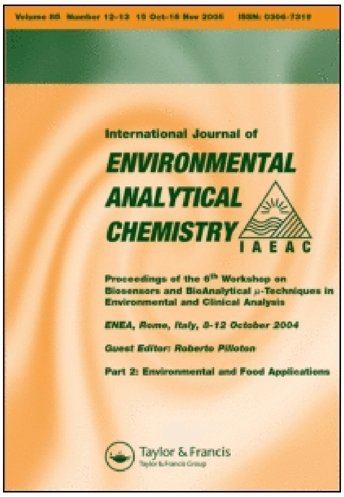

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The Sampling and Gas Chromatographic Analysis of Organic Vapours in Landfill Sites

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A technique has been devised for the sampling of organic vapours in landfill sites. The vapours are concentrated on an active carbon adsorbent and subsequently desorbed with carbon disulphide. The resulting solution is analysed by gas chromatography. Amounts of selected compounds which are recovered using the technique have been calculated.

Using the technique landfill sites have been monitored for organic vapours in general as well as for specific compounds. Landfill sites where decomposition is well into the methogenic stage show no significant concentrations of organic vapours. Where compounds are observed from the chromatogram their distribution throughout a site can be determined, as can their variation in concentration with time.

KEY WORDS: Gas chromatography, landfill sites, organic vapours

INTRODUCTION

For many years landfill has been a preferred method for the disposal of industrial and domestic refuse. Thus suitable sites are progressively filled with successive layers of refuse and inert material until the site reaches ground level when it is normally covered with a final layer of topsoil and left. Such methods have been used for many decades and still possess many advantages over more recently developed methods of refuse disposal.

However, problems arise when the land is eventually required for some other use. No definitive information is available regarding the length of time required for complete decomposition of refuse in landfill sites, and indeed the decomposition mechanism is not well understood. Frequently the previous history of the site is poorly recorded, so even if information on the rate of decomposition was available, the exact state of the processes proceeding below the surface might only be postulated. Before any development of landfill sites can be considered the positive safety of such development must be proved. Possibly the most hazardous substance likely to be present as a result of refuse decomposition is methane. A technique for the analysis of methane and some associated gases in landfill sites has previously been reported.[1] However, methane is one of the final products of refuse decomposition, being produced in the methogenic stage.[2] Before this ultimate stage, which requires the presence of specific bacteria, a much less specific process must take place. This involves the enzymatic breakdown of the complex organic compounds present to smaller organic compounds.[3,4] The nature of the compounds produced is not clear, although previous work in these laboratories[5] and elsewhere[4,6] has shown that fatty acids are present. It may well be that the compounds formed will vary from site to site depending on a number of factors, predominant among these, being the nature of the refuse which has been deposited, and the conditions within the site.

The aim of the work here reported was to develop a method which could be applied generally to the analysis of organic compounds present interstitially in landfill sites. This would fill a gap between the permanent gases such as methane and carbon dioxide, which may be analysed directly,[1] and other organic species such as fatty acids which can be analysed after concentration by some specific chemical reaction.[5] A non-specific method would be a useful technique for the analysis of organic compounds with an appreciable vapour pressure which are present in the landfill site. In many cases the identification of the individual compounds although theoretically desirable may not be necessary in practice. Comparison of one site with another may be all that is required.

In order to reduce the number of operations required for the analysis of a particular landfill site it was decided that the method would be based on the sampling system previously described for the analysis of methane and the fatty acids.[1,5] It was assumed that the concentration of any organic compounds present would be at such a low level that concentration would be a pre-requisite. A number of choices are available for the concentration of organic vapours, involving either absorption or adsorption. Absorption has proved satisfactory for the concentration of selected landfill vapours, but it is very much more convenient to deal with an adsorption system, involving the manipulation of a solid adsorbent, than absorption, which involves the handling of quantities of liquid absorbent on site. Thus adsorption was the selected means of concentration.

A number of adsorbents have been used in the analysis of organic vapours. Among those widely used are silica gel,[7,8] active carbon,[9,10] graphitised carbon black[11] and more recently porous polymers.[12,13] The choice between these alternatives depends among other factors on the method adopted for desorption of the organic compounds once adsorbed. Heat desorption requires that the adsorbent be heated to a temperature sufficiently high to desorb the adsorbed compounds without chemically altering the adsorbate, or producing artifacts as a result of the adsorbent. Solvent desorption involves manipulating the smallest volume of solvent to effectively wash the adsorbate from the surface of the adsorbent. This markedly reduces any possibility of catalytic processes producing chemical reaction on the adsorbent surface. Such processes would give rise to different compounds being desorbed compared with those adsorbed. However, with the porous polymers solvent desorption would lead to dissolution of the adsorbent.

The choice of adsorbent is also affected by the conditions during adsorption. Vapours from landfill sites may be very damp, especially after periods of rain, so the effect of water on the efficiency of the adsorbent is an important consideration. Active carbon has proved capable of adsorbing organic compounds from a stream of steam,[14] a far more severe test than that likely to be encountered with gases from landfill sites. Active carbon was thus chosen as the concentration medium. Desorption from active carbon with carbon disulphide has been shown to be a very efficient means of recovering the adsorbate.[10,14]

The method selected from the analysis of the adsorbate was gas chromatography. The choice of carbon disulphide as the desorbing medium was entirely compatible with the use of gas chromatography since carbon disulphide gives a relatively small response in the widely used flame ionisation detector (F.I.D.), a factor reducing the problems in interpreting the chromatogram.

EXPERIMENTAL AND RESULTS

The sampling technique was identical to that used for the analysis of methane in landfill sites.[1] An aluminium tube, 1.2 cm diameter, 0.8 cm bore, and 2 m in length with 0.3 cm diameter holes bored through the wall at 25 cm intervals was used. This was inserted in the ground with the aid of a stainless steel rod 2.05 m long, 0.6 cm diameter, and ground to a point at one end. A circular block 5 cm long and 2.5 cm diameter was welded to the other end of the rod. This head enabled the rod once inserted in the tube, to be hammered into the ground. When the sampling tube was in the ground to its full length the rod was withdrawn. The presence of a

0.6 cm diameter hole through the head of the rod, through which another rod could be placed, aided this withdrawal.

The active carbon adsorbent was contained in 8 cm long 0.6 cm outer diameter glass tubes drawn to a fine jet at one end. Glass fibre yarn held the adsorbent in place. With the adsorbent in place there was a 2 cm length of empty tube which could contain the desorption solvent when it was added.

The recovery from the traps of selected compounds was measured by spiking the traps with known volumes of the organic compounds using a microlitre syringe. Desorption was achieved with the minimum volume of carbon disulphide. A piece of P.T.F.E. tube was connected to the wide end of the trap and a volume of carbon disulphide (100–500 μl) placed on top of the carbon with a dropping pipette. A second dropping pipette with rubber teat was connected to the trap by the P.T.F.E. tube. Gentle pressure was applied by squeezing the rubber teat. By applying successively pressure and suction from the rubber teat it was possible to draw the carbon disulphide back and forth over the active carbon, until eventually it reached the jet at the end of the trap and was collected in a calibrated tube. The recoveries of spiked samples of selected compounds are shown in Table I. These were calculated by comparison of the areas on a gas chromatogram of the pure substance directly injected and the corresponding area from the solution of adsorbate.

The percentage recovery which might be obtained following adsorption of the compounds from a gas stream was also measured. A known volume of selected compounds was introduced into a 20 l glass flask fitted with inlet and outlet tubes. Air was drawn from the flask over an adsorbent trap using a Factory Inspectorate battery powered portable pump. Sampling was continued for 30 min at constant flowrate between 1 and 2 l min^{-1}. At the end of the sampling period the adsorbate was desorbed as previously described. The percentage recoveries are also listed in Table I.

The traps have been used on a number of landfill sites. In all cases the sampling has been carried out using a Factory Inspectorate pump. Sampling was largely carried out on landfill sites where there was no measurable methane production, and in all these cases there was no measurable trace on the chromatogram of other organic compounds. On one occasion when sampling was carried out in an area of suspected phenolic contamination the chromatogram did show peaks which could be correlated with suspected compounds.

The solutions after desorption were examined using two different stationary phases, one polar and one non-polar. The polar stationary phase was 5% Carbowax 20 M coated on 80/100 mesh Chromosorb W

TABLE I

Recovery (%) of selected compounds from active carbon traps

Adsorbate	Direct spiking		Adsorption from gas phase	
	1st Wash	2nd Wash	1st Wash	2nd Wash
n-hexane	98	99	97	98
n-decane	99	99	96	97
Benzene	100	100	97	97
Ethyl benzene	100	100	96	96
Phenol	96	97	92	93
o-cresol	95	96	90	91
1,2-dichlorobenzene	100	100	94	94
Ethanol	95	95	96	96
n-hexanol	92	94	94	95
Methyl ethyl ketone	94	95	92	93
Methyl *n*-butyl ketone	94	96	92	92
Ethyl acetate	94	95	92	92
Ethyl benzoate	92	94	90	92
Acetic acid	95	95	88	90
Propionic acid	94	95	88	90
Butyric acid	92	94	88	90

packed in a 2 metre column of $\frac{1}{4}$ in outer diameter. This was programmed from 50°C to 200°C at 4°C min^{-1}, with a nitrogen carrier gas flowrate of 20 ml min^{-1}, and an injection temperature of 200°C. The non-polar column was 5% OV17 coated on 80/100 mesh Chromosorb W packed in a 2 metre column of $\frac{1}{4}$ in outer diameter. This was programmed from 50°C to 250°C at 4°C min^{-1} with a nitrogen carrier gas flowrate of 20 ml min^{-1} and an injection temperature of 250°C. The gas chromatograph used was a Perkin Elmer F11 fitted with a F.I.D. and an electron capture detector (E.C.D.). The column effluent was split in a 1:1 ratio between the two detectors.

DISCUSSION

The use of active carbon adsorption presents a method for the analysis of interstitial soil gases while creating the minimum disturbance to the processes which are proceeding. Sampling using this adsorption system is relatively simple, and once the sampling tubes are in position few problems are encountered. The adsorbent traps used are very small, and the only other equipment required is a portable pump such as the Factory Inspectorate design which was employed in this work.

However, both the scope and limitation of the technique should be appreciated before significance is given to the results obtained. It should not be anticipated that an accurate quantitative analysis of all the compounds present in the soil will necessarily result. Although it has been shown that the percentages of adsorption and desorption are generally satisfactory, and the problem of lower percentage recoveries can be alleviated by the use of a suitable internal standard, there are other limiting factors in obtaining an accurate analysis of the compounds present. In addition to the actual concentration of a particular compound in the gas phase its vapour pressure also makes a significant contribution to its measured concentration. The concentration of a compound in the interstitial gases will at equilibrium be related to its vapour pressure. When the equilibrium is disturbed, as during this sampling process, the vapour pressure will determine how quickly more of the compound will move into the gas phase. Hence a compound with a high vapour pressure will be found to have a greater concentration than a compound actually present in the same amount, but having a lower vapour pressure, always assuming that the compounds are not both entirely in the gas phase initially. Compounds which are present in the solid matrix and which possess very low vapour pressures would not be detected, and this method is not suitable for their estimation. In such a case extraction of the compounds from a soil sample would be necessary. However, for a wide range of compounds with intermediate vapour pressures, this method should prove very useful.

Although it may not be possible to obtain an accurate quantitative analysis of a particular compound this need not be a serious drawback. In many cases it may be necessary only to know whether the compound is present, in which event a comparison can be made both between different boreholes at one time and the same boreholes at different times. In this way a profile of the concentration throughout a landfill site can be built up and studied, even though the precise concentrations are not known.

The majority of landfill sites examined in this study have shown negligible concentrations of organic compounds in the range here considered. This is not surprising since operations had finished at least thirty years ago, and it would be expected that the methogenic stage was close to completion. Concentration measurements of methane verified this, being very close to zero. However, on one site where phenolic and cresylic waste was thought to have been deposited quite recently, the presence of the soil of gases of these types of compounds was shown, showing that the method should prove very useful in monitoring such situations.

In the absence of specific information and when peaks are observed on the chromatogram identification may prove difficult. However, if the purpose is merely to monitor the landfill site before considering development the identification of the compounds may not be necessary. Only in the absence of peaks on the chromatogram could the site unequivocally be called safe. The presence of organic compounds in the gases should at least warrant serious further investigation before development. It may be simply as an initial monitoring technique that the method will find its greatest application.

It must be said that it is a good deal more difficult to obtain negative chromatograms than positive ones. In the hands of inexperienced operators contamination from a multitude of sources is very easy. Thus should positive results be obtained the importance of blank analyses is critical. Such a blank could be produced by passing a suitable volume of inert gas from a cylinder through an analytical trap, the gas itself having been purified by passing through an initial active carbon adsorbent. If desorption from the analytical trap then produces a blank solution when examined under the same conditions as the test solution, the peaks in the test solution can be considered genuine.

The results of such analyses, taken with measurement of the concentration of methane and carbon dioxide should enable rational decisions to be made regarding the advisability of developing the landfill site.

References

1. S. Thorburn, B. A. Colenutt and S. D. Douglas, *Int. J. Env. Anal. Chem.* **6,** 245 (1979)
2. M. Alexander, *Microbiol. Ecology,* Wiley Inc. (1971).
3. A. A. Imshenetskii, *The Ecology of Soil Bacteria,* Edited T. R. G. Gray and D. Parkinson, Int. Symp. Univ. Liverpool, Univ. Toronto Press (1968).
4. D. F. Toerien, W. H. J. Hattingh, J. P. Kotze, P. G. Thiel and M. L. Siebert, *Water Res.* **3,** 129 (1969).
5. B. A. Colenutt, *Int. J. Env. Anal. Chem.* **7,** 71 (1979).
6. C. W. Bird and P. M. Molton, *Topics in Lipid Chem.* **3,** 125 (1972).
7. A. P. Altshuller, T. A. Bellar and C. A. Clemons, *Ind. Hyg. J.* **23,** 164 (1962).
8. N. E. Whitman and A. E. Johnston, *Ind. Hyg. J.* **25,** 646 (1964).
9. L. D. White, D. G. Taylor, P. A. Mauer and R. E. Kupel, *Ind. Hyg. J.* **31,** 225 (1970).
10. K. Grob and G. Grob, *J. Chromatogr.* **62,** 1 (1971).
11. A. Raymond and G. Guichon, *Environ. Sci. Technol.* **8,** 143 (1974).
12. W. Bertsch, R. C. Chang and A. Zlatkis, *J. Chromatogr. Sci.* **12,** 175 (1974).
13. J. P. Mieure and M. W. Dietrich, *J. Chromatogr. Sci.* **11,** 559 (1973).
14. K. Grob, *J. Chromatogr.* **84,** 225 (1973).