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Publisher *Taylor & Francis*

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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 Thorburn, S. , Colenutt, B. A. and Douglas, S. G.(1979) 'The Sampling and Gas Chromatographic Analysis of Gases from Landfill Sites', International Journal of Environmental Analytical Chemistry, 6: 3, 245 – 254

To link to this Article: DOI: 10.1080/03067317908071177

URL: <http://dx.doi.org/10.1080/03067317908071177>

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The Sampling and Gas Chromatographic Analysis of Gases from Landfill Sites

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(Received August 1, 1978)

The safe development of landfill sites is daily increasing in importance. In this context the analysis of soil gases, especially for methane, is vital. Techniques have been developed for the sampling of such gases, and their subsequent analysis at the v.p.m. level by gas chromatography. Factors affecting the gas concentrations are considered.

KEY WORDS: Landfill, gas chromatography, methane, catalytic reduction, carbon monoxide, carbon dioxide.

INTRODUCTION

In England and Wales alone over 14 million tons of domestic and industrial waste are produced annually. For many years this has been disposed of by depositing in landfill sites. Although methods such as incineration have been developed, controlled landfill is acknowledged to be the cheapest method of disposal, and is still widely used. Recommendations¹ and reviews^{2,3} on controlled landfilling have been published. Landfill sites are often huge holes left as a result of mining or other excavation work. After successive alternate layers of refuse and inert material, a top layer of soil would be made and the site then abandoned.

Today many such sites are little more than wasteland. With increasing demands for land it has become necessary to make the maximum use of all that is available, including the reclamation of landfill sites. Many factors have to be taken into consideration before such sites can be safely developed. One such factor is the state of decomposition of the refuse. During decomposition of refuse toxic and hazardous gases may be produced. The actual products will vary with the precise nature of the refuse and the conditions prevailing in the site but methane, carbon

monoxide, and carbon dioxide are some of the most likely gases. There can be no question, of course, of a development on a site where methane is being produced, but as yet no work has been reported on the analysis of landfill gases. This paper describes how gas samples have been taken from a number of landfill sites, and the techniques used for their analysis by gas chromatography.

The major problems to the analyst are first to ensure that valid samples are obtained and ultimately that a significant analysis, both qualitative and quantitative, is produced. A katharometer detector is capable of detecting the permanent gases, but has limited sensitivity. Although in ideal conditions a concentration of 100 volumes per million (v.p.m.) of methane can be monitored, it may be necessary here to deal with much lower concentrations routinely. The flame ionisation detector (F.I.D.) is much preferred in trace analysis because of its higher sensitivity and wide linear response. However, it responds not at all to carbon monoxide and carbon dioxide. Wisniewski⁴ suggested that carbon dioxide could be hydrogenated to methane which could be estimated by means of the F.I.D. The method was later applied to carbon monoxide⁵ and Ajetian⁶ proposed the technique for the analysis of atmospheric air samples. A wide variety of catalysts capable of reducing carbon monoxide and carbon dioxide to methane have been produced and reviewed.⁷ Not all of the catalysts are necessarily adaptable to this chromatographic system. The gases must be reduced after they have been separated, otherwise only a total analysis is obtained. The catalyst is therefore inserted in the system between the column outlet and the detector inlet. The catalyst used here was one developed by Bond and Turnham⁸ using ruthenium and copper. This had the advantages of good stability, a uniformly high conversion rate over a wide concentration range, and a relatively low temperature of reaction.

The problem of obtaining significant samples is a difficult one, and depends largely on the nature of the site considered. In many cases accurate records of landfill were not kept or are lost, so the history of the site may be unknown. In the first instance a concentration of 1 sample per acre would seem a reasonable compromise, although this may well be varied in the light of results.

EXPERIMENTAL

Sampling

Samples of the gases were obtained by means of tubes inserted into the ground. The apparatus is illustrated in Figure 1. The tubes used were aluminium, 1.2 cm diameter, 0.8 cm bore, and 2 m long. 0.3 cm holes were

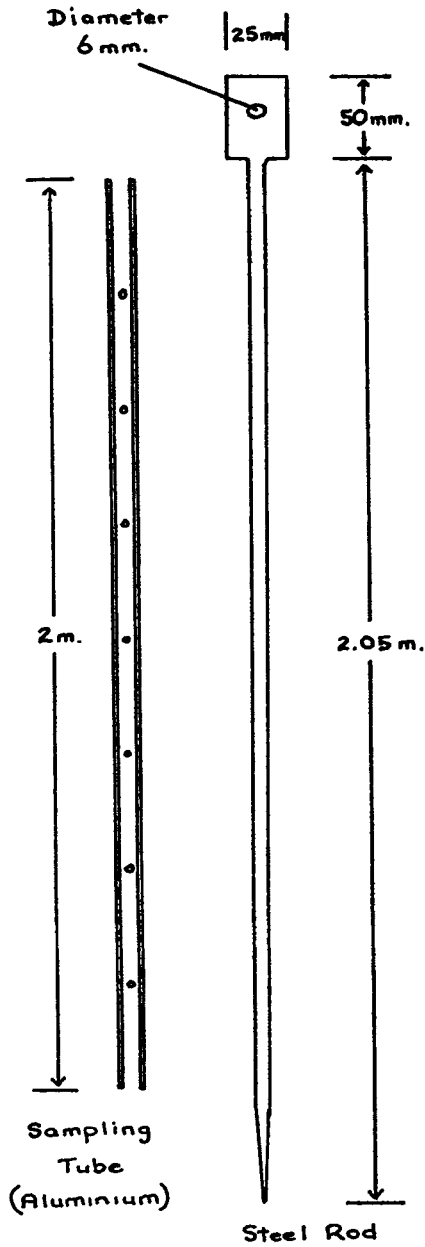


FIGURE 1 Diagram of apparatus for sampling landfill gases (not to scale).

bored through the wall at 25 cm intervals so that gas could be drawn in at other than the bottom of the tube. A stainless steel rod was used as an aid to the insertion of the tubes. The rod was 2.05 m long, was ground to a point at one end and fitted comfortably in the bore of the tube. A circular block 5 cm long and 2.5 cm diameter was welded onto the other end. This head enabled the rod to be hammered into the ground together with the tube. The head had a 6 mm hole drilled through its diameter into which a rod could be put to aid removal from the ground.

To insert the tube, the rod was first pushed into the tube, and the rod and tube together hammered into the ground. Information about the composition of the site could sometimes be gained from the manner in which the rod entered the ground. When the tube was in the ground to its full length the central rod was withdrawn with the aid of a 6 mm diameter rod through the hole in the head of the rod. The tubes were stoppered after insertion, although if they were on open sites the bungs were frequently lost.

Samples of gas were taken from the tube by means of evacuated glass flasks fitted with Teflon taps. The tube had a volume of approximately 25 c.c., and to ensure that gas from around the tube was taken, the flasks had a volume of at least 100 c.c. The flasks were connected to the open end of the tube by a suitable piece of rubber pressure tubing and the valve opened. After sampling, the flasks were returned to the laboratory for analysis. A minimum of three gas samples were taken from each tube, at intervals of not less than seven days.

ANALYSIS OF THE GASES

Two systems were used and are described here. The first used a normal F.I.D. for the analysis of methane alone. The second used the catalytic reduction system to convert carbon monoxide and carbon dioxide after separation to methane, which was estimated by the F.I.D.

(a) Methane

A Pye GCD gas chromatograph with a F.I.D. was used. The column was 1.5 m long, 3 mm inner diameter glass packed with Chromosorb 102. The oven temperature was 60°C and nitrogen carrier gas flowrate of 30 mls.min⁻¹. The injector and detector temperatures were 100°C and 200°C respectively. Standard atmospheres were produced by injecting measured volumes of methane into flasks of known volume. Calibration graphs were produced by injecting 1 ml. aliquots of the standard atmospheres into the gas chromatograph. Using this system 1 v.p.m. could be

readily determined, and the calibration plot was linear up to 500,000 v.p.m. methane.

(b) Methane, carbon monoxide and carbon dioxide

The system was constructed in the laboratory, and is illustrated in Figure 2. The ruthenium-copper catalyst was prepared by adding calculated amounts of 0.5M $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ to silica gel (10g) with much stirring. The silica was dried under vacuum in a rotary evaporator and then reduced in a stream of hydrogen and nitrogen (6% H_2 , 94% N_2) for four hours at 525°K. After cooling, the required amount of catalyst (~4g) was packed into a spiral glass tube which was to be the catalytic chamber in the system. The packed chamber was heated overnight at 673°K with the nitrogen hydrogen gas mixture flowing. Following this conditioning the catalyst was ready to use.

The oven in which the catalyst chamber was maintained at 660°K was constructed from quartz tube of 3 cm diameter, and 20 cm long. Nichrome wire was wound around the tube and embedded in "Pyruma" fireclay. Further windings of nichrome wire were made and similarly embedded. The oven was electrically heated through a Variac variable voltage device. The thermocouple was incorporated in the glass spiral of the catalyst chamber to ensure that the correct temperature was maintained.

The column used was 2 m long 1.5 mm inner diameter stainless steel packed with Carbosieve B. This was operated at room temperature and was able to separate carbon monoxide from nitrogen and oxygen which were eluted together. The injector and detector temperatures were 100°C and 150°C respectively. The nitrogen carrier gas flowrate was 12 ml.min⁻¹. At the end of the column hydrogen for the reduction was mixed with the gases at a flowrate of 50 ml.min⁻¹ and passed over the catalyst into the F.I.D.

The system was calibrated in the same manner as was described earlier for methane. The percentage conversion of carbon monoxide and carbon dioxide was calculated on the assumption that equal volumes of the gases would yield equal volumes of methane which would produce the equivalent response as the same amount of natural methane.

It was observed that calibration problems arose when plastic disposable syringes were used for injections of carbon monoxide. The syringes, once used, had a memory effect which could not be eradicated. Thus glass syringes were used at all times.

RESULTS AND DISCUSSION

Gas analysis techniques

The methane determination was simple and straightforward and gave

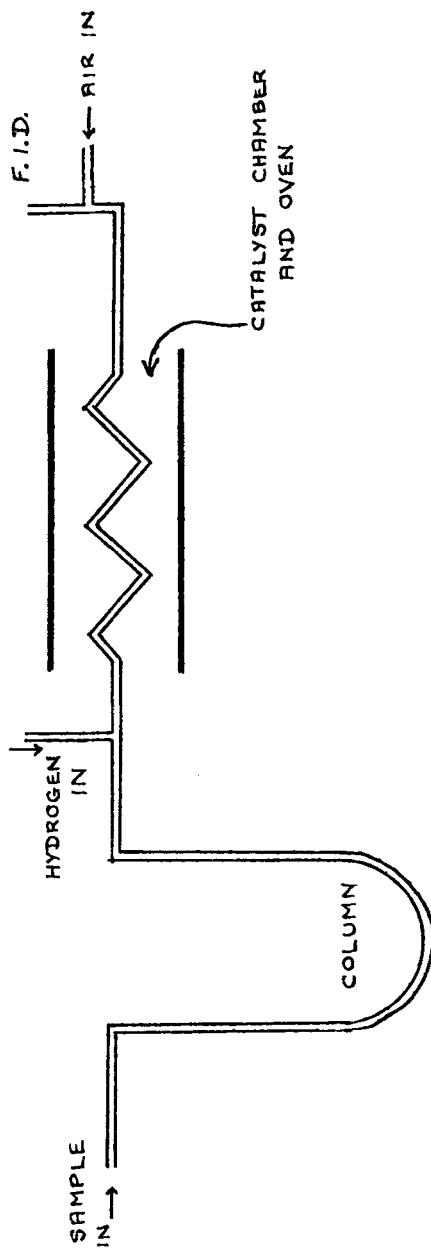


FIGURE 2 Schematic diagram of system for F.I.D. estimation of carbon monoxide and carbon dioxide.

unambiguous results. There were no peaks due to other compounds in any gas samples examined. The catalytic conversion system also worked well giving 98% conversion of both carbon monoxide and carbon dioxide. Whilst higher energy is required for the hydrogenation of carbon dioxide than carbon monoxide, it is with the latter that problems can arise. In the presence of large amounts of air, or more precisely oxygen, an interfering effect occurs. Thus it may not be entirely suitable for analysis of carbon monoxide in aerobic landfill gases, although in such situations the formation of carbon monoxide is unlikely. The problem arises because oxygen reacts on the catalyst, saturating it if sufficient oxygen is present. The response may be due to reaction between the oxygen and carbon particles within the catalyst to form an oxide which is subsequently reduced to methane and passed into the detector. Certainly in the presence of large amounts of oxygen such as may be found in an atmospheric air sample, the catalyst is deactivated for a short period of time. It is during this period that carbon monoxide is eluted. The separation of carbon monoxide from oxygen is difficult to achieve but can be accomplished on Carbosieve B. However, the length of column used here meant that the two compounds were eluted very close together. The catalyst is effectively deactivated for about 30 secs after the passing of oxygen, and if carbon monoxide is eluted with at least this spacing, full conversion is obtained. The problem is readily solved by increasing the length of the column to separate carbon monoxide from oxygen by the appropriate amount. It would then be necessary to adopt a temperature programming procedure to obtain elution of carbon dioxide in a reasonable time. In practice the interference was not important, and the system was used as described. In fact the information regarding the presence of oxygen in a sample is useful. (Figure 3 shows a typical chromatogram.)

Gas concentrations

The concentrations of gases which were measured varied over a wide range, and the quoting of particular results would be of little value here. However, concentrations of methane determined varied from less than 5 v.p.m. to 80%. At a concentration of 5 v.p.m. the level is similar to that of the gas in ambient air and is regarded as insignificant. Concentrations above 10 v.p.m. indicate the possibility of significant concentrations either being present or being produced. On some sites a level of 10 to 40 v.p.m. was observed at the first time of sampling, a level which fell to less than 5 v.p.m. at second and subsequent samplings (often five or more over several weeks). This was taken as an indication that the tube had broken into small pockets of gas which having been released on the first occasion

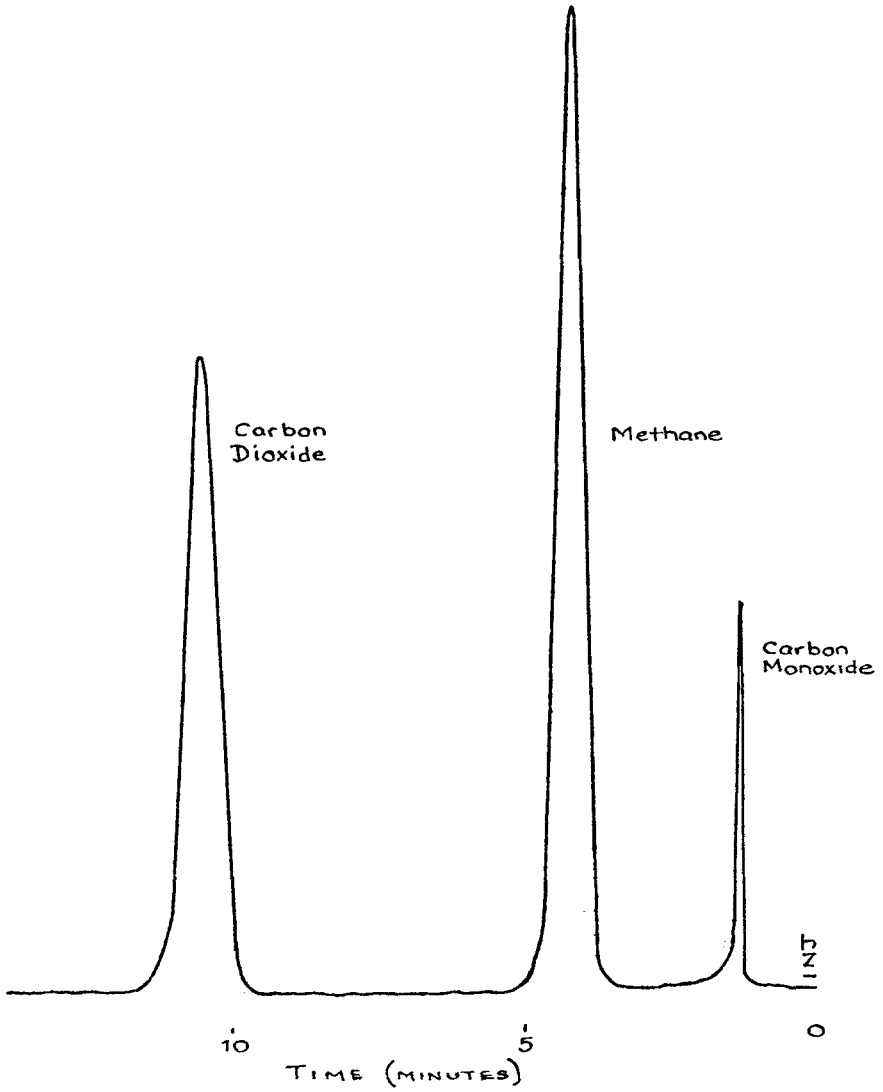


FIGURE 3 Typical chromatogram of standard gases.

were not replenished. This suggested either a very slow or zero rate of production of the gas, a strong indication that decomposition was complete.

At the other end of the scale sites have been sampled where levels of 80% methane in the interstitial gas has been determined. If sufficient oxygen were able to enter, these areas would represent a serious fire risk. Generally in such situations the concentration of methane was uniformly high, varying little during the minimum three week sampling period. In this situation the decomposition is far from complete.

The presence of carbon monoxide in samples was infrequent, but carbon dioxide was observed more often. Concentrations of up to 20% carbon dioxide were noted, always in the presence of some methane. A complicating factor was the variation of results. Results of duplicates taken from the same sample site at the same time were excellent, but variation from week to week was not exceptional. This is considered to be a result of environmental factors, predominantly water in the tip as a result of rainfall.

Rainfall between the taking of samples from a single site invariably leads to a higher concentration in the second sample compared with the first. Skinner⁹ has reported that waterlogging of soils increased gas production in general and methane in particular. This evidence correlates with the observation that the methane concentration was at a minimum during spells of dry weather, and increased markedly after periods of rain. We have noted methane concentrations increase by a factor of ten during a period of seven days with rain in the intervening period. It is therefore essential that the sampling is spread over a sufficiently long period to remove the possibility of erroneous conclusions.

Homogeneity of landfill sites

Sample tubes have normally been inserted at a spacing of 1 per acre. This can give a good indication of the homogeneity of the site. If adjacent tubes give similar results this spacing is probably sufficient. However, in the investigation of particular landfill sites considerable variation has been observed in the composition of gas samples taken at adjacent sampling points, perhaps only 50 m apart. In this situation a greater density of sampling points is required. It is possible to draw concentration profiles by joining areas of similar concentration, and this may serve as a guide to where further samples should be taken.

The temperature at the bottom of the sampling tube may also be of some significance. This is simply measured by lowering a thermometer to the bottom of the tube. Although the temperature difference may be only a

degree or two, we have found a significant fall away from zones of highest methane concentration.

Significance of results

The only unambiguous results are those where no methane is measured. Providing a sufficient sampling density has been used the site is regarded as free of methane. This is essentially the only safe concentration. With the inherent variation in gas concentrations as a result of internal and external tip conditions, any value is only an indicator. In this situation any level of methane must be regarded with suspicion unless evidence shows otherwise.

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