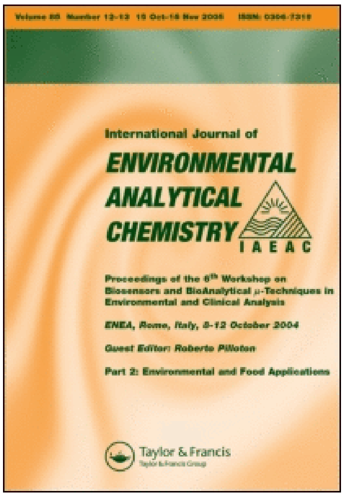

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Colenutt, B. A.(1979) 'The Sampling and Gas Chromato-graphic Analysis of Fatty Acids from Landfill Sites', International Journal of Environmental Analytical Chemistry, 7: 1, 71 — 77

To link to this Article: DOI: 10.1080/03067317908071479

URL: http://dx.doi.org/10.1080/03067317908071479

Intern. J. Environ. Anal. Chem., 1979, Vol. 7, pp. 71–77
0306-7319/79/0701-0071 $04.50/0

Printed in Great Britain

The Sampling and Gas Chromatographic Analysis of Fatty Acids from Landfill Sites

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A gas chromatographic technique has been developed and applied to the qualitative and quantitative analysis of fatty acids in the interstitial gases of landfill sites. Acetic, propionic, and butyric acids were those shown to be present in the highest concentrations. The fatty acid concentrations were higher at a site where landfill had been completed two years ago than at a site where operations had finished twenty-five years ago.

The concentrations of fatty acids measured were well above the odour thresholds. These compounds may be responsible for the unpleasant smells frequently associated with landfill gases.

KEY WORDS: Landfill, gas chromatography, fatty acids

INTRODUCTION

Landfill is a method which has been used extensively for the disposal of industrial and domestic refuse. Its major advantages are cheapness and simplicity. In general after the landfill has been completed the site is covered and left for a number of years before development is considered. Increasing demand for land has meant that old landfill sites are now required for other uses, providing that such uses present no hazards. In this context, the prime consideration is that the decomposition of the refuse has gone to completion.

The process of decomposition in landfill areas is not well understood. Attempts have been made to simulate in the laboratory the conditions existing in a landfill site but a major problem in the elucidation of the mechanism is the infinitely variable nature both of the refuse itself and the conditions prevailing within the landfill site. The reaction will be affected by the nature of the refuse, and for example the pH of the medium and the presence or absence of oxygen. When the site is sealed at the completion of landfill activities oxygen is present, but this is consumed as the reactions proceed and eventually an anaerobic stage is reached. Once the site is closed the supply of further oxygen depends on the permeability of the seal, although since the gas pressure within is normally above atmospheric pressure, the direction of gas flow is likely to be from the site rather than into the site.

Ultimately a point will be reached where an anaerobic process assumes major importance. This proceeds in two stages. The first stage involves the breakdown of complex organic compounds to smaller compounds under the action of enzymes.[1,2] Although there is some disagreement[3] over the nature and amounts of the products, it is reported that fatty acids, notably acetic acid, are formed.[2,4,5]

Whilst this stage can be brought about by a wide variety of soil bacteria,[6] the second stage is very much more specific, and requires the presence of methanobacteria.[5] In this stage methane and carbon dioxide are major products from the subsequent reaction of the products of the first stage.

Work in these laboratories to analyse methane and other associated gases has been described earlier.[7] These gases are of major importance in determining the safety of a landfill site for development. The analysis of the products and intermediates in the earlier stages of reaction is also important for a number of reasons.

It is possible that a knowledge of the type and amount of these compounds will help in the elucidation of the nature of the decomposition mechanism. The information could also be useful in determining the state of decomposition of a site of unknown or uncertain history.

Leakage of the gases into the atmosphere may occur, and in some situations there could be washout into natural water courses. A knowledge of the range of compounds present is necessary to understand their potential toxicity. Traces of the compounds may also remain when a landfill site is developed, and for this reason their nature and toxicity is again an important consideration. In some instances residents near landfill sites complain of unpleasant odours, and these compounds may be responsible for this nuisance.

Although methane and some other associated gases has been analysed by direct injection of the interstitial gases into a suitable gas chromatograph system, this method is unlikely to yield any information as far as the fatty acids are concerned. Their concentrations in the gas are likely to be so low that they are undetectable without concentration. Thus a concentration technique has been devised prior to the analysis of the acids by gas chromatography.

EXPERIMENTAL

Sampling

Aluminium tubes 2 m long, 13 mm outer diameter and 9 mm bore were inserted into the ground in the manner previously described.[7] Gases from the tubes were drawn through two Dreschel bottles each containing 200 ml of 0.5 M sodium hydroxide. A Factory Inspectorate battery powered portable pump was used to draw the gases through the liquid at a flowrate of 1 litre min^{-1} for periods of up to 1 hr. The sodium hydroxide solutions were returned to the laboratory for analysis.

Gas chromatography

The fatty acids were liberated by the addition of dilute sulphuric acid to the sodium hydroxide solutions, and subsequently extracted into diethyl ether (2 × 25 ml). After concentration the ether solutions were examined by gas chromatography.

A 2 m stainless steel column of 3 mm outer diameter packed with 10% FFAP (free fatty acid phase) coated on 60–80 mesh acid washed Chromasorb W was operated at 80°C with nitrogen carrier gas at a flowrate of 30 ml min^{-1}. The injection temperature and detector temperature were 250°C. Injections of standard solutions of the fatty acids showed that those from acetic to *n*-heptanoic could be analysed under these conditions.

The use of two alkaline solutions in series was a useful measure of the efficiency of the trapping system. Any acid passing through the first trap would be collected in the second trap. In practice negligible traces of fatty acids were ever found in the second trap.

The efficiency of the extraction technique was measured by adding known masses of each acid to 200 ml 0.5 M sodium hydroxide. The acids were then released with dilute sulphuric acid, extracted into diethyl ether, concentrated, and analysed under the conditions described. The recoveries of the fatty acids at a level equivalent to 5 mg m^{-3} in the gas stream are given in Table I. The recoveries are satisfactory, and serve to show that all these fatty acids could be analysed in this manner. Acetic acid recovery is lowest at 72%. This is as a result of the concentration stage, where acetic acid is lost together with diethyl ether. Concentration is usually necessary to bring the fatty acid concentrations to detectable levels. A higher percentage recovery is achieved with acids of higher boiling point.

RESULTS AND DISCUSSION

The technique has been used to analyse the fatty acid concentrations on two landfill sites of differing histories. At site A filling operations ceased approximately twenty-five years ago, and development was being considered. Filling has been carried on since the beginning of the twentieth

TABLE I

Percentage recovery of fatty acids from sodium hydroxide solutions

Acid	Boiling point (°C)	Percentage recovery
Ethanoic acid (acetic acid)	118	72
Propionic acid	141	78
n-butyric acid	164	84
2-methyl propionic acid (iso-butyric acid)	154	82
n-pentanoic acid (valeric acid)	187	88
3-methylbutyric acid (iso-valeric acid)	177	85
n-hexanoic acid	205	90
n-heptanoic acid	223	92

century and was largely with household refuse, although there had been limited filling with industrial refuse. Site B was one where filling had stopped only a few years previously. On this site a larger proportion of industrial refuse had been used, but there was also a large amount of household refuse.

Prior to and during this work tests were carried out to measure the methane concentration of the interstitial gases at both sites. The same boreholes were used as sampling points for the fatty acids. The results, together with the methane concentrations are given in Table II.

All of the fatty acids listed in Table I were found in the vapours from the most recent landfill site. The acids in greatest concentration were acetic, propionic and butyric. The straight chain isomers of both butyric and valeric acid were found in much greater concentrations than the corresponding branched chain acid. In general there was a marked decrease in concentration as the molecular weight of the fatty acid increased. There appears to be little correlation between the concentration of methane and the fatty acid concentrations. Borehole 4, which consistently gave the highest methane levels also produced the lowest concentration of most of the fatty acids. The problems of correlation are increased because of the variation in methane levels which have been previously reported.[7] Samples of gases for fatty acid determinations were taken during suitable dry spells so that sufficient gas could be withdrawn from the site without drawing up water which would interfere with the analysis. Fatty acid concentrations were much more consistent than the methane levels, but it is possible that if the samples were taken in different weather conditions more variable results would be observed.

TABLE II

Concentrations of fatty acids in gases from landfill sites

	Site A					Site B			
Borehole No.	1	2	3	4	5	1	2	3	4
Methane (v.p.m.)	< 10	< 10	< 10	< 10	< 10	40–60%	20–50%	40 50%	50 80%
Acetic acid (mg . m^3)	0.08	0.06	0.04	0.01	0.03	3.81	3.91	4.26	2.00
Propionic acid (mg . m^3)	0.09	0.06	0.05	0.01	0.03	2.98	4.22	5.05	3.13
n-butyric acid	0.11	0.07	0.06	0.03	0.06	3.80	4.19	4.62	2.14
Iso-butyric acid	0.01	0.01	—	—	—	0.63	0.87	0.72	0.51
n-valeric acid	0.02	0.01	0.01	0.01	0.01	1.42	1.80	1.74	1.10
Iso-valeric acid	—	—	—	—	—	0.40	0.52	0.67	0.43
n-caproic acid	—	—	—	—	—	0.95	1.16	0.82	0.95
n-caprylic acid	—	—	—	—	—	0.12	0.22	0.20	0.14

The absence of data indicates that the concentrations were less than 0.01 mg . m^{-3}.

In fact, when there were instances of water being drawn into flasks during methane sampling, the water was sometimes analysed for the fatty acids. The concentrations in the water samples are shown in Table III. This evidence shows that acetic acid is present in the highest concentrations, the concentration of the other fatty acids decreasing with increasing molecular weight. The solubility of the fatty acids must be considered here, since above *n*-butyric acid the solubility in water decreases markedly. Thus the analysis of the water samples may not give a reliable analysis of the concentrations prevailing in the site.

TABLE III

Concentrations of fatty acids in water from landfill sites

	Site A					Site B			
Borehole No.	1	2	3	4	5	1	2	3	4
Acetic acid (p.p.m.)	0.82	—	0.78	0.42	—	5.74	8.41	7.92	4.30
Propionic acid	0.51	—	0.39	0.21	—	4.80	6.78	6.50	3.10
n-butyric acid	0.42	—	0.40	0.18	—	3.35	4.50	3.95	2.45
Iso-butyric acid	0.13	—	0.21	0.16	—	1.85	2.90	2.45	1.55
n-valeric acid	0.05	—	0.12	0.04	—	0.37	1.15	0.95	0.25
Iso-valeric acid	0.02	—	0.08	0.01	—	0.13	0.25	0.40	0.10
n-caproic acid	0.01	—	0.03	0.01	—	0.02	0.08	0.10	0.01
n-caprylic acid	0.01	—	0.01	0.01	—	0.01	0.05	0.05	0.01

No data are available for Site A, boreholes 2 and 5.

The results from the older landfill site. A, show that although the methane concentration was insignificant, there remained measureable quantities of some of the fatty acids. However, their concentrations were an order of magnitude lower than those at the newer site and acids above *n*-valeric acid were not detected. It may be that those detected represent residual traces of the acids which are reacting slowly, the rate of evolution of methane being too low to measure significantly. The concentrations of fatty acid measured seem, like the methane concentrations, to give a guide to the state of decomposition of the landfill site, and have the advantage of giving more consistent values for a series of analyses at a single borehole.

The method used here enables a comparison between sites to be made, but does not necessarily reflect accurately the concentration within the refuse matrix. This may not be a disadvantage since the landfill site is by its nature heterogeneous. Comparison of the concentrations measured at different boreholes on the same site show this to be so.

The concentrations measured here are comparable with the concentrations of fatty acids which could be released into the atmosphere in the event of a leakage. The fatty acids generally have unpleasant odours, and their release from landfill sites could be responsible for complaints by people in the vicinity. A thorough study of the odour threshold of the fatty acids has been carried out,[8] demonstrating that butyric and valeric acid could be detected at concentrations well below those measured here. Even when dilution with atmospheric gases is considered these fatty acids still cause an odour problem in some cases.

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