±.03	70	60					76
68 Isobutylmethyl-1,3-propa- nediyl methyl propanoate	19.11	78						
69 Isopropenyl benzene	13.10		<50					
70 Isopropyl benzene	9.07		86					
71 Isoquinoline	15.13							83
72 Methoxy-1,2-benzenediol	15.15						<50	
73 Methyl benzofuran (7- ?)	11.95	81	89			93		
(2- ?)	12.13	<50						
74 Methyl benzonitrile	11.76±.14	86	83				71	
75 Methyl biphenyl	17.91		79					63
	19.76							<50
76 Methyl dibenzofuran	19.93							70
	20.12							81
	20.42							79
77 Methyl ethenyl benzene	11.16							74
78 Methyl ethylcyclopentane	6.65		52					
79 Methyl ethyl disulfide	11.73		<50					
80 Methylenehydride)-bicyclo [2.2.1]hepta 2-(1-	14.09	<50						
81 Methylene naphthalene	19.08							65
82 Methyl fluorene	20.83							67
83 Methyl indene	13.16							70
84 Methyl Indole	16.30		71					
85 Methyl (1-methylene) benzene	10.80		89					

Table 3 Continued

Sample Compounds	RET. TIME	2A		4A		4B		Coal tar ADS
		ADS	DTS	ADS	DTS	ADS	DTS	
86 Methyl naphthalene (2-?)	15.62±.13 10.01	78			76		83	60
87 Methyl-2-nitrophenol (4- ?)	14.58	83						
88 Methylpentyl cyclopropane	8.37						79	
89 Methyl phenanthrene	23.32							70
90 Methyl phenol (2- ?)	11.46±.19		79			94	89	88
91 Methylphenyl pyrrolo [2,3b] pyridine	25.52							<50
92 Methylpropanal (2- ?)	9.54						<50	
93 Methyl pyrene	26.85							63
94 Methyl pyridine (2- ?)	7.06			94	87			
95 Methyl quinoline (2- ?)	15.48					96		
96 Methyl quinoline 7-?	16.32							93
97 Methyl quinoline (5- ?)	16.16					<50		
98 Methyl thiophene (3- ?)	6.40		95					
99 Naphthalene	13.95							81
100 Nitrobenzaldehyde, oxime	17.29	<50						
101 Nitrobenzoic acid (2- ?)	16.07	<50						
(3- ?)	16.71	<50						
102 Nonanal	12.07						86	
103 Octene	6.54					76		
104 Pentanone (2-	4.76	60						
105 Phenalene	19.18							<50
106 Phenanthrene	22.30							70
107 Phenol	9.99							52
108 Phenylmethylene indene	22.75							51
109 Phenylmethylhydrazine carboxylate	9.62	<50						
110 Propyl benzene	9.60		89					
111 Pyrene	25.90							58
112 Pyridine	5.93±.28					89	87	
113 Quinoline	14.76							87
114 Styrene	8.46							58
115 Toluene	6.10±.14	84	89			81	87	
116 Trimethyl benzenes	9.74 9.85	87 71	81 89					

Table 3 Continued

Sample Compounds	RET. TIME	2A		4A		4B		Coal tar ADS
		ADS	DTS	ADS	DTS	ADS	DTS	
117 Trimethyl cyclopentane	10.35	87	79			81		
(1,1,2- ?)	6.70						52	
118 Trimethyl heptane	4.78					60		
119 Trimethyl naphthalene	18.25		<50					78
120 Trimethyl octane	27.33							<50
121 Trimethyl phenol (2,4,5- ?)	14.09		83					
	14.77		87			97		<50
122 Trimethyl pyridine 2,4,6-	10.75							86
123 Trimethyl thiophene								
(2,3,4- ?)	10.70		62					
124 Trimethylheptane	10.69	70						
125 Xylyl isocyanide (3,5- ?)	13.63						<50	

Table 4 Groundwater samples from the Ville-Mercier Quebec, dumpsite.
Quantitative result DTS and ADS.

Samples Compounds	VILM-R2-3		VILM-R6-3	VILM-R6-6
	ADS	DTS	ADS	INJ
1 Bis-dichloroethyl ether	0.5	0.01	2.2	1.1
2 Naphthalene	0.3	0.20	1.2	0.6
3 Phenol			1.9	
4 1,3-dichlorobenzene		0.06		
5 Bis-2-chloroisopropyl ether		0.01		
6 N-nitroso-di-n-propylamine		0.12		
7 Hexachloroethene		0.12		
8 Nitrobenzene		0.02		
9 Isophorone		0.05	0.7	
10 Nitrobenzene		0.03		
11 2,5-Dimethyl phenol		0.07		
12 Acenaphthylene		0.01		
13 Acenaphthene		0.01		
14 4-Nitrophenol		3.7		
15 2,4-Dinitrotoluene		0.15		
16 Diethyl phthalate		0.08		
17 Phenanthrene		0.02		

Table 5 Groundwater samples from the Ville-Mercier dumpsite. Comparison of library searches, percent confidence.

Sample Technique	RET TIME	R2-3		R6-3	R6-6
		DTS	ADS	ADS	ADS
1 Benzaldehyde	9.76			x	x
2 Benzene	4.50		94	94	80
3 Benzo[b]thiophene	13.72	<50			
4 Biphenyl	16.54	73			
5 Bromochlorocyclobutane	12.53		<50		
6 Bromochloropropane	8.84	<50			
7 C-4 alkylbenzene	11.09	<50			
8 Chlorobenzene	1.40	49		67	
9 Chlorobicyclooctene					<50
10 Chloro-1,3-butadiene 2-	3.58		74	60	88
	3.85		87		
11 Chlorobutene 3-	6.50	<50			
12 Chloroethyl benzene 2-	12.11	90	<50	87	67
13 Chloro-6-methylphenol 2-	11.45	89	59	<50	
14 (4-chlorophenyl)-ethanone 1-	14.23	96			
15 Chloropropane					<50
16 Chloropropene	6.51		60	60	<50
17 Chloro-thieno[3,2-c]pyridine 2-	15.40	60			
18 Cis-1,2-dichloroethene			89	89	87
19 Cyclooctatetraene 1,3,5,7-	5.65	95	94	94	94
20 Dichlorobutane 1,2-	6.84		76	76	<50
1,3-	7.34		87	87	89
21 Dichloro-2-butene 2,3	5.99		<50	<50	<50
Dichloro-1-butene 1,4-	2.60	55	59	53	55
Dichloro-2-butene 1,4-	5.16	60	<50	52	60
22 Dichlorocyclobutane 1,3-	7.42		70	60	70
23 Dichlorocyclopentane 1,3-	13.14	<50			
24 Dichloroethane 1,2-	4.27			51	
25 Dichloroethene trans-1,2-	3.30		87	89	89
Dichloroethene 1,2 cis	3.77		87		
26 Dichloropropene 2,3-	5.32	71			
1,3-	8.35		76	<50	58
27 Dihydro-5-methyl indene 2,3-	12.67	83			
28 Dimethyl benzene 1,2-	3.47	84			71
1,3-	4.25	71	97	97	97
1,4-	5.75	70			
29 Dimethyl naphthalene 1,3-	17.15	97			
1,2-	17.45	78			
30 Dimethyl pentane 2,4-	4.98				<50
31 Ethylaminoethanol	5.98			x	

Table 5 Continued

Sample Technique	RET. TIME	R2-3		R6-3	R6-6
		DTS	ADS.	ADS.	ADS.
32 Ethyl methyl benzene	8.47	76	67	70	60
33 Ethyl naphthalene	16.77	88			
34 Hexane	4.96		<50		
35 Hexanone 2-	5.65		70		
36 Indene	10.87	81	70		
37 Isopropyl benzene	9.03	<50			
38 Limonene	10.29	71			
39 Methyl benzo[b]thiophene	15.27	<50			
40 Methyl-2-butanone 3-	4.77			52	70
41 Methyl-indene	12.98	96			
42 Methyl-3-methylethyl benzene	11.38	86			
43 Methyl naphthalene 2-	15.34	76			
	15.63	67			
44 Methyl-2-pentanone 4-	5.63			77	89
45 Pentanone	4.81		60	<50	
46 Phenyl ethanone	11.20	64			
47 (2-Propenyl)-naphthalene 1-	17.97	76			
48 Quinolinol	13.93	<50			
49 Sulfur dioxide	3.21				78
50 Tetrachloroethane 1,1,2,2,-	6.71	93			
51 Tetrachloroethene	7.01		83	83	86
52 Tetradecanoic acid	21.63	<50			
53 Trichlorobutane	8.93	52	83	78	76
54 Trichloroethane 1,1,2	6.26		73	73	74
55 Trichloroethene	5.04		93	86	95
56 Trichloropropane 1,1,2-	7.61		78		
57 Trichlorotrifluoropropane	13.35	x	x		
	14.14	x			
	14.61	x			
58 Trimethyl benzene 1,2,3-	10.17	89	83	81	81
1,2,4-	8.42	87			
59 Trimethyl naphthalene 1,4,5-	18.62	52			

Table 6 Groundwater samples from monitoring wells on the Uniroyal Chemicals limited in Elmira, Ontario. Results of library searches.

SAMPLE Compound	ELM-50		ELM-54		ELM-55	
	R.T.	CONF. LEVEL	R.T.	CONF. LEVEL	R.T.	CONF. LEVEL
1 Acetic acid			8.86	83	6.76	<50
2 4-Acetyl morpholine			13.98	58		
3 Alkyl amine ? m. wt 365					26.66	
4 Alkyl amine ? m.wt. 351					26.31	
5 Aniline			9.66	81	10.17	<50
6 1,3-Benzodioxolone					13.37	<50
7 Benzothiazole	13.59	74	14.40	88	14.31	89
8 Benzothiazolone			20.93	79		
9 4-(2-benzothiazolylthio)-morpholine			24.19	76		
10 Carboxin			25.91	93		
11 m-Chloroaniline			12.59	76		
12 Dichlorophenol 2,4-	12.41	86				
13 Dimethyl-3,8-decane			24.94	<50		
14 Dimethyl-3-phenyl-2,5-cyclohexadien-1-one 4,4-			22.36	<50		
15 Dithiane 1,3-			11.50	71		
16 Dithiane 1,4-			11.56	<50	11.61	89
17 Dithio-bis-ethanol 2,2'-			17.70	79		
18 [1,2-Ethanedylbis(thio)bis-ethanol 2,2-			21.04	52		
19 Ethyl furanone 5-			13.43	<50		
20 Ethyl hexanol 2-			10.60	60		
21 Ethyl morpholine 4-					12.74	<50
22 Ethyl hexylamine					13.75	<50
23 Hexadecane			25.33	78		
24 Hydroxy-5-nitro-benzaldehyde 2-			23.47	<50		
25 Isoquinoline			14.51	79		
26 Methyl benzisothiazole			15.31	58		
27 Methyl quinoline			15.60	<50		
28 Methyl silane			8.14	<50		
29 Methyl sulfinyl ethene					8.91	<50
30 Methyl tetrahydro-pyran-2-one			13.10	<50		
31 2-Methylthiobenzothiazole			19.58	<50		
32 Morpholine			9.37	<50	8.42	52
33 N-(2-hydroxyethyl)-N'-phenylthiourea	13.16	86				
34 N-phenyl acetamide			16.94	51	16.57	60
35 N-phenyl benzenamine	19.48	71			19.58	100
36 N-propyl benzamide			16.30	<50		
37 N-phenyl formamide			15.91	<50		
38 Toluene	6.37	78	5.94	87	5.94	87
39 2,4,5-Trichlorophenol	15.80	79				

Table 7 Municipal landfill leachate from Guelph, Ontario. Quantitation of priority pollutants and comparison of confidence level of library searches

COMPOUND	RET TIME	CONF LEVEL	DTS	ADS
1 Acenaphthene	18.06	100	62 µg/L	
	18.08	75		
2 Acenaphthylene	17.61	100	7 µg/L	
	17.59	86		
3 Bis (2-methoxyethyl) 1,2-benzenedicarboxyla	23.26	88		
4 Di-n-butyl phthalate	23.26	100	1.0 mg/L	
5 Diethyl phthalate	19.12	100		18.8 mg/L
	19.14	100	722 µg/L	
6 Dimethyl phenol (2,5-)	13.03	100		35.9 mg/L
	12.87	100	1.5 mg/L	
7 Fluorene	19.32	100	9 µg/L	
	19.32	<50		
8 Isophorone	12.60	100	87 µg/L	
9 Trimethyl 2-cyclohexen-1-one 3,3,5- [isoph	12.60	70		
10 Naphthalene	13.70	100	116 µg/L	
11 Phenol	9.96	75		
	9.96	100	4.9 mg/L	
	10.20	100		19.4 mg/L
	10.45	<50		

Table 8 Municipal landfill leachate, Guelph, Ontario. Result of library searches.

COMPOUND	ADS		DTS	
	R.T.	CONF. LEVEL	R.T.	CONF. LEVEL
1 Acetic acid	6.35	52		
2 Biphenyl			16.51	<50
3 Butanoic acid	8.72	58		
4 Butanone 2-	3.56	60		
5 Cineole			11.03	83
6 Dibenzofuran			18.45	79
7 Diethyl phenol			14.88	52
8 Diethyl phosphate	12.64	70		
9 Dimethyl benzene			8.52	59
Dimethyl benzene 1,2-			8.06	95
10 Dimethyl benzenemethanol α,α -	12.12	89	11.94	82
11 Dimethyl disulfide	5.69	71		
12 Dimethyl naphthalene 1,6- or 1,7			16.88	96
1,7- or 1,8-			17.12	95
2,7- or 2,6-			17.16	67
13 Dimethyl pentene 4,4-	11.01	<50		
14 Dimethyl phenol 2,3-			13.17	76
2,6-			12.23	95
15 Dimethylethyl-2methyl-1,3propanediyl metpr			19.09	87
16 Ethyl benzene			7.91	95
17 Ethyl pentanol	9.03	<50		
18 Ethyl phenol 2-	13.35	86	12.66	86
19 Ethyl-2-methyl phenol 4-			14.24	76
Ethyl-5-methyl phenol 3-			14.60	75
Ethyl methyl phenol	14.71	<50		
20 Ethylidene indene			15.62	89
21 Hexanol 2-	5.92	52		
22 Hexanone 3-			6.44	<50
23 Hexen-1-ol 2-			8.35	53
25 Hydroxy-3-propyl hexan-2-one 4-			6.50	70
25 Isobutanoic acid	8.36	<50		
26 Methoxy-4-(methylethyl) benzene			15.14	<50
27 Methyl 2-(methylethyl) cyclohexanol	13.43	83		
28 Methyl benzo-b-thiophene			15.49	<50
29 Methyl butan-2-one 3-	4.32	70		
30 Methyl butanoic acid	9.34	67		
31 Methyl hexanoic acid	11.55	58		
32 Methyl hexanone 5-			7.75	<50

Table 8 Continued

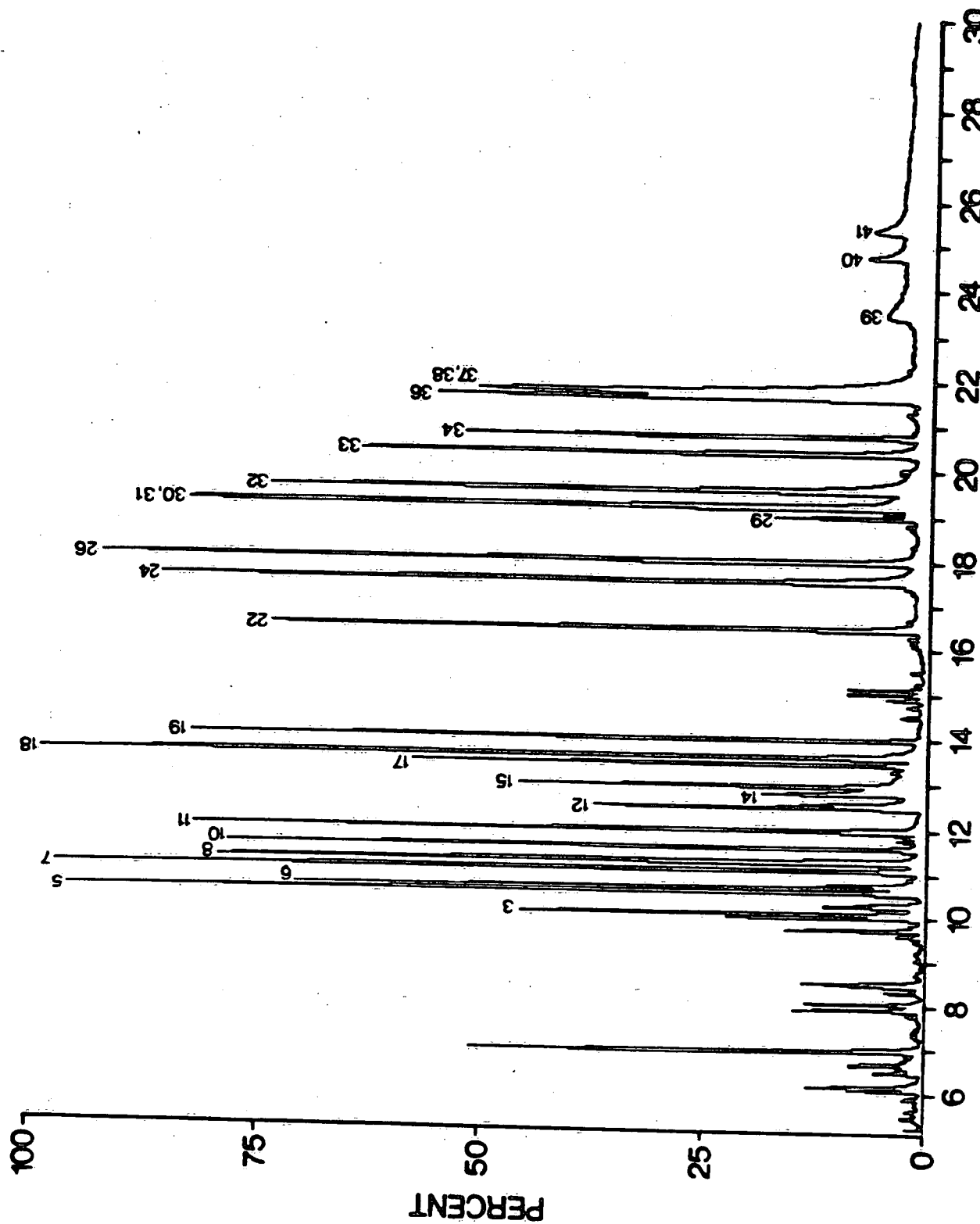
COMPOUND	ADS		DTS	
	R.T.	CONF. LEVEL	R.T.	CONF. LEVEL
33 Methyl naphthalene			15.34	67
34 Methyl pentan-2-one 4-			5.63	86
Methyl pentan-2-one 4-	5.55	69		
35 Methyl phenol 2-			11.31	84
3-	12.04	74	11.66	79
4-	11.88	84		
36 Methyl propanal 2-	3.17	78		
37 Methyl pyridine			7.10	<50
38 Methyl pyrrolidin-2-one 1-	11.67	86		
39 Methyl-1-(methylethyl)-3-cyclohexen-1-ol 4			13.47	70
40 Methyl-2-(methylethyl)-cyclohexanol 1 α ,2 β ,			13.36	67
41 Methyl-2-(methylethyl)benzene			10.84	89
42 Methyl-4-(methylethenyl) cyclohexane			10.14	84
43 Methyl-4-(methylethyl)oxabicyclo[2.2.1]hep			10.70	71
44 Methyl-5-(methylethyl) benzene 2-			15.20	<50
45 Methyl-5-(methylethyl) phenol			16.13	<50
46 Morpholine			7.33	52
47 N-methyl pentanamine	8.55	<50		
48 Octanone 3-			9.29	<50
49 Pentanoic acid	9.65	<50		
50 Pentanone -2	4.70	70		
51 Propanoic acid	5.24	<50	5.48	60
	7.35	70		
52 Propanone 2-			9.52	<50
53 Propyl phenol 4-			13.96	<50
54 Tetradecanoic acid	21.50	<50	21.52	<50
55 Toluene			6.19	89
56 Trimethyl 1,3,6-heptatriene 2,5,5-			9.60	79
57 Trimethyl 3-cyclohexene-1-methanol α , α ,4-	13.73	52	13.66	56
58 Trimethyl benzene 1,2,3-			10.33	58
59 Trimethyl bicyclo[2.2.1]hept-2-ene 1,7,7-			10.93	94
60 Trimethyl bicyclo[2.2.1]heptan-2-one 1,3,3			12.04	81
1,7,7	13.08	55	13.04	96
62 Trimethyl cyclohexanemethanol α , α ,4	13.01	63	12.92	76
63 Trimethyl cyclohexanone 3,3,5-	11.28	58	11.16	76
64 Trimethyl phenol 2,3,5-			14.73	62
2,4,5-			14.80	86
3,4,5-			13.79	86

Table 9 Correlation of the results using DTS and ADS: number of compounds identified.

SAMPLE	DTS	ADS	OVERLAP
PRIORITY POLLUTANT	30	40	30
SYDNEY (4B)	44	28	20
VILLE-MERCIER (R2-3)	59	33	14
GUELPH	63	33	14
ELMIRA (54)	28*	30	10
* not DTS, but solvent extraction			

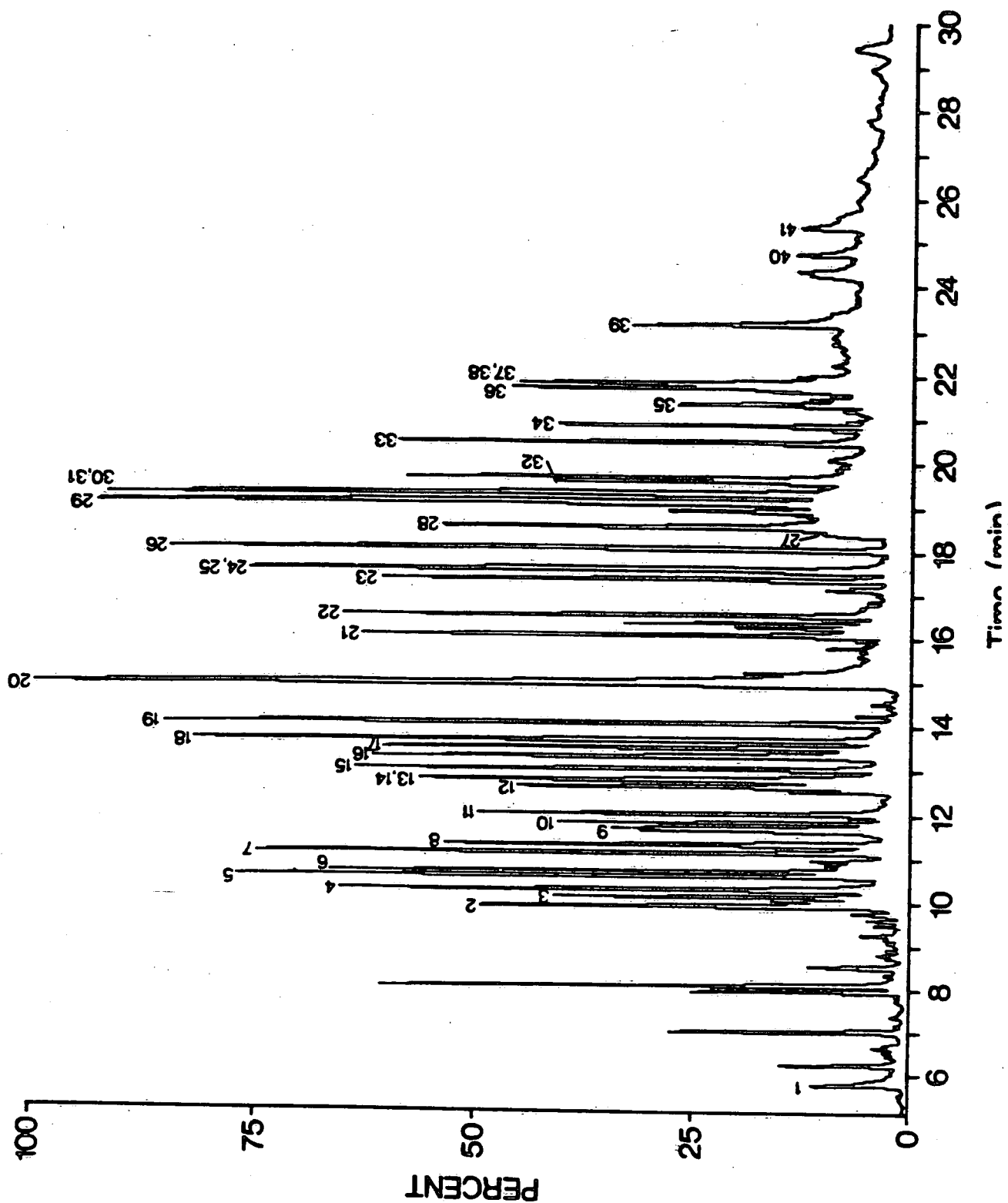
PRIORITY POLLUTANTS BY DTS

Figure 1



PRIORITY POLLUTANTS BY ADS

Figure 2



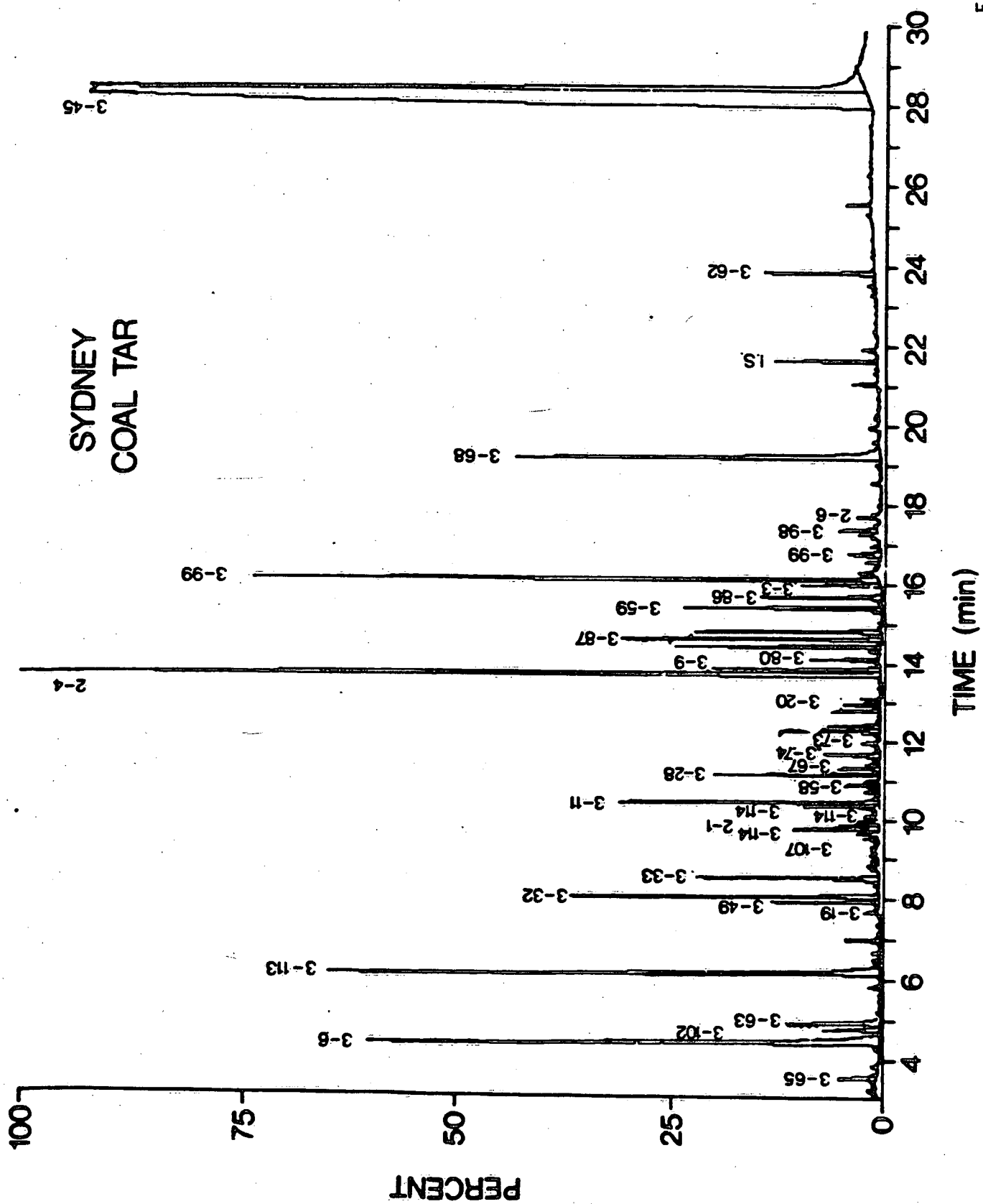


Figure 3

VILLE-MERCIER

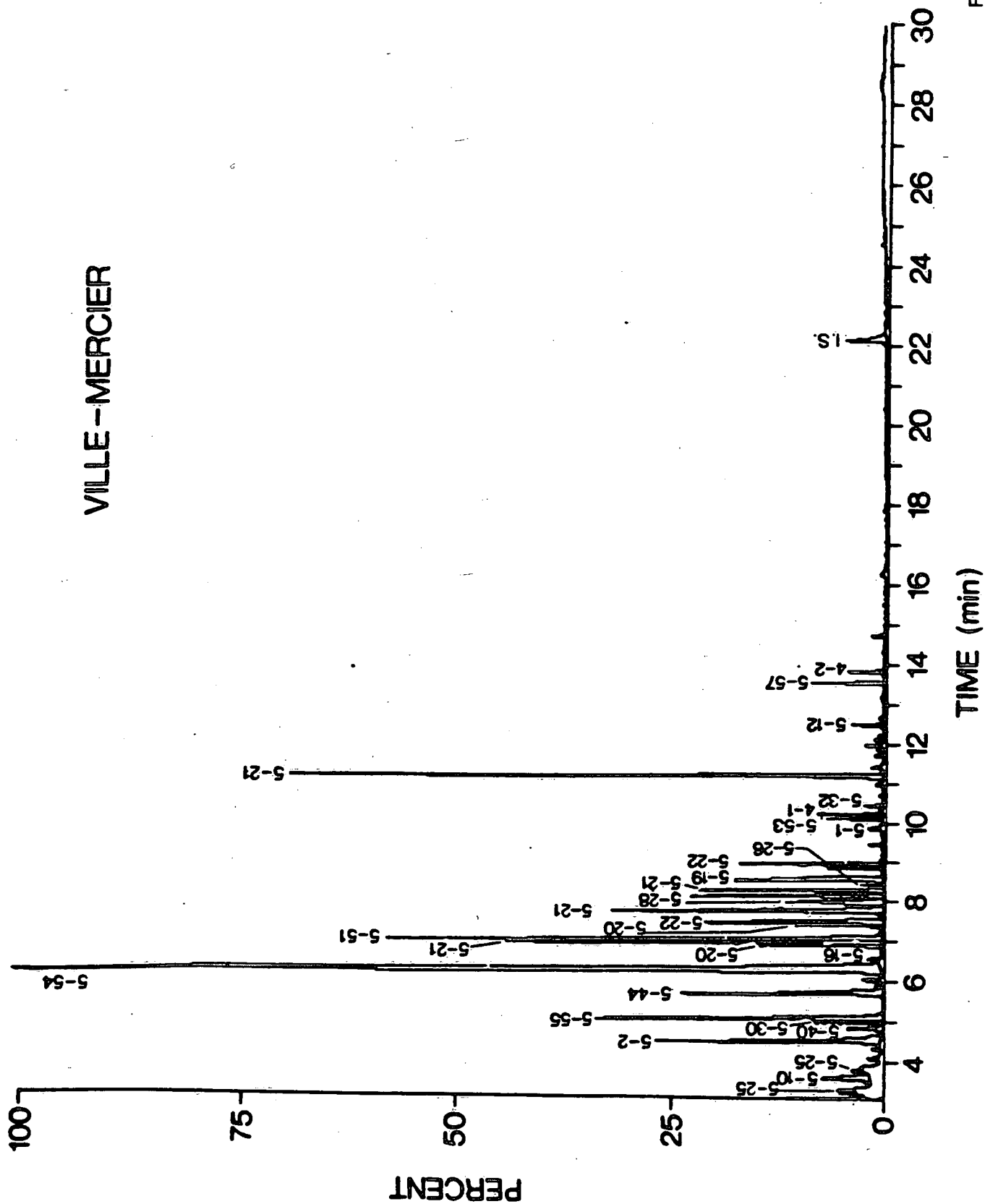


Figure 4

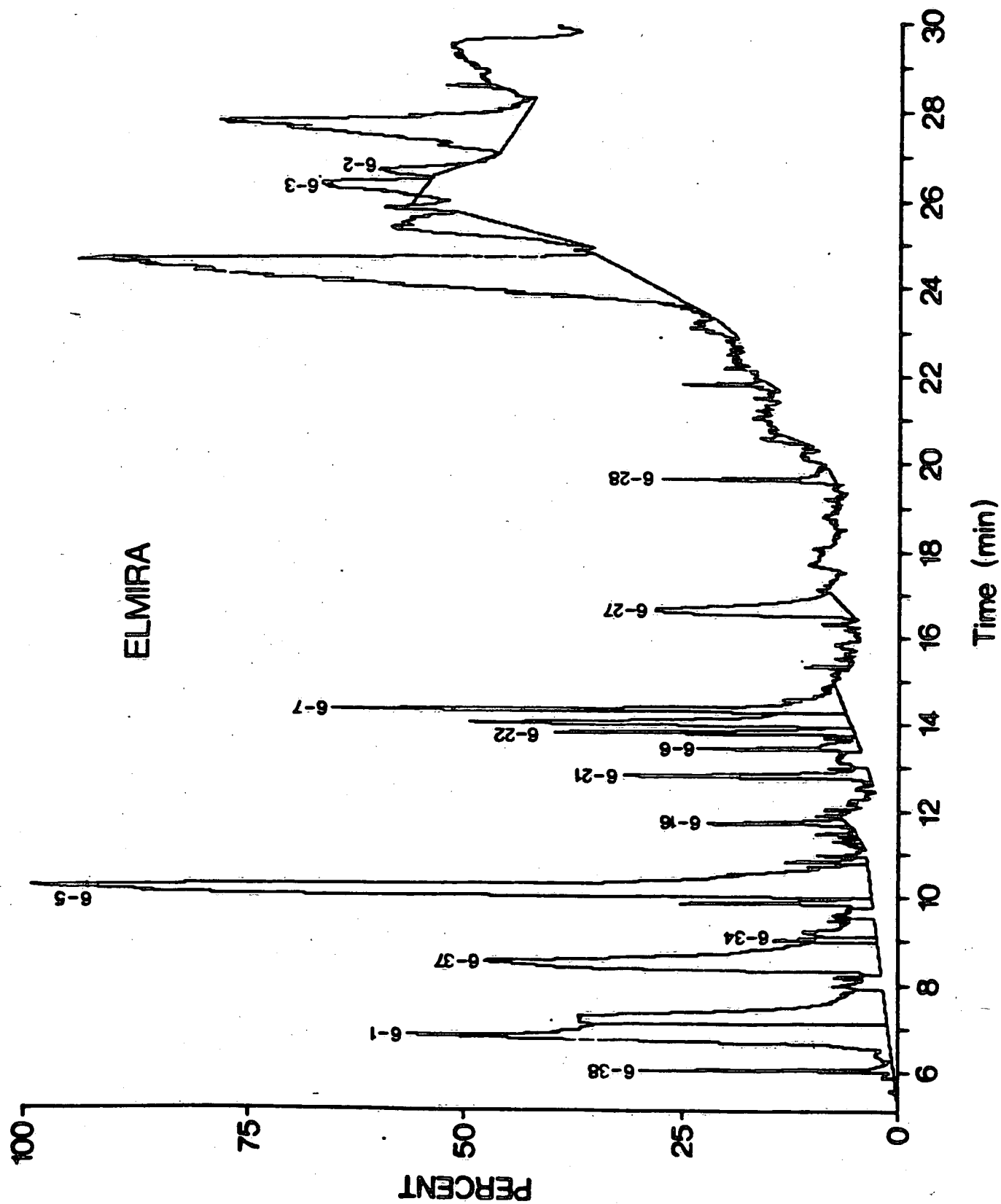


Figure 5

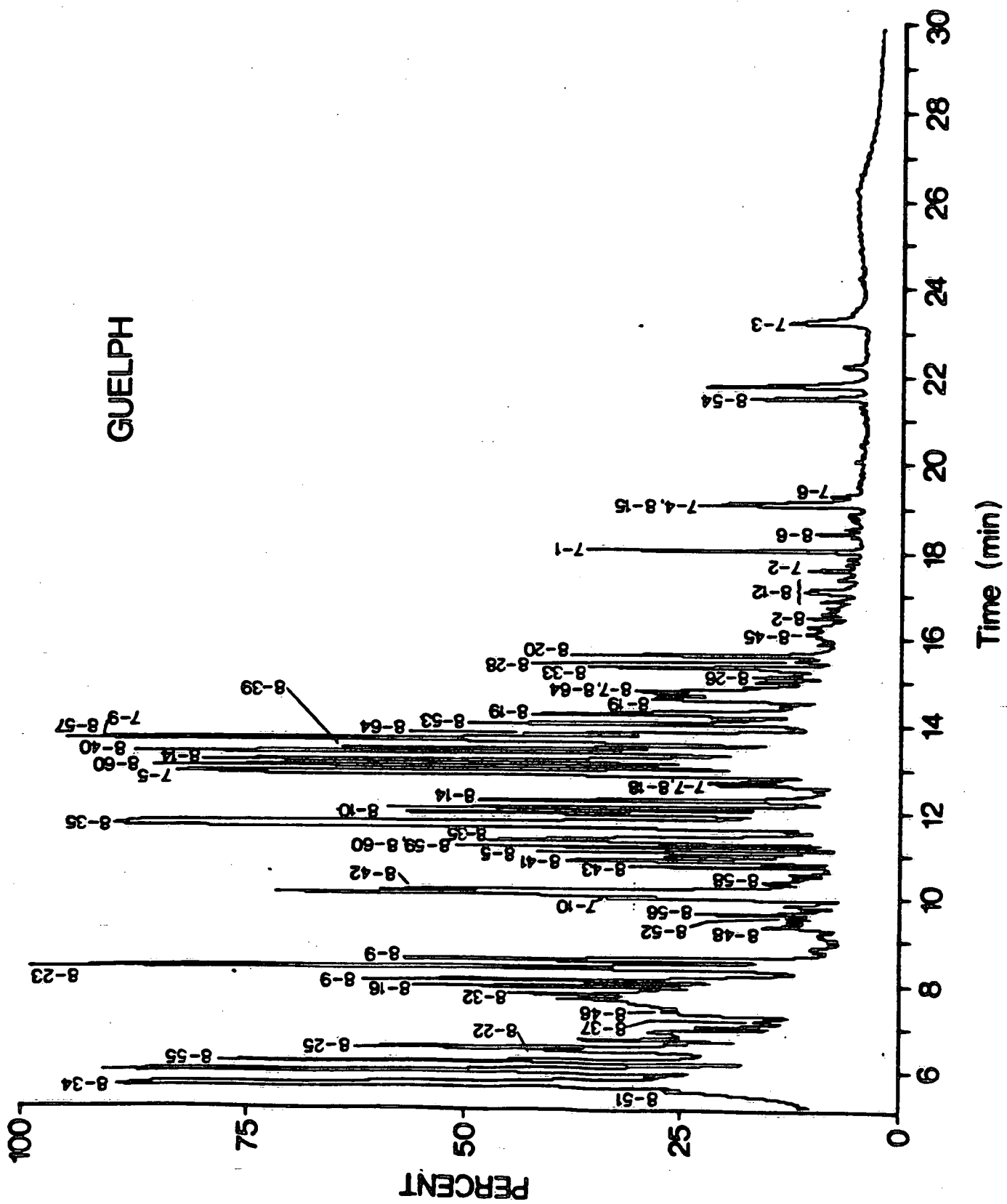


Figure 6