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CHARACTERIZATION OF GROUNDWATER CONTAMINANTS AT ELMIRA, ONTARIO, BY THERMAL DESORPTION, SOLVENT EXTRACTION GC-MS AND HPLC

by

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ABSTRACT

Contaminated groundwater samples were characterized using on-line thermal desorption GC-MS analysis. The results were compared with conventional solvent extraction followed by GC-MS. Thermal desorption gave similar results for most compounds and was found to be superior for the analysis of water-miscible compounds. HPLC with a diode-array detector was used to measure phenol in the presence of large quantities of aniline.

RÉSUME

Des échantillons d'eau souterraine contaminée ont été analysés par un système intégre de désorption thermique, chromatographie en phase gaseuse et spectrométrie de masse (CG-SM). Les résultats sont comparés à ceux obtenus par la méthode conventionnelle d'extraction par solvant suivi de l'analyse par CG-SM. La désorption thermique a donné des résultats comparables pour la plupart des composés et s'est avérée supérieure pour l'analyse des composés miscibles à l'eau. La chromatographie en phase liquide avec un détecteur à faisceau-diode a permis l'analyse du phénol en présence de grandes quantités d'aniline.

MANAGEMENT PERSPECTIVE

This work arose out of an instituted proposal supported by DSS and DOE to develop aquifer restoration techniques for organically-polluted systems.

Contaminated groundwater samples from the Uniroyal Plant site in Elmira, Ontario, were analysed using a variety of analytical techniques. On-line thermal desorption GC-MS gave similar results to the more time consuming solvent extraction technique for the analysis of heavily contaminated groundwater. The contaminants identified could all be traced back to historical manufacturing and waste disposal practises. This study supports an earlier Environment Canada report on the source of contaminants of the Canagagigue Creek.

PERSPECTIVE POUR LA GESTION

Cette étude découle d'une proposition spontanée supportée par Environnement Canada et Approvisionnement et Services Canada visant à développer des techniques de restauration des aquifères contaminés par des produits organiques.

Des échantillons d'eau souterraine contaminée provenant des terrains de l'usine de la compagnie Uniroyal à Elmira en Ontario ont été analysés par plusieurs méthodes. L'analyse par un système intégré de désorption thermique CG-SM a donné des résultats semblables à la méthode conventionnelle tout en étant plus rapide et moins coûteuse. Les contaminants identifiés étaient tous imputables à des procédés de manufacture et de gestion des déchets antérieurs. Cette étude confirme un rapport précédent d'Environnement Canada reliant la contamination du ruisseau Canagagigue à celle de l'eau souterraine adjacente.

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 byproducts are codisposed over a very long period of time. 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 (Swallow et al., 1988). 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 EPA methods 624 and 625 (Rheinhard et al., 1984). In wastewater effluents and municipal landfill leachates, this discrepancy is largely accounted for by the high level of naturally occurring compounds such as short chain fatty acids. The leachate from industrial landfills would not be expected to contain much organic matter of natural origin, hence, the rest of the DOC must be comprised of non-volatile or non-extractable compounds. Techniques such as LC-MS have been employed to analyse such samples. Unfortunately, this technique is not as widely available as GC-MS and thus an alternative was sought to identify some of the poorly extractable compounds.

The samples were taken from three monitoring wells located on the property of the Uniroyal Chemical Company in Elmira, Ontario. The wells were installed beside or into former waste disposal lagoons.

Previous studies in the area had indicated that there was significant contamination of the shallow aquifer. The investigation was conducted as a preliminary to a groundwater remediation demonstration project. The chemical characterization was therefore essential to the design of the treatment plant.

SAMPLING

The monitoring wells were pumped with peristaltic pumps at the rate of approximately 1 L/min. Samples for volatiles were collected in 40 mL vials with a teflon coated septum and acidified with dilute nitric acid. Samples for semi-volatiles were collected in 1 L glass bottles and were refrigerated. Samples were collected from three wells situated beside an existing and former waste holding lagoon (50 and 54) and into a former disposal lagoon (55). The well screens were located in a shallow aquifer at 6, 5 and 5 meters respectively.

ANALYSIS

Volatiles

The analysis for volatile organic compounds was conducted within one week of sampling. Because of the expected high level of contamination, 100 µL aliquots were used for analyses and diluted to 10 mLs with uncontaminated groundwater. The analysis was conducted on a Unacon-810 purge and trap concentrator directly interfaced to a

Hewlett-Packard model 5890-5970 GC-MSD. The analytical column was a J&W DB-624 fused silica capillary column, 30 m in length, 0.32 mm i.d., 1 µm film thickness. The GC was cooled to -15°C wth CO_2 and ramped to 130°C at 10°/min. Chlorobenzene-d5 and difluorobenzene were used as internal standards. Standard solutions were prepared from the purest available chemicals. All compounds reported were analysed against a standard.

Semi-volatiles

Solvent extraction

Semi-volatile compounds were extracted by EPA method 625 with the following modifications:

- 500 mL of each sample were spiked with the following surrogates: phenol-d5, trifluoro-m-cresol, nitrobenzene-d5, 2-fluorobiphenyl, p-terphenyl-d14

- because of the high level of contamination, the final extract volumes were adjusted as follows:

  - well 50: base-neutral fraction = 33 mLs
    acid fraction = 112 mLs

  - well 54: base-neutral fraction = 140 mLs
    acid fraction = 405 mLs

Pentafluorophenol, 1-fluoronaphthalene and anthracene-d10 were added to the extracts prior to analysis on a Finnigan OWA GC-MS. A splitless injection was performed into the gas chromatograph which was equipped with a J&W DB-5 capillary column, 30 m x 0.25 mm i.d., 0.25 µm film thickness, directly interfaced in the ion source of the mass spectrometer. The gas chromatograph temperature program was started at 35°C for 1 min., then ramped at 4.5°C/min to 295°C and held for 30 min. The mass spectrometer was scanned from 46 to 450 a.m.u. every second.

Thermal Desorption

Semi-volatile compounds were also analysed by thermal desorption from the Unacon-810 tube desorber accessory connected on-line to the GC-MSD described above in the volatiles section. The samples (100 µL) were injected onto Carbotrap/Carbotrap C adsorbent (Supelco Canada Limited) packed into a 20 cm long, 6 mm i.d. quartz tube. One µL of a 100 µg/mL solution of d-10-anthracene in methanol was also added as an internal standard. The sample tube was dried by a gentle flow of nitrogen for 5 min. while kept in a heated sleeve at 50°C. The tube was desorbed by heating rapidly to 350°C in the tube desorber. 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). The gas chromatograph was ramped from 35°C to 275°C at the rate of 10°/min. Mass spectral data was acquired

from 45 to 450 a.m.u. at the rate of 1 scan/sec. Priority pollutant standards were obtained from Bio-Scientific Lab Supplies (Mississauga, Ontario) as injection-ready mixtures. One µL of each mixture made in methanol was injected on the sorbent tube and then treated as described above for the samples.

HPLC

HPLC was performed on a Waters system consisting of two 501 pumps, an autosampler and a Waters 990 diode array detector. The analytical column was a 3.9 mm x 30 cm stainless steel µBondapak^{R} C_{18}. The eluant was composed of a multistep gradient from 36% to 100% acetonitrile and water modified with 0.005 M acetic acid. The flow rate was 1.0 mL/min. The sample from well 54 was filtered and injected directly into the system. Identification and quantification was done by comparison to known standards.

SITE HISTORY

The plant located in Elmira was known to have manufactured over 200 different chemicals over almost fifty years. Disposal practices improved with the years as more knowledge of environmental impact became available (Jackman et al., 1985). Monitoring wells 54 and 55 were installed in waste pond RPW5. This pond was first installed in 1948, but was emptied and redesigned several times over the history of

the plant. In 1969, the sludge was removed and buried elsewhere and the pond was clay lined. Well 50 was installed besides lagoon 8 which was formed as a lined equalization pond in 1966. These ponds were used to balance waste strength for the discharge to an adjacent municipal sewage treatment plant, and as preliminary settling ponds.

A list of some of the chemicals deposited in the lagoons prior to 1969 is shown in Table 1. It is by no means exhaustive, but served as an indicator of the type of contaminants expected to have leached into groundwater prior to the installation of the clay liner. A subsequent study by Carey et al. (1983) identified contaminants (Table 2) in the adjacent creek. Because of their seasonal fluctuations, these contaminants were attributed to shallow groundwater seepage.

RESULTS AND DISCUSSION

(a) Volatiles. The results of the volatile analyses are listed in Table 3. Results are expressed in mg/L to better reflect the precision of the analyses which were conducted on 100 µL of sample. Even at this dilution the results for toluene should be considered as a minimum concentration since there was evidence of saturation of the chromatographic peak. No other unidentified peaks were found in the chromatograms. The solvents found in the groundwater were in agreement with the solvent usage at the plant. Their high concentration in groundwater may be surprising however since the lagoons were completely open to the atmosphere and most of them would

have been expected to volatilize. The fact this did not happen could be because many semi-volatile compounds having a higher density than water were mixed with the solvent, thus producing a denser non-miscible phase which could then leach through the bottom of the lagoons and contaminate the groundwater.

(b) Semi-volatiles by Extraction GC-MS. Semi-volatiles which were identified in wells 50 and 54 are listed in Table 4 for U.S. EPA priority pollutants and Table 5 for other compounds. Quantitation for priority pollutants was done by the internal standard method, whereas for the compounds which were tentatively identified using comparison with computerized library of spectra, the quantities reported were estimates based on the area of the base peak in the spectrum compared to the surrogate response factor and do not reflect individual compound response factors in the mass spectrometer.

There are several points which are noteworthy in the quantitative results obtained using this method. First, the compound reported as N-nitroso-diphenylamine is most probably diphenylamine and not the nitroso derivative. The two are indistinguishable in this analysis since the nitroso compound is thermally unstable and is degraded to diphenylamine in the gas chromatograph injector. This compound was produced at the plant (Jackman et al., 1985) and was identified in the creek (Table 2).

Secondly, final volume adjustments of the extracts were necessary in order to allow identification of as many components as possible. In both analyses, the aniline peaks were overloaded.

Saturation of the base peak and quantitation using a surrogate response factor may have resulted in estimates differing greatly from the actual concentration of aniline.

Thirdly, due to the high amount of aniline present, it was not possible to confirm the presence of phenol. As a result of the mass overlap (Fig. 1) and the close elution of phenol and anline, if a lesser amount of phenol was present in the extracts, it would be obscured by the M+1 peak of anline. The fragment ions are also the same for both compounds, which precludes their differentiation. Aniline also interferes with the colorimetric analysis used for total phenols (Welcher, 1963).

(c) Semi-volatiles by Thermal Desorption GC-MS. The results for thermal desorption analysis are listed in Table 6. Except for di- and trichlorophenol, which were based on comparison with standards, the estimated concentrations were based on the area of the peak in the total ion chromatogram compared to the area of the internal standard.

Qualitatively the results obtained by solvent extraction and thermal desorption were very similar. The compounds that were identified by both methods are flagged by an asterisk in Tables 4-6. In one case, the spectra of two best matches were virtually identical to each other, and an assignment of the unknown could not be made to either method. Considering that these are tentative identifications and that the chromatograms are very complex, the correlation is very good, especially for sample 54. For sample 50, the discrepancies were greater, although every compound found by thermal desorption was also identified by solvent extraction, the latter method allowed the identification of more compounds.

There are several possible reasons for this discrepancy. Although these samples came from the same monitoring wells, they were collected sequentially and are not true duplicates. The aquifer is relatively small, and the well was not yielding very much ground water, which means that the samples may represent different zones of the aquifer. Indeed, there seem to be a high degree of heterogeneity at the site as can be seen by comparing samples 54 and 55 (Table 6). The two monitoring wells were less than 10 m apart, yet their composition is significantly different. Also, the sample size used for thermal elution may have not been sufficient to identify several of the components present in lower concentrations. In retrospect, it was possible to find in the thermal desorption chromatogram masses characteristic of some of the compounds that had been identified by the solvent extraction, but they were either too low in intensity or not resolved from other peaks to allow their identification in the initial analysis.

The DOC for samples 54 and 50 were reported as 3370 and 491 mg/L (Canviro Laboratories, 1989). Although the analyses using thermal desorption do not account for the total, the proportion for sample 54 was higher than what was obtained by solvent extraction. This is probably because a large proportion of organic compounds in this sample are water soluble and partition poorly into dichloromethane, hence when the extraction step is omitted, the recoveries improve. For sample 50, most of the contaminants were very amenable to the conventional extraction technique and thus the results are reversed.

The thermal desorption method of analysis has the advantage of requiring little sample preparation, and similarly to the current practise for the GC-MS analysis of extracts, it allows for the simultaneous analysis of neutral, acidic and basic compounds. Also, water miscible compounds such as dithiane, morpholine and 2,2'dithio-bis-ethanol would not be detected using the conventional solvent extraction technique. Increasing the range of compounds extracted however has the effect of producing much more complex chromatograms which can create problems with unresolved peaks. Further, method development will be necessary to address this problem. Thermal desorption-GC-MSD could provide a cost effective method of estimation of groundwater contamination potential.

(d) HPLC. As with the extraction method, thermal desorption did not permit to verify the presence of phenol in the samples, since the analytical columns were similar and the same coelution problems were encountered. It was therefore necessary to rely on HPLC to obtain confirmation and quantitation of both. The results are shown in Table 7.

Using the diode array detector, it was possible to differentiate between aniline and phenol, since their U.V. absorbance spectra are significantly different even though the two peaks are chromatographically only partially resolved (Fig. 2). By examining the contour diagram for the sample (Fig. 3a) and comparing it to that of pure aniline (Fig. 3b), a spectral shift can be detected as a light area at 6.36 minutes. This spectral shift can be seen even though phenol is present in much lower concentration than aniline.

It was also possible to confirm the presence of benzothiazole and mercaptobenzothiazole. The latter compound is thermally unstable and thus indistinguishable from benzothiazole in the GC-MS analysis.

(e) Relevance to the Site. Most of the compounds identified in the groundwater samples could be traced to some of the processes used at the plant and known to have been disposed of in the lagoons. Aniline was the major contaminant identified, yet it had never been reported until now. This is probably because the analytical techniques used did not permit its detection. Acetic acid had also never been reported for the same reason. It is a known product of anaerobic biological degradation, and its presence would not be surprising in such a contaminated aquifer. However, it is usually accompanied by other acids such as propionic and butyric (Harmsen, 1983) which were absent from the samples. Monochloroacetic acid is a product used at the plant (Morrison Beatty, 1989), and it could conceivably be transformed to acetic acid by reductive dechlorination.

Benzothiazole was a known waste product for the plant, and it had also been identified in the creek (Table 2). The chlorinated phenols were mostly found in well 50 and were also expected. Diphenylamine was found in all samples, and had also previously been found in the creek. Carboxin is the chemical name for the pesticide Vitavax^{R} 2,2'-Dithio-bis-ethanol could be formed by the condensation of 2-mercaptoethanol used in the synthesis of carboxin. Morpholine had not been identified previously, but is a chemical associated with the plant, as is benzothiazolylthio-morpholine. Chloroaniline, methyl quinoline and isoquinoline are present in the current pesticide manufacturing waste streams.

CONCLUSIONS

These analyses provided a good means of characterization of the contaminated groundwater. Most of the products identified using computerized library searches could be related to the known products of the plant. Thermal desorption GC-MS was found to be a rapid cost effective method for the assessment of the groundwater contaminants, providing similar results to the traditional solvent extraction technique but much less labor intensive. It was also found superior for the identification of water soluble components as the results compared well with those obtained by HPLC. This study supports an earlier hypothesis that many of the creek contaminants were due to groundwater seepage.

REFERENCES

Carey, J.H., M.E. Fox, B.G. Brownlee, J.L. Metcalfe, P.D. Mason, and W.H. Yerex. 1983. The fate and effects of contaminants in Canagagigue Creek: Stream ecology and identification of major contaminants. IWD Scientific Series No. 135, Environment Canada.

Harmsen, J. 1983. Identification of Organic Compounds in Leachate from a Waste Tip. Water Res., 17(6):699-705.

Jackman, W., J. Ralston and A.F. Smith. 1985. A history of Uniroyal waste management at Elmira. Ontario Ministry of the Environment Report.

Reinhard, M., N.L. Goodman and J.F. Barker. 1984. Occurrence and distribution of organic chemicals in two landfill leachate plumes. ES&T, 18:953-961.

Swallow, K.C., N.S. Shifrin and P.J. Doherty. 1988. Hazardous organic compound analysis. ES&T, 22:136-142.

Welcher, F.J. (ed.). 1963. Standard methods of chemical analysis. 6th edition. Van Nostrand Reinhold Co., N.Y., pp. 2464-2465.

Figures

Figure 1:

Mass spectra of aniline and phenol; mass 94 is common to both.

Figure 2:

U.V. Absorbance spectra for phenol and aniline.

Figure 3:

Contour diagram of the HPLC-diode array chromatogram:

a) sample 54: b) aniline standard

Table 1. Some of the wastes known to have been deposited in the unlined ponds prior to 1969 (Jackman et al., 1985)

- Aniline process sludge; iron oxide and cutting oils
- Nonylated phenol, paracresol filter cake, thiocarbamate filter cake, mercaptobenzothiazole tars, gelled polyester resin, Vitavax^{R} still bottom tars
- Chlorophenolics mixed with shellsol
- Aromatic amine tars from the production of diethyltoluamide
- Phenyl β-naphthylamine and other aromatic amines and hard tars
- Toluene still residues

Table 2. Chemicals identified in Canagagigue Creek (Carey *et al.*, 1983)

- Dichlorophenols: 2,4-, 2,6- and 3,4-
- Trichlorophenols: 2,4,5- and 2,4,6-
- 2,3,4,6-Tetrachlorophenol
- Pentachlorophenol

- Benzothiazole
- Diphenylamine
- 2-(Methyl sulfinyl)benzothiazole
- 2-(Methyl sulfonyl)benzothiazole
- 2-(Methylthio)benzothiazole
- Dioctyl phthalate
- Nonyl phenol
- Butyl butoxyethylphthalate
- Tributyl phosphate
- 2-Hydroxybenzothiazole

Table 3. Results of the analysis for volatiles. A blank indicates none detected.

Well Number	50	54	55
Concentration	mg/L	mg/L	mg/L
Dilution Factor	100X	100X	100X
Chloromethane	0.1	0.1	0.09
1,1-Dichloroethene			0.16
Dichloromethane	0.02		0.06
Chloroform	0.07	0.12	0.04
Benzene	0.46	0.21	0.08
Toluene	3.9[a]	3.1[a]	2.4[a]
Chlorobenzene	4,0	0.27	
Ethyl benzene	1.2	0.07	0.02
m+p-Xylene	3.1	0.2	0.04
o-Xylene	1.7	0.06	
Styrene	0.07		
Cumene	0.05		
Propylbenzene	0.08		
3+4-Ethyltoluene	0.37	0.05	
2-Ethyltoluene	0.15		
Trimethyl benzene	0.87	0.03	
1,2-Diethylbenzene	0.03		
[b] SURROGATE RECOVERY			
Bromochloromethane	91%	86%	89%

- Results were corrected for blank
[a] Peak was saturated and represents minimum concentration
[b] Surrogate was spiked at 100 µg/L

Table 4. Results for semi-volatile EPA priority pollutants

Base Neutral Group	Well 50 (µg/L)	Well 54 (µg/L)
Naphthalene	62	18
1,3-Dichlorobenzene	4	
N-nitrosodiphenylamine	*1386	420
Di-n-butylphthalate	58	2249
Di-n-octylphthalate	5	50
Bis(2-ethylhexyl)phthalate	47	47
Total	1562	2784
Acid Group		
p-Chloro-m-cresol	416	
2-Chlorophenol	584	99
2,4-Dichlorophenol	*16815	662
Pentachlorophenol	21	
Phenol	a	a
2,4,6-Trichlorophenol	*2027	81
Total	19863	842
SURROGATES	(%RECOVERY)	
Phenol-d5	129	85
Trifluoro-m-cresol	132	105
Nitrobenzene-d5	75	45
2-Fluorobiphenyl	99	107
p-Terphenyl-d14	86	91

a - unable to verify the presence of phenol because of aniline interference

* compound also identified by thermal desorption; see Table 6

Table 5. Other pollutants tentatively identified by solvent extraction-GC/MS (estimated)

Sample Number	Compound Name	Rel. Ret. Time	Approximate[a] Concentration (mg/L)
50	Aniline	0.324	33
	Trimethylbenzene	0.333	1.1
	Trimethylbenzene	0.361	0.7
	Cresol	0.394	0.7
	Cresol	0.416	1.4
	N-(1-Methylethyl)aniline	0.490	0.3
	Chlorophenol	0.535	11
	* Isothiocyanatobenzene or N-(2-hydroxyethyl)-N'-phenylthiourea	0.535	4.2
	* Dichlorophenol	0.535	3.7
	* Benzothiazole	0.556	4.5
	1,2,3-Benzothiodiazole	0.580	0.1
	2-Methylbenzothiazole	0.619	0.4
	* Trichlorophenol	0.675	6.7
	N-Phenylacetamide	0.692	0.9
	3,6-Dichloro-4-methylpyridazine	0.730	0.2
	3-Methyl-2(3H)-Benzothiazolethione	0.868	0.1
	2-Benzothiazolamine	0.869	0.1
	2(3H)-Benzothiazolone	0.920	2.3
	N,N'-Methanetetraylbisbenzeneamine	0.992	0.8
	2,2'-Dithiobisbenzothiazole	1.113	2.4
	Carboxin	1.254	3.8
	N,N'-Diphenylurea	1.268	3.7
	N,N',N"-Triphenylguanidine	1.469	0.7
	TOTAL (including Table 4)		104
54*	Aniline	0.327	97
	Cresol	0.397	0.2
	Cresol	0.419	0.6
	4-Nitrosomorpholine	0.408	0.4
	o-Chloroaniline	0.466	1.3
	Isothiocyanatobenzene	0.534	1.4
	* m-Chloroaniline	0.537	1.3
	* Benzothiazole	0.558	9.4
	3-Aminooximebenzaldehyde	0.558	3.2
	* Isoquinoline	0.568	0.6
	1-(2-Methyl-1,3-dithiolan-2-yl) ethanone	0.608	0.4
	2-Methylbenzothiazole	0.620	0.8
	* 2-Methylquinoline	0.632	0.1
	Trichlorophenol	0.676	0.3
	* N-Phenylacetamide	0.695	10.0
	* 2(3H)-Benzothiazolone	0.917	3.2
	* 2,2'-Dithiobisbenzothiazole	1.115	10.8
	4-(Methoxymethyl)-2,6-dimethylphenol	1.115	30.0
	* 4-(2-Benzothiazolylthio)morpholine	1.147	3.0
	* Carboxin	1.252	5.6
	TOTAL (including Table 4)		183

[a]These are TENTATIVE identifications. The concentration reported ar ESTIMATES based on response factors of surrogates.
[b]This peak was saturated, amount estimated is a minimum.
*Compound also identified by thermal desorption; see Table 6.

Table 6. Tentative identification of unknowns using thermal desorption-GC-MS.

Compound	Rel. Ret. time	Approx. Conc.[a] mg/L
Sample: 50		
Toluene	0.293	0.5
*[b] 2,4-Dichlorophenol	0.571	30
* N-(2-hydroxyethyl)-N'-phenyl-thiourea or Isothiocyanatobenzene	0.606	1.3
* Benzothiazole	0.626	4
* 2,4,5-Trichlorophenol	0.728	11
Diphenylamine	0.897	1.7
TOTAL CONCENTRATION		48.5 mg/L
Sample: 54		
Toluene	0.272	22
Acetic Acid	0.407	150
Morpholine	0.430	n.r.[c]
* Aniline	0.443	300
2-Ethyl hexanol	0.486	16
1,3-Dithiane	0.528	38
1,4-Dithiane	0.530	n.r.
* m-Chloroaniline	0.578	3.5
Methyl tetrahydro-pyran-2-one	0.601	19
5-Ethyl-furanone	0.616	14
Acetyl morpholine	0.642	11
* Benzothiazole	0.661	110
* Isoquinoline	0.666	<10
Methyl benzisothiazole	0.703	8.5
* Methylquinoline	0.716	17
N-phenylformamide	0.730	13
N-propylbenzamide	0.748	4.9
* N-phenylacetamide	0.777	42
2,2'-dithio-bis-ethanol	0.812	51
2-Methylthio-benzothiazole	0.898	0.6
* Benzothiazolone	0.960	17
2,2-[1,2-ethanediylbis(thio) bis-thanol	0.966	10
4,4-dimethyl-3-phenyl-2,5-cychexadien-1-one	1.026	
* 2,2'-Dithiobisbenzothiazole	1.077	6
* 4-(2-benzothiazolylthio)-morpholine	1.110	5
Dimethyl-3,8-decane	1.145	80
Hexadecane	1.162	n.r.
* Carboxin	1.189	6.5
TOTAL CONCENTRATION		945 mg/L
Sample: 55		
Toluene	0.273	2
Acetic acid	0.310	25
Morpholine	0.387	23
Methyl sulfinyl ethene	0.409	1.6
Aniline	0.467	41
1,4-Dithiane	0.533	1.7
4-Ethyl-morpholine	0.585	3.8
1,3-Benzodioxolone	0.614	2.2
Acetyl morpholine	0.632	3.6
Methyl oxathiane	0.643	
Benzothiazole	0.658	8.8
N-phenyl acetamide	0.761	8.1
Diphenylamine	0.900	3
TOTAL CONCENTRATION		123.8 mg/L

[a] These are estimates based on the d-10 anthracene response factor.
[b] *Compound also identified by solvent extraction; see Tables 4 and 5.
[c] n.r. = not resolved

Table 7. Analysis of sample 54 by HPLC

Aniline	299 mg/L
Benzothiazole	17 mg/L
Mercaptobenzothiazole	22 mg/L
Phenol	3 mg/L

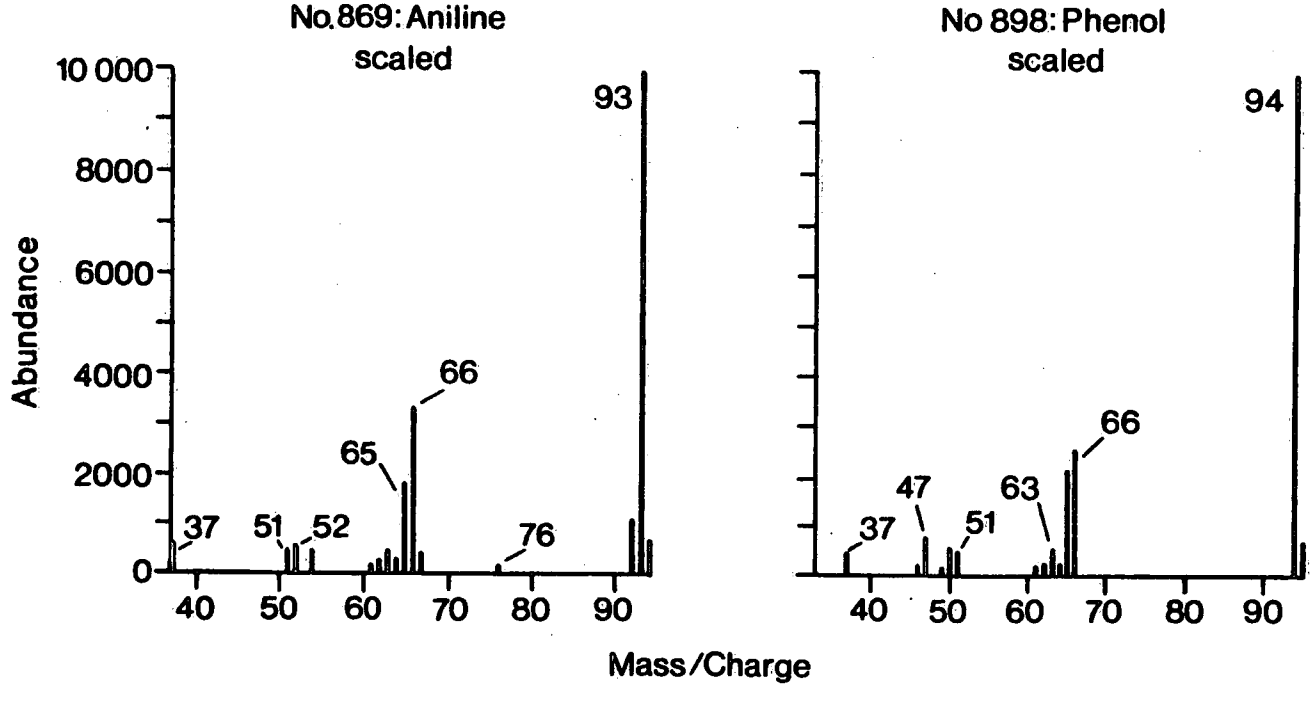
No.869: Aniline
scaled
No 898: Phenol
scaled
Abundance
10 000
8000
6000
4000
2000
0
93
66
65
37
51
52
76
94
66
47
63
37
51
40
50
60
70
80
90
Mass/Charge

Figure 1

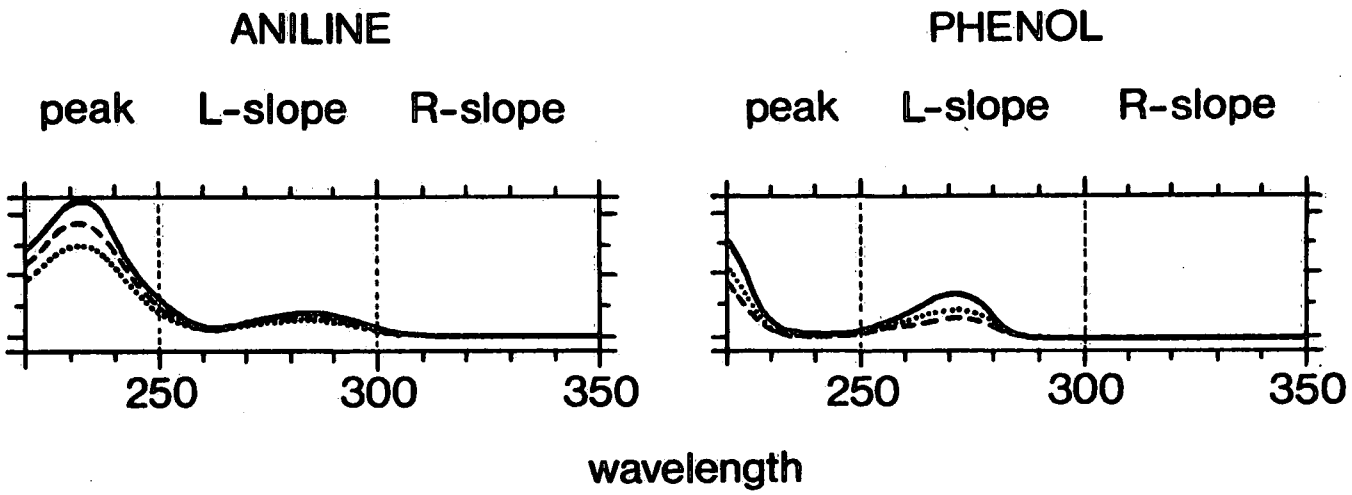
ANILINE
peak
L-slope
R-slope
250
300
350
PHENOL
peak
L-slope
R-slope
250
300
350
wavelength

Figure 2

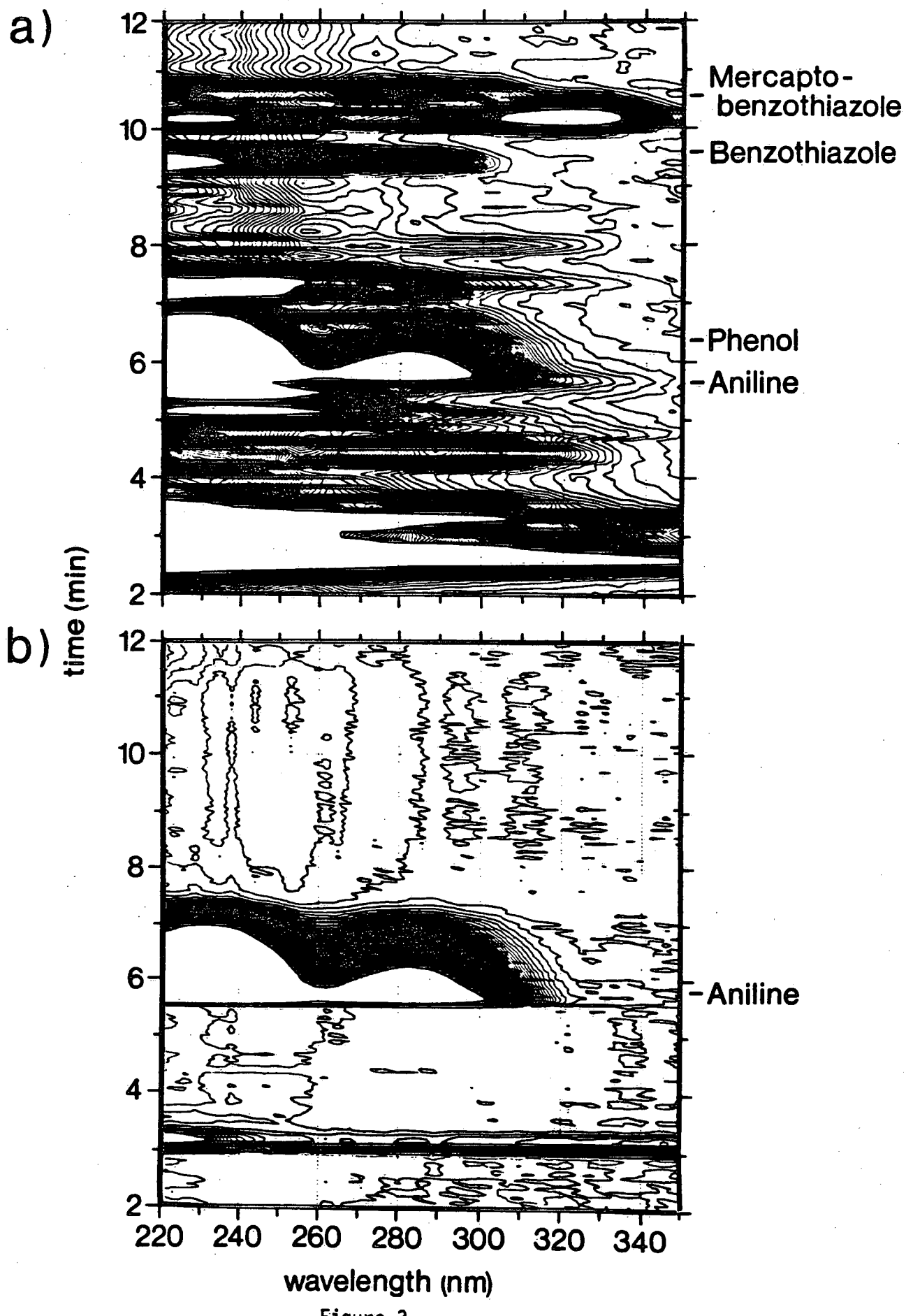
a)
b)
12
10
8
6
4
2
time (min)
Mercapto-
benzothiazole
Benzothiazole
Phenol
Aniline
Aniline
220
240
260
280
300
320
340
wavelength (nm)

Figure 3