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IDENTIFICATION OF ORGANIC COMPOUNDS IN THE LEACHATE OF A WASTE TIP

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ABSTRACT

Two different types of leachate from a waste tip have been researched. For that purpose some analytical methods were developed. The first type of leachate was sampled from a waste tip in the acidification stage. In this leachate the larger part of the organic load consists of free volatile acids (95 to 100% of the COD). Volatile amines and ethanol (1.2% respectively 1% of the COD) were also present. The leachate was extracted with hexane and the extract was analyzed with infrared and nuclear magnetic resonance spectrometrie and a gaschromatograph - mass spectrometer combination. In the extract alcohols, oil, esters, terpenes and phtalates have been identified. High molecular compounds were only present in a low concentration.

The second leachate, taken from a waste tip in the methane fermentation stage contained much more high molecular compounds. About 32% of the organic carbon consists of compounds with a molecular weight over 1000. In this water no acids, amines and alcohols could be detected. This means that the organic compounds were end products of degradation processes.

Furthermore there was a remarkable difference in heavy metal content between the two leachate types.

INTRODUCTION

In the Netherlands a large part of the municipal refuse is deposited at waste tips. The dumped refuse is leached by percolating rainwater and the leached contaminants may penetrate the groundwater system. Therefore it is important to know which compounds are present in the leachate. The presence of organic compounds is of particular

interest as they play a role in the transport of heavy metals: metal ions may become very mobile in the soil when they form water soluble complexes with organic substances.

In the presented research two types of leachate were investigated. The first one (leachate I) was collected at a nine-year old part of the waste tip of Ambt-Delden, situated in the region of Twente in the eastern Netherlands. The waste tip is a controlled one, i.e. the refuse is daily compacted and covered with sand. The leachate samples have been taken from a tile drainage system just beneath the tip.

The second type (leachate II) was collected at the waste tip of Wijster in the northern part of the Netherlands. The refuse at the sampling point was about two years old. On this tip the refuse is not compacted and only covered with sand. The samples have been taken in the same way as in Delden.

Earlier research on organic compounds in leachates from waste tips was carried out by ROBERTSON et al. (1), CHIAN and DE WALLE (2) and HARMSSEN (3).

The here presented research shows that there are large differences in the organic load of leachate, depending on the fermentation stage of the refuse. In general there are two main types of leachate. This article described the presence of different organic compounds in these two types of leachate and the analytical methods used.

ORGANIC CONTAMINATION OF THE LEACHATE

The organic load of the two types of leachate is completely different (Table 1). The leachate from Delden, further on called leachate I, has very high COD (Chemical Oxygen Demand), TOC (Total Organic Carbon)

Table 1. COD, TOC and BOD values of the leachates

	Leachate I	Leachate II
COD $\text{mg}\cdot\text{l}^{-1} \text{O}_2$	60,000	7000
TOC $\text{mg}\cdot\text{l}^{-1} \text{C}$	20,000	2100
BOD $\text{mg}\cdot\text{l}^{-1} \text{O}_2$	30,000	50

and BOD (Biological Oxygen Demand) values. For leachate II from Wijster these values are much lower, especially the low BOD value is remarkable. This shows that the organic compounds are more or less end products of the degradation.

Research of HOEKS and BORST (4) has indicated that the organic load of leachate I drastically changed in a soil column by methane fermentation. The organic load of the effluent is comparable with leachate II. In a waste tip the process of methane fermentation also takes place.

Leachate I is produced in the acidification stage and leachate II in the methane fermentation stage. These stages have been described by FARQUHAR and ROVERS (5).

In the acidification stage, complex organic compounds are fermented anaerobically, yielding soluble organic acids (free volatile fatty acids), amino acids and other low molecular compounds and gases like H_2 and CO_2 . In the methane fermentation stage free volatile acids are fermented yielding CH_4 and CO_2 gas as end products.

The organic load also influences the pH. In leachate I the pH is 5.7 and in leachate II about 7. At the higher pH the solubility of the produced CO_2 is higher. The bicarbonate content in leachate I is $17 \text{ mg.l}^{-1} \text{ HCO}_3^-$ and in leachate II $12,000 \text{ mg.l}^{-1} \text{ HCO}_3^-$.

FREE VOLATILE FATTY ACIDS

The organic load of leachate I was very high, as appeared from the COD which amounted to about $60,000 \text{ mg.l}^{-1} \text{ O}_2$. The larger part of these oxidizable compounds can easily be determined by gas chromatography. This is especially true for the free volatile fatty acids (C_2 to and including C_6). In this case the water sample can directly be injected into the gas chromatograph (for a result see Fig. 1).

A problem with the analysis of fatty acids is the pollution of the injection part of the chromatograph, which causes so-called ghost peaks when water is injected afterwards. Because of their polar character the acids are adsorbed in the injection port. When water is injected the acids desorb and give peaks at the same place as the acids

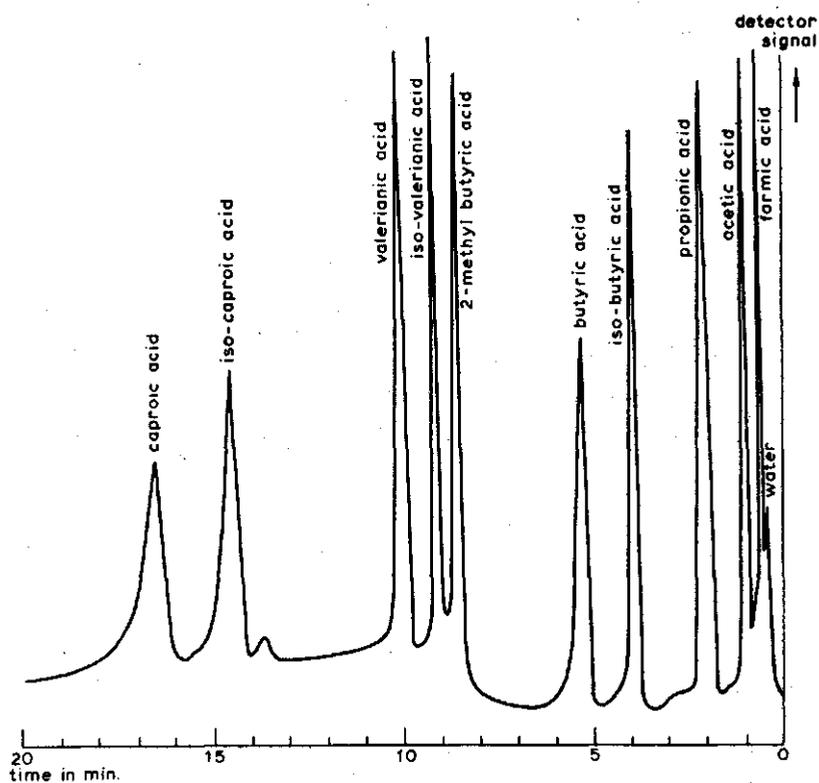


Fig. 1. Gas chromatogram of C_1-C_6 acids. Column 3% Carbowax 20 M; 0.5% H_3PO_4 on Carbopack B; 6 feet x 1/8 inch glass. Carrier gas N_2 40 ml. min^{-1} . Temp. column 170°C during 7 min.; in 1 minute to 210°C . Sample $1 \mu\text{l}$ of 0.01% of each acid in 1% formic acid.

to be analyzed. The ghosting largely can be avoided by adding 1 ml of formic acid to a 100 ml sample. The formic acid is more polar than the other acids and is therefore preferentially adsorbed, thereby reducing the ghosting to an acceptable level (HARMSSEN, 6).

With the method developed the acids, acetic acid up to and including capronic acid, have been analyzed. VAN ENGERS (7) has also determined enanthic acid. The results are given in Table 2. The accuracy of these analyses is about 5 to 10%. Referring to Table 2 the conclusion is that the acids represent 95 to 100% of the total COD.

In leachate II no volatile acids could be detected.

Table 2. Free volatile fatty acids in leachate I (COD 65,000 mg.l⁻¹ O₂)

Acid	Conc. in mg.l ⁻¹	COD caused by the acid in mg.l ⁻¹ O ₂	Percentage of total COD
acetic acid	11,000	11,730	17.9
propionic acid	3,760	5,690	8.7
iso-butyric acid	520	950	1.4
butyric acid	9,890	17,980	27.4
2-methyl butyric acid	350	710	1.1
iso-valeric acid	320	650	1.0
valeric acid	2,510	5,118	7.8
iso-caproic acid	70	150	0.2
caproic acid	5,770	12,730	19.4
enanthic acid	5,200	12,160	18.5
total			103.4

VOLATILE AMINES

The amines in leachate can also be determined by gas chromatography without concentrating them beforehand (MUYLAERT, 8). An example is given in Fig. 2.

Again ghosting is a problem, because the amines are polar. The ghost peaks can be reduced to an acceptable level by adding 1 g of KOH and 20 ml of 25% ammonia to 100 ml of sample. Results concerning leachate I are given in Table 3.

With this column ethanol is also determined. The ethanol concentration was 277 ml.l⁻¹, which represents 1% of the COD. In leachate II no amines and ethanol were detected.

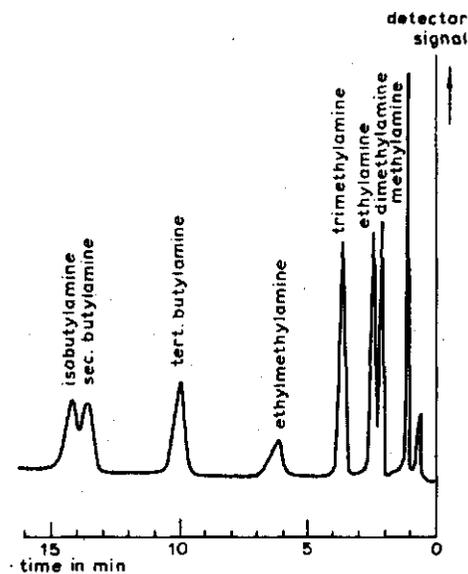


Fig. 2. Gas chromatogram of volatile amines. Column 4% Carbowax 20 M; 0.8% KOH on Carbopack B; 6 feet x 1/8 inch glass. Carrier gas N_2 20 ml.min⁻¹; temp. column 70°C during 5 min.; with 4°C per min. to 150°C. Sample 0.5 μ l of 0.01% of each amine in 5% NH_3 and 1% KOH

Table 3. Volatile amines in the leachate I (COD 56,000 mg.l⁻¹ O₂)

Amine	Conc. in mg.l ⁻¹	COD caused by the amines in mg.l ⁻¹ O ₂	Percentage of total COD
methanamine	6	9	0.02
trimethylamine	83	201	0.36
t-butylamine	43	114	0.20
sec-butylamine	102	268	0.48
iso-butylamine	32	83	0.15
total			1.21

HIGH MOLECULAR COMPOUNDS

With membrane filtration and gel permeation the presence of high molecular compounds can be established. This was done by Chian and De

Walle. Using membrane filtration they found that 11.1% of the TOC had a molecular weight over 100,000. With gelpermeation they found only 6% of the TOC having a molecular weight of more than 50,000. They did not explain the difference. From the here described experiments it appeared that membrane filtration did not give satisfying results when applied to leachate I, because the free volatile acids adsorbed in the filters and the filterhousing. This is the reason why the reduction in COD after filtering cannot be attributed to the presence of high molecular compounds (BEKER, 9). Possible Chian and De Walle have had the same problems, because in their leachate volatile acids were also present. Probably their results with gelpermeation will be more reliable.

In this case gelpermeation has given good results. The leachates were supplied to a gelpermeation column (Sephadex G-75). The effluent was sampled by a fraction collector and the fractions were analyzed for TOC. The results are given in Fig. 3. The first peak is caused by high molecular compounds with a molecular weight of more than 50,000, the last peak by low molecular ones with a molecular weight of less or about 1000. Since a small part of the Sephadex was leached from the column, the background value of the TOC was about 10 mg.l^{-1} C.

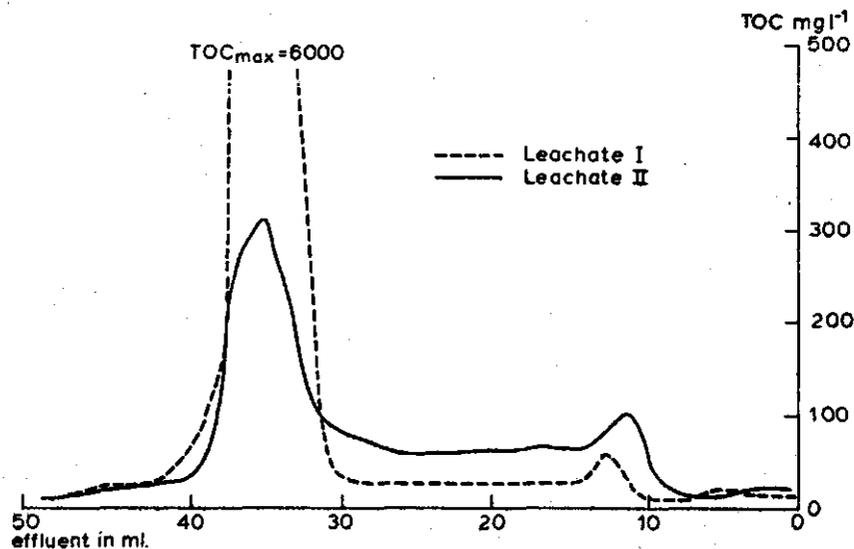


Fig. 3. TOC values in fractions of leachate passed through a Sephadex G-75 column (column dimension 60 x 1 cm; eluant: distilled water 2 ml.hr^{-1} sample 1 ml, fractioning every 30 minutes).

Leachate I contained only a relative small amount of high molecular compounds compared with the low molecular compounds like acids and amines. The high molecular compounds represented only 0.5% of the TOC. About 0.8% of the TOC was attributable to compounds with a molecular weight between 1000 and 50,000. The rest of the TOC was related with low molecular compounds.

In leachate II about 12% of the TOC could be attributed to the presence of compounds with a molecular weight of more than 50,000 and 20% to compounds with a molecular weight between 1000 and 50,000. The remaining part consisted of low molecular compounds.

Comparing leachate I and II it can be concluded that the absolute amount of high molecular compounds is increased by a factor of 2.6, when going from leachate I to II. The absolute amount of low molecular ones is decreased by a factor of 10.

The amount of high molecular compounds (> 50,000) in the leachate as reported by Chian and De Walle, amounted to 6% of the TOC, while the volatile acids were still present. This indicates that the leachate investigated by them was in a fermentation stage somewhere between the acidification and methane fermentation stage.

The high molecular compounds in leachate II will be of humic origin. Also the low molecular compounds will partly consist of humic and fulvic acids, since 40% of the COD precipitates when the water is acidified. At 300°C 75% is still non-volatile.

CHIAN (10) has reported some more details on the molecular weight distribution. He observed that the amount of volatile acids and high molecular compounds decreased with time, when comparing waste tips of different ages. His results do not completely agree with the results published here, because these results show that the amount of high molecular compounds increased with decreasing amount of acids. It is, however, likely that on the long run the amount of high molecular compounds also will decrease. Therefore not only the stage of fermentation, but ultimately also the age of the waste tip will influence the amount of organics in the leachate.

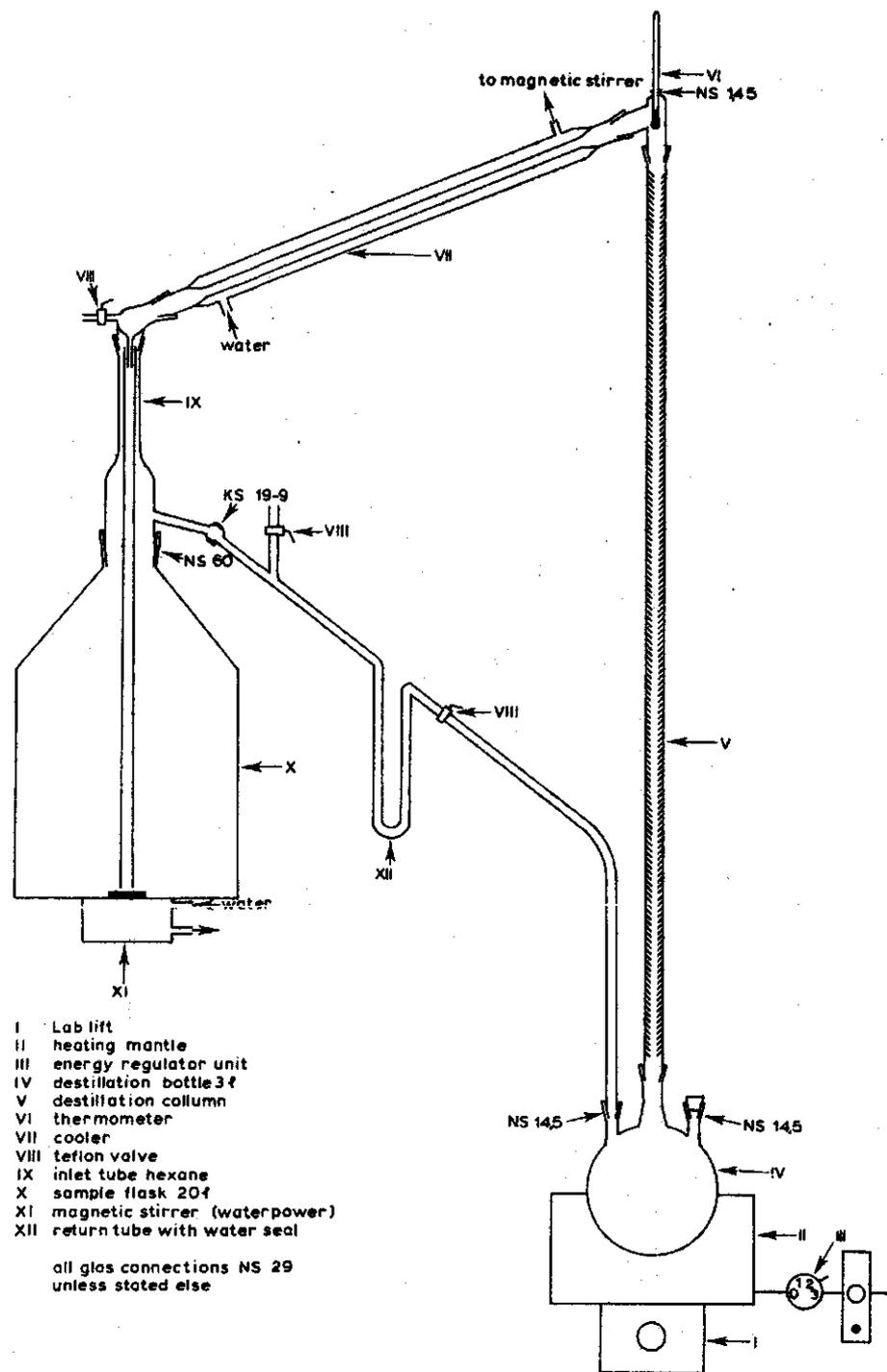


Fig. 4. Apparatus for continuous extraction of water samples

ALIPHATIC, AROMATIC AND POLAR COMPOUNDS

The remaining compounds have been investigated by extracting the leachate with hexane. To this purpose an apparatus for continuous extraction was constructed (see Fig. 4). A similar apparatus has been used by MEIJERS and VAN DER LEER (11).

The hexane solution is concentrated by evaporation and the acids and bases are removed by extraction with diluted HCl and NaOH. Next the extract is added to a column of silica-gel (Fisher S662). The aliphatic compounds (oil) are eluted with hexane, the aromatic ones with benzene and the polar compounds (the so-called 'oxys') with chloroform-methanol (1:1).

Table 4. With hexane extractable compounds in the leachate in mg.l^{-1}

	Leachate I	Leachate II
aliphatic compounds	0.64	0.09
aromatic compounds	1.21	0.38
oxys	12.5	4.38

The eluted fractions have been investigated by gas chromatography. The results are given in Table 4. Since hexane only poorly extracts the more polar components, the actual concentrations in the leachate, as far as aromatic compounds and oxys are concerned, will be higher as reported here.

ALIPHATIC COMPOUNDS

The aliphatics are easily identified in the chromatogram. They could be named with the aid of standards. The chromatogram of leachate I is given in Fig. 5. From this figure it appears that the aliphatics may originate from light to heavy gas oil (C_{13} - C_{25}) and lubricants and waxes (C_{25} - C_{30}).

The chromatogram of leachate II is completely identical, indicating that the same aliphatics are found. Only the total amount of aliphatics is much smaller in leachate I (Table 4). This may be caused by the high amount of volatile acids in leachate I, because the solubility of hydrocarbons is raised by the presence of these acids.

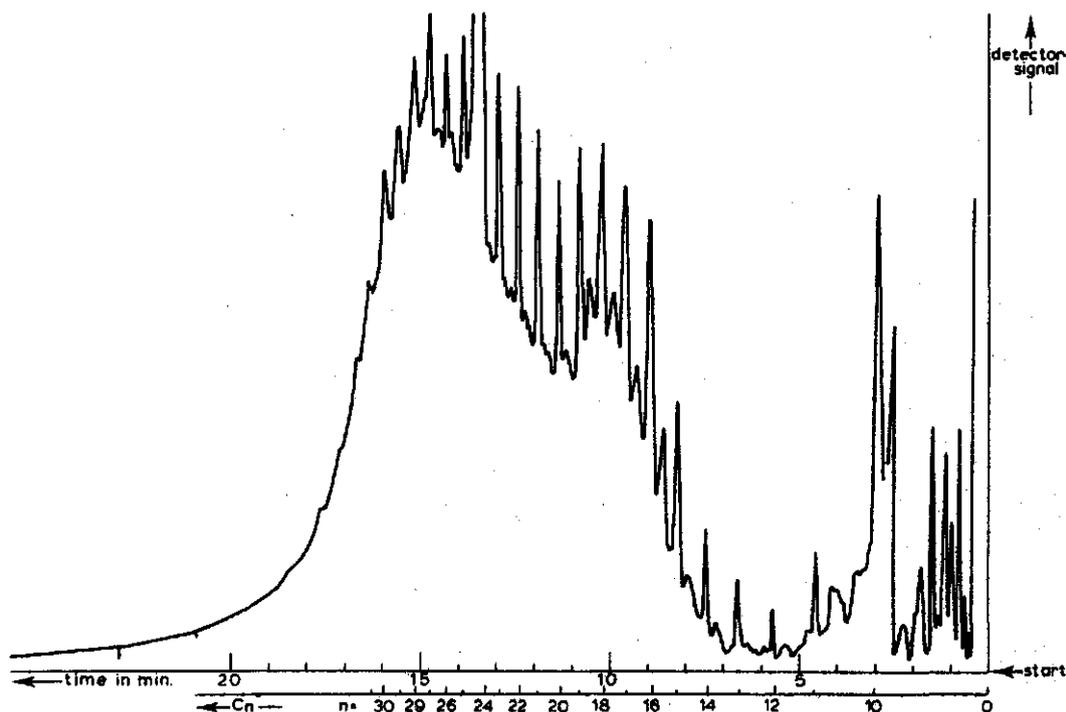


Fig. 5. Gas chromatogram aliphatic compounds in leachate I

AROMATIC COMPOUNDS

The aromatics in the gas chromatograms cannot easily be named. For the identification of these compounds other detection methods are needed. In this research the aromatic fractions were investigated by infrared spectrometry and nuclear magnetic resonance. The spectra of leachate I are given in Figs. 6 and 7. For leachate II the concentrations were too low to give clear peaks. In the NMR spectrum only a peak for aromatics and in the IR spectrum a peak for the $C=O$ group was to be seen in the hexane extract of the leachate. Because of the little informations got from the spectra, the spectra of leachate II are not presented.

In the NMR spectra 6-III and 6-IV the peaks are found at somewhat lower δ -value (0.1 ppm) because of the effect of the benzene solvent. The peak at 1.6 ppm in spectrum 5-III indicates the existence of a $-C=C-H_3$ group, the peak at 2.1 ppm refers to a $-C-CH_2-C=C$ group and the one at 2.2 ppm to CH_3 substituted to an aromatic ring. The peaks

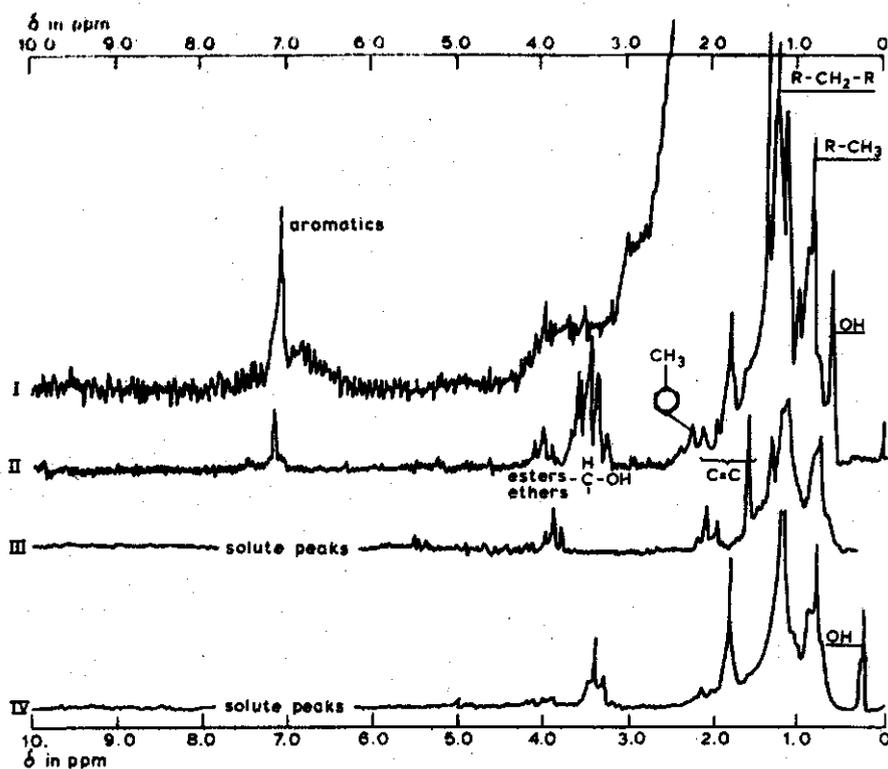


Fig. 6. NMR spectra of leachate I. I, with hexane extracted compounds; II, after removing acids and bases; III, aromatic compounds; IV, oxys

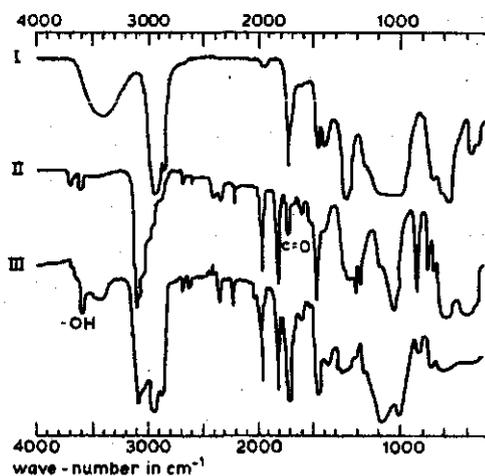


Fig. 7. Infrared spectra of leachate I. I, extract after removing acids and bases; II, aromatic compounds; III, oxys

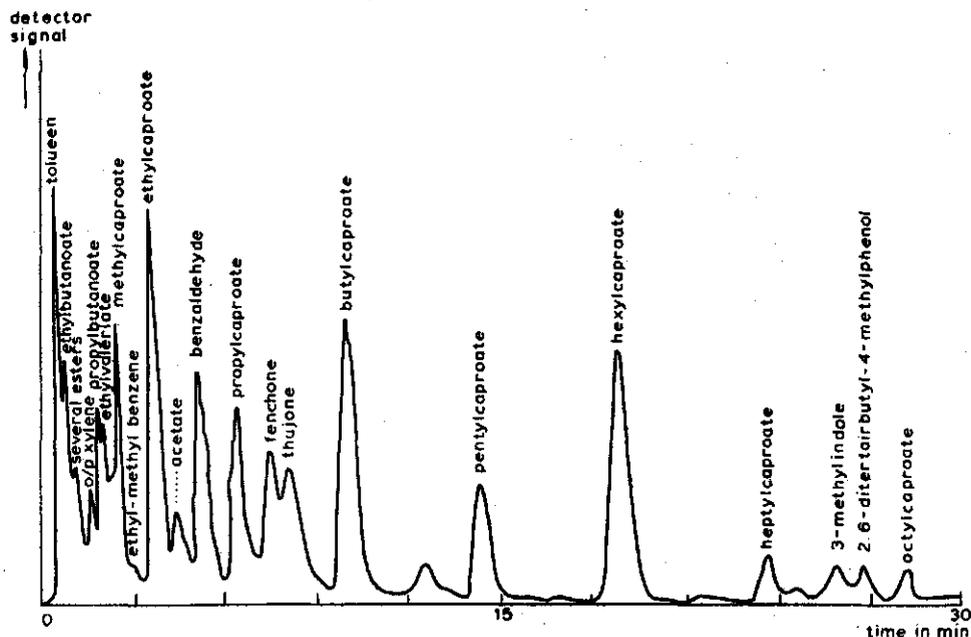


Fig. 8. Gas chromatogram of the aromatic compounds in leachate I, mentioning those that have been identified by GC-MS. Column OV 17; 5 feet x 1/4 inch glass. Carrier gas He 30 ml.min⁻¹; temp. column 70-200°C; 8°C.min⁻¹. Detection with VG Micromass 70-70

at 4.0 ppm refer to both esters and ethers. The presence of esters is confirmed by the peak at 1700 cm⁻¹ in the infrared spectrum 7-II.

Fig. 6 also shows that after removing acids and bases, the peak of the aromatics at 7.0 ppm becomes smaller. It must be concluded therefore that aromatic bases or acids are present in the leachate.

The aromatic fraction of leachate I has also been investigated with the aid of a gas chromatograph mass-spectrometer combination VG Micromass 70-70. The results are given in Fig. 8. A typical problem was met in the mass-spectra of several peaks in the chromatogram. They all had in common mass peaks at 99 and 117. These spectra belong to ester of caproic acid.

In Fig. 8 small aromatic compounds detected by gas chromatography are mentioned. The eluate which was obtained by percolating the silicagel column with benzene was referred to as the aromatic fraction, because the aromatic hydrocarbons are present in this fraction. Of course also other non-aromatic compounds with a polarity comparable to the aromatics may be present. This is quite clear from the chromatogram in Fig. 8.

As the experiments with NMR and IR did show aromatic compounds they will be present in the extract, but probably they cannot be determined with the gas chromatographic method used. Capillary or liquid chromatography will most probably give better results.

Unfortunately there was no opportunity to analyze leachate II with mass-spectrometry, since at the time of the experiments the GC-MS was not available.

POLAR, OXIDIZED COMPOUNDS

The oxys have also been investigated with infrared spectrometry, NMR and mass-spectrometry. Since methanol does influence the IR and NMR spectra, the oxys were eluted with chloroform instead of chloroform-methanol. This change in eluant did not influence the chromatogram.

In the IR and NMR spectra the benzene solvent is also visible. The results of leachate I are presented in Figs. 6 and 7. The NMR peaks at 4.0 ppm refer to esters and ethers, at 3.5 ppm to alcohols ($-\text{CH}_2\text{-OH}$ or $-\text{CH-OH}$), at 2 ppm to double bounds and the peaks at 0.9 and 1.5 ppm to $-\text{CH}_2-$ and $-\text{CH}_3$. The peak of the $-\text{OH}$ group can be found at about 0.5 ppm. This δ -value is very low, because of the low concentration of the $-\text{OH}$ groups. At higher $-\text{OH}$ concentration there will be interaction between different OH groups, resulting in a higher δ -value. The presence of esters and alcohols is confirmed by the IR spectrum 7-III because of the presence of the $\text{C} = \text{O}$ peak at 1700 cm^{-1} and the $-\text{OH}$ peak at 3400 cm^{-1} .

As already mentioned the NMR and IR spectra of leachate II are not presented here because there were only a few peaks present. The absence of the OH peak in the IR spectrum indicates that alcohols are not present in leachate II.

In both leachates n-butylphtalate and iso-octylphtalate could be identified which is in accordance with the presence of the $\text{C} = \text{O}$ peak in the IR spectra.

The oxys in leachate I were investigated with GC-MS. The results are presented in Fig. 9.

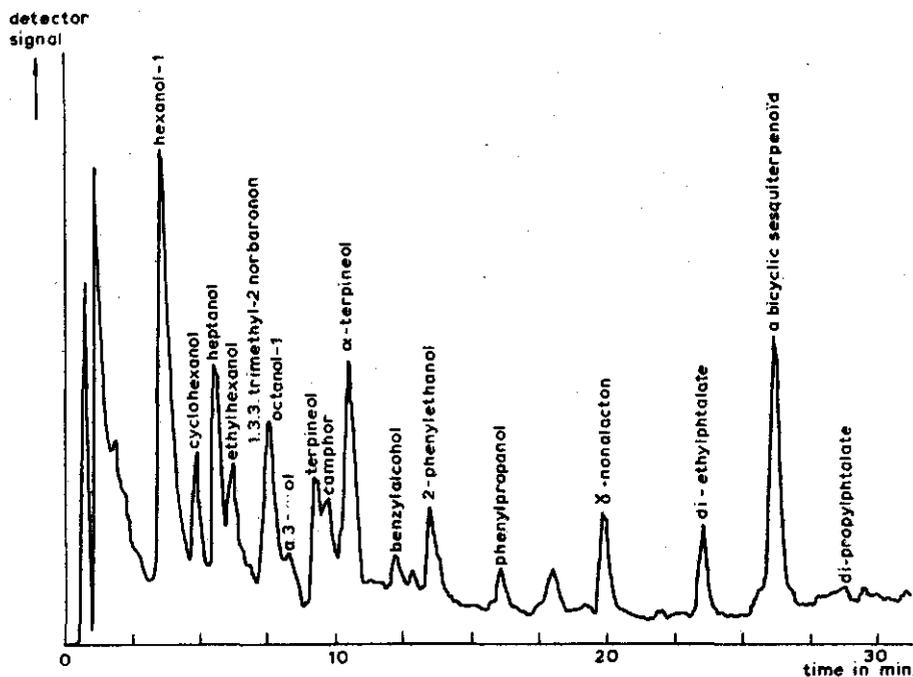


Fig. 9. Gas chromatogram of the oxys in leachate I, mentioning those identified by GC-MS. Column Silar 5C; 5 feet x 1/4 inch glass. Carrier gas He 30 ml.min⁻¹. Temp. column 80-250°C; 8°C.min⁻¹. Detection with VG Micromass 70-70

COMPLEXATION OF HEAVY METALS WITH ORGANIC COMPOUNDS

There was a remarkable difference in heavy metal content between the two types of leachate (Table 5). This difference is related to the organic load in the leachate.

Table 5. Heavy metals in the leachates in mg.l⁻¹

	Leachate I	Leachate II
Fe	1120	40
Mn	53	0.24
Cd	0.01	0.02
Cu	0.65	0.20
Ni	1.04	0.40
Pb	0.17	1.0
Zn	54	1.6

During the acidification stage in the waste tip (leachate I) the metals are kept in solution by complexation with the free volatile acids. In the methane fermentation stage (leachate II) the acids disappear and there is only a relative small amount of organic compounds left with differing complexing features. This gives a change in the metal concentrations. Lead for instance is known as a metal which forms very stable complexes with humic acids and this may be the reason that lead is present in a higher concentration in leachate II. More details about the behaviour of the heavy metals are published by HOEKS and BEKER (12).

The effluent of the Sephadex column which was used to study the molecular weight distribution in leachate II, is also investigated with respect to a few heavy metals. The results are given in Fig. 10.

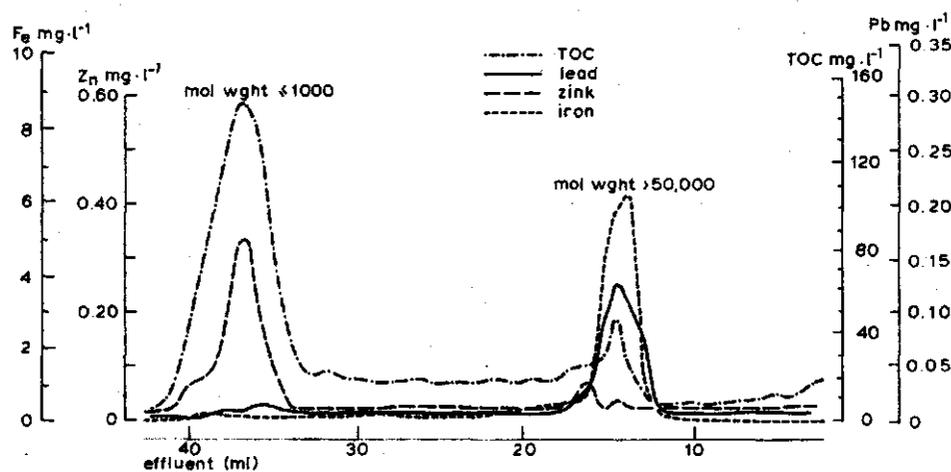


Fig. 10. Heavy metals in fractions of leachate II passed through a Sephadex G75 column (column and eluant as in Fig. 3, sample 0.5 ml, fractioning every 30 minutes)

It is clear that iron and lead have formed complexes mainly with the high molecular compounds, while zinc is associated with the low molecular ones.

More about this subject will be published in future.

ACKNOWLEDGEMENT

It is gratefully acknowledged that for IR, NMR and GC-MS analyses use was made of the facilities of the Department of Organic Chemistry of the Agricultural University in Wageningen. In particular the author wishes to thank Dr. M. Posthumus for his aid with the GC-MS combination.

SUMMARY

Two characteristic types of leachates of a waste tip have been investigated with respect to organic compounds. For that purpose some analytical methods were developed.

The first type of leachate was collected from a waste tip in the acidification stage. The larger part of the organics in this leachate, 95 to 100% of the COD, appeared to consist of free volatile fatty acids. The acids have been analyzed by gas chromatography. Ghosting was a problem, but this could largely be eliminated by the addition of formic acid.

The volatile amines could be analyzed in a similar way as the acids. They represent about 1.2% of the COD. Ethanol, 1% of the COD, could also be analyzed with the column used for amines.

The remainder part of the COD was investigated by extracting the leachate with hexane. The extract was separated into an aliphatic, an aromatic and a more polar fraction by column chromatography. These fractions were analyzed by gas chromatography, IR, NMR and also by a gas chromatograph mass-spectrometer combination. Several compounds have been identified, among which oil, alcohols, esters, terpenes and phthalates.

It was not possible to establish the presence of high molecular compounds with membrane filters, because the acids were adsorbed in the filters. Gel permeation gave more reliable results. About 0.5% of the TOC had a molecular weight more than 50,000 and 0.8% between 1000 and 50,000.

In the second leachate, taken from a waste tip in the methane fermentation stage, about 12% of the TOC had a molecular weight of more

than 50,000 and 20% between 1000 and 50,000.

In this leachate no volatile acids, amines and alcohols could be identified. The organic load was relatively low and because of the remarkable low BOD-value (high COD/BOD ratio) it is concluded that the organic compounds present are more or less end products of the degradation process. Probably most of the organics consist of humic and fulvic acids.

Not only the nature of the organic compounds in the two types of leachate differs, but also the amount of heavy metals complexed by these compounds. This can be explained by different complexing features of the organic compounds. With gelpermeation it is shown that some metals are better complexed by high molecular compounds and some by low molecular ones.

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