The Analysis of Sludge Digester Gas (1979 version)

Methods for the Examination of Waters and Associated Materials

Contents

London Her Majesty's Stationery Office

Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in a properly equipped laboratory. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards for others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. One such publication is 'Code of Practice for Chemical Laboratories' issued by the Royal Institute of Chemistry, London. Another such publication, which includes biological hazards, is 'Safety in Biological Laboratories' (editors E Hartree and V Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London.

Where the committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life, but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of the correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first aid, fire-fighting, and rescue equipment. If in doubt it is safer to assume that a hazard may exist and take reasonable precautions rather, than to assume that no hazard exists until proved otherwise.

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About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes, inevitably, took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis
9.0 Radiochemical methods

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977

About this booklet

1 Two methods are described in this book for the analysis of sludge digester gas based on (A) Gas – Solid Chromatography and (B) The Volumetric Orsat Technique.

2 Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of the materials and apparatus used. The method therefore mentions the actual materials used for the evaluation tests. This in no way endorses these materials as superior to other similar materials. Equivalent materials are acceptable but it must be understood that the performance characteristics may be different and may vary with batch. It is left to the senior supervising analyst to evaluate and choose from the appropriate brands available.

The Analysis of Sludge Digester Gas

Introduction

The anaerobic decomposition of organic matter in sludge generates gas which consists mainly of methane and carbon dioxide together with minor quantities of nitrogen, oxygen, hydrogen sulphide, hydrogen and traces of volatile hydrocarbons. The analysis of the gas is normally carried out for the following purposes:

a. to control the digestion process,

b. to ensure that the gas mixture is free of oxygen following purging operations on plant and equipment,

c. to estimate the calorific value of digester gas.

Comprehensive details of the properties and composition of digester gas are given by Burgess and Wood[1]. Background information about the Orsat apparatus and technique is given by Wilson and Wilson[2] and the British Standards Institution[3]. General information about gas analysis by gas chromatography is given by Jeffery and Kipping[4] and the method used at the Water Research Centre is described in detail by Mosey *et al*[5]. Alternative methods of analysing digester gas have been discussed by Wood and Fossey[6].

Method A – gas-solid chromatography is used for the determination of methane, carbon dioxide, oxygen, nitrogen, hydrogen and hydrogen sulphide.

Method B – volumetric determination by the Orsat technique of oxygen and carbon dioxide: methane plus nitrogen is estimated indirectly by difference.

Method A Gas-Solid Chromatography

A1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristscs see a publication in this series).

(Throughout this method, concentrations are expressed as per cent by volume).

A1.1	Substances determined	Methane, carbon dioxide, oxygen, nitrogen, hydrogen and hydrogen sulphide.
A1.2	Type of sample	Gas produced by anaerobic digestion of organic sludges. Digestion plant purge gas.
A1.3	Basis of method	Chromatographic separation of the component gases followed by their detection using a katharometer.
A1.4	Range of application	Up to 100%
A1.5	Calibration curves	Linear. (See Section A7.6 and A7.7, note c).
A1.6	Standard deviations* (within batch)	These were each measured from ten replicate injections (ie 9 degrees of freedom)

(a) *Using argon as carrier gas and 0·15 ml samples*

Gas	Concentration (per cent by volume)			
	100	10	1	0·1
CH_4	1·5	0·26	0·12	—
CO_2	6·6	0·21	0·21	—
O_2	1·9	0·19	0·11	—
N_2	0·9	0·35	0·19	—
H_2	0·0	1·53	0·034	0·0054
H_2S	1·2	0·21	0·23	—

(b) *Using argon as carrier gas and 10 ml samples*
For hydrogen at 0·01 $\%^{V}/_{V}$ the standard deviation was 0·001 $\%^{V}/_{V}$ and at 0·001 $\%^{V}/_{V}$ it was 0·000325 $\%^{V}/_{V}$.

(c) *Using helium as carrier gas and 0·15 ml samples*

Gas	Concentration (per cent by volume)			
	100	10	1	0·1
CH_4	1·3	0·2	0·052	0·018
CO_2	0·24	0·16	0·034	0·01
O_2	0·82	0·2	0·057	0·01
N_2	1·3	0·15	0·045	0·0058
H_2	0·63	0·37	0·11	—
H_2S	0·67	0·77	0·11	0·017

(d) *Using helium as carrier gas and 10 ml samples*
For hydrogen sulphide at 0·01 $\%^{V}/_{V}$ standard deviation was 0·00243 $\%^{V}/_{V}$ and at 0·001 $\%^{V}/_{V}$ it was 0·000282 $\%^{V}/_{V}$.

* These data supplied by the Water Research Centre (Stevenage Laboratory).

A1.7	Limits of detection†	(a) *Using argon as carrier gas and 0·15 ml samples* Methane 0·1% (1000 ppm) Carbon dioxide 0·1% (1000 ppm) Oxygen 0·1% (1000 ppm) Nitrogen 0·2% (2000 ppm) Hydrogen 0·001% (10 ppm) Hydrogen sulphide 0·5% (5000 ppm) (b) *Using argon as carrier gas and 10 ml samples* Hydrogen 0·0002% (2 ppm) (c) *Using helium as carrier gas and 0·15 ml samples* Methane 0·1% (1000 ppm) Carbon dioxide 0·005% (50 ppm) Oxygen 0·01% (100 ppm) Nitrogen 0·005% (50 ppm) Hydrogen 0·5% (5000 ppm) Hydrogen sulphide 0·02% (200 ppm) (d) *Using helium as carrier gas and 10 ml samples* Hydrogen sulphide 0·001% (10 ppm)
A1.8	Bias	The mean total concentrations of hydrogen, oxygen, nitrogen, methane, carbon dioxide and hydrogen sulphide in 258 samples was 99·6 per cent with a standard deviation of 4·5. If one assumes the concentration of water vapour in the samples to have been 2·3 per cent (saturation at 20°C) then the correct total for the other gases would be 97·7 per cent.
A1.9	Interferences	None.
A1.10	Time required for analysis*	(a) For determination of methane, carbon dioxide, oxygen and nitrogen. To warm up instrument and set carrier gas flow rates – 30 minutes. To calibrate instrument for these four gases – 2 hours. Thereafter each sample can be analyzed for these four components in about 20 minutes. (b) For determination of hydrogen *or* hydrogen sulphide in trace concentrations. To change carrier gas, reset flow rates and warm up detector – 30 minutes. To calibrate instrument – 45 minutes. Thereafter each sample can be analysed for hydrogen *or* hydrogen sulphide in 10 minutes.

† As judged by the sensitivity of the analytical method

A2 Principle

The components of the sample are separated in a gas chromatograph and then detected by a katharometer. Concentrations are determined by comparison with standard gas mixtures. At present, there is no single column packing which will satisfactorily separate all six components in an isothermal chromatograph and it is necessary to use two different columns. The preferred arrangement is to install permanently both columns in the same chromatograph oven and to connect one column to each half of the katharometer head as shown in Figure 1.

* Data supplied by the Water Research Centre (Stevenage Laboratory).

A3 Interferences

None.

A4 Hazards

The normal precautions for the storage and use of compressed gases should be observed. Hydrogen and methane are flammable. Hydrogen sulphide is also flammable and very poisonous[7].

Digester and purge gases may contain high concentrations of methane and therefore great care should be taken to ensure that explosive mixtures of methane-enriched gas with air are not allowed to form in confined areas around the digestion plant and in the laboratory. A NO SMOKING, NO NAKED LIGHTS policy should always be operated.

A5 Reagents

The only reagents required are the calibration and carrier gases. Calibration gases may be either pure gases from which the analyst prepares his own calibration mixtures or ready-prepared calibration mixtures purchased especially for that purpose. The choice of carrier gas is dictated largely by the trace gases which the analyst is required to determine. The carrier gas should be hydrogen or helium for the determination of traces of hydrogen sulphide. Of the two, helium is preferred because it is non-flammable. A wide range of carrier gases may be used to determine traces of hydrogen. Argon is preferred because it permits determination of all the other gases.

A6 Apparatus

A6.1 The gas chromatograph

This should be an isothermal gas chromatograph fitted with gas sampling valves, the necessary columns and a katharometer detector. Oven temperatures for the separations are usually low (100°C or less) and providing the columns and detector head are well insulated to prevent temperature fluctuations the separations may even be carried out at room temperature. The operating conditions and instrument settings will vary according to the instrument used, the dimensions of the columns and the precise nature of the packing materials. As a guide, a selection of operating conditions that have been successfully used by different analysts together with some specimen traces are shown in the appendix. The preferred packing materials for the columns are Molecular Sieve 5A or 13X to separate hydrogen, oxygen, nitrogen and methane, and Porapak to separate methane, carbon dioxide, hydrogen sulphide and water vapour from a combined oxygen/nitrogen peak. Porapak Q, S and T have all been successfully used. Silica gel is also an acceptable packing material for the separation of methane and carbon dioxide. A typical layout of the gas chromatograph is given in Figure 1.

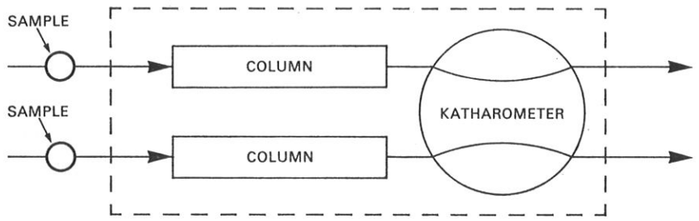

Figure 1 Gas chromatograph, typical layout of the instrument

A6.2 Gas sampling valves

The analyst is recommended to use gas sampling valves rather than direct injection to introduce the samples.

These are valves which permit a short section of pipe of known internal volume to be connected alternately to a stream of process gas and to a stream of carrier gas thus permitting a sample of the process gas to be instantaneously transferred to the carrier gas stream and they are recommended even where direct injection from a syringe would normally be used because they provide a more reproducible means of transferring the sample. The analyst is recommended not to construct his own sampling valves from glass tubing and stopcocks but to purchase proprietary valves from the manufacturer of his instrument. These valves are usually constructed from stainless steel with rubber or plastic seals. To protect these seals from damage, and to ensure that the samples are at ambient temperature, the valves are usually located outside the chromatograph oven. The layout of the instrument (Figure 1) requires two sampling valves, but a single set of sample loops can usually serve both valves. Non-standard loops can be easily constructed by the analyst from a section of chromatograph pipe and a pair of couplings.

Where the instrument is not permanently connected to the stream of process gas, the sample outlet port should be connected to the atmosphere via a long narrow pipe to minimize back-diffusion of air. If samples are collected in a glass vessel as shown in Figure 2 or a collapsible container then this vessel or container may be connected directly to the sample inlet port of the valve. Alternatively, a chromatograph septum may be fitted to the sample inlet port of the valve to permit samples or standards to be

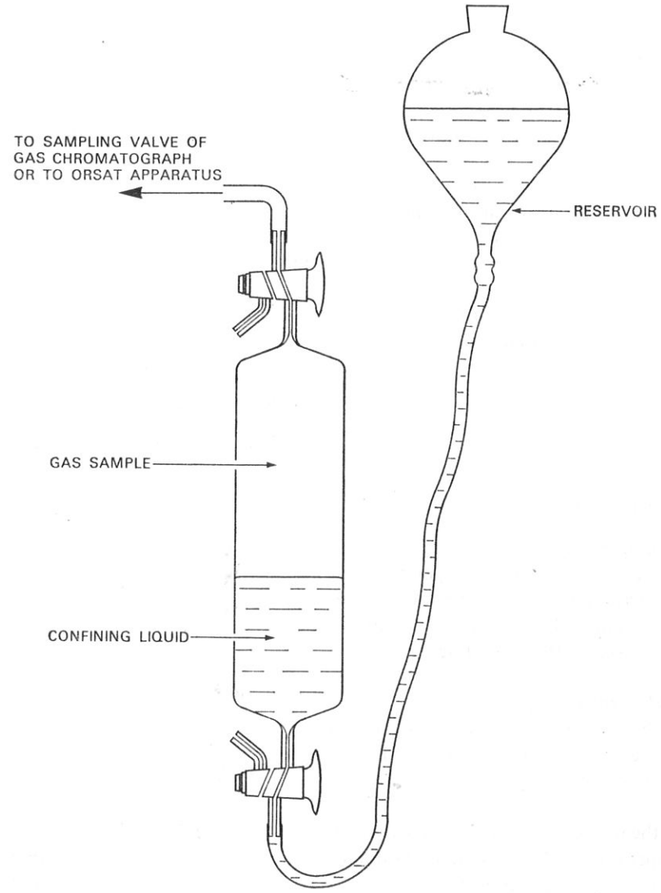

Figure 2 Gas collection apparatus

injected into that port from a syringe or a pressurized can. In either case, sufficient sample should be transferred to fill completely the loop and purge the valve; for example, use a 10 ml syringe to fill a 1 ml sample loop.

A6.3 Gas sampling equipment

Collection, transport and introduction of the samples are the major sources of error in the analysis. For small laboratory digesters the most convenient method is to fit a chromatograph septum to the gas line on the digester and another septum to the sample inlet port of the sampling valve and to transfer the sample using a syringe. The quality of this syringe is critical. Ordinary medical-type all glass syringes are not suitable. The analyst is recommended to use high quality gas syringes with PTFE seals similar to those used for high performance liquid chromatography.

To collect gas samples from full-scale digesters, sampling vessels similar to the one shown in Figure 2 or collapsible containers, eg football bladders are more suitable, however hydrogen sulphide reacts chemically with some types of rubber and plastic and the analyst should be alert for losses of hydrogen sulphide on storage of samples. According to the wishes of the analyst, the samples may be analyzed either as received or after drying. It is, of course, necessary when reporting the results to state whether the sample was dried before analysis (Table 2 in the appendix provides a guide to the water content of samples).

A7 Analytical Procedure

Step	Analytical procedure	Notes
	Preparing the instrument for use (note a)	
A7.1	Select the carrier gas and set the inlet pressure to obtain an approximately correct flow rate. Switch on chromatograph oven and potentiometric recorder. *Do not switch on the katharometer yet* (note b). Allow the instrument to warm up.	(a) See Table 1 in the appendix for some typical operating conditions. (b) Switching on the katharometer without an adequate flow of carrier gas may burn out the filaments in the detector head.
A7.2	Measure and, if necessary, adjust the flow of carrier gas to that appropriate for the instrument.	
A7.3	Switch on the katharometer and allow it to warm up.	
A7.4	Check that the instrument is producing a satisfactory baseline on its lowest attenuator setting (note c).	(c) If the baseline is unacceptable, check for leaks, or for draughts and check the electrical connections to the recorder, and then allow about 30 minutes for the fault to correct itself. If the fault persists refer to the instrument manual or send for the service engineer.
	Activating the columns	
A7.5	Silica gel and molecular sieve both irreversibly adsorb water at normal oven temperatures. Molecular sieves also irreversibly adsorb carbon dioxide and hydrogen sulphide. This causes them gradually to lose resolving power for the other gases.	
	As and when necessary	
A7.5.1	Activate the silica gel column by raising the oven temperature to 105°C for a few hours whilst purging the column with carrier gas.	
A7.5.2	Activate the molecular sieve column by raising the oven temperature to 350°C for a few hours whilst purging with carrier gas (note d).	(d) Porapak needs no activation and decomposes at around 200°C. Remove the Porapak colunm from the instrument when activating the molecular sieve column.
	Calibrating the instrument	
A7.6	When first using the method or when changing to a new instrument the analyst should inject a sufficient number of calibration gas mixtures to establish the slope of the calibration curve for each determinand (note e).	(e) With careful selection of operating conditions it should be possible to obtain linear calibration curves using peak heights. Linearity of calibration curves is improved by reducing the volume of the samples and the flow of the carrier gas and by reducing the temperature of the chromatograph oven, at the expense of a reduction in sensitivity and an increase in the time required to obtain the chromatograms.
A7.7	Once the shape of the calibrating curve has been established, routine analyses may be performed with a minimum of calibration mixtures. Calibration mixtures may be purchased or prepared from pure gases by the analyst using a syringe. Providing the plunger is moved rapidly to ensure turbulence, the gases mix instantaneously and completely in the syringe.	

Step	Analytical procedure	Notes
	Alternative methods for preparing calibration mixtures are given by Wood and Fossey (6). For trace gases (H_2 and H_2S) the analyst is recommended to purchase calibration mixtures.	
	Injecting the samples	
A7.8	Select a sample loop for the gas sampling valve. For major components the loop should be small (1 ml or less) to provide good resolution – for minor components (H_2 or H_2S) a larger loop may be necessary.	
A7.9	Switch on the chart drive of the potentiometric recorder and pass sufficient gas through the sampling valve to fill the loop and purge the valve.	
A7.10	Operate the valve and mark the start time on the trace.	
A7.11	Run the chromatogram adjusting the output attenuator when necessary to obtain an easily measurable peak for each determinand.	
A7.12	Identify the components of the sample by the retention times of the peaks on the chromatogram (note f).	(f) The specimen chromatograms given in Figures 3, 4 and 5 may prove useful.
A7.13	Determine the concentrations by comparing the heights of peaks on chromatograms from the samples and from the standard gas mixtures.	
A7.14	Express results as *per cent by volume*. State whether the results refer to concentrations in wet or dry gas.	

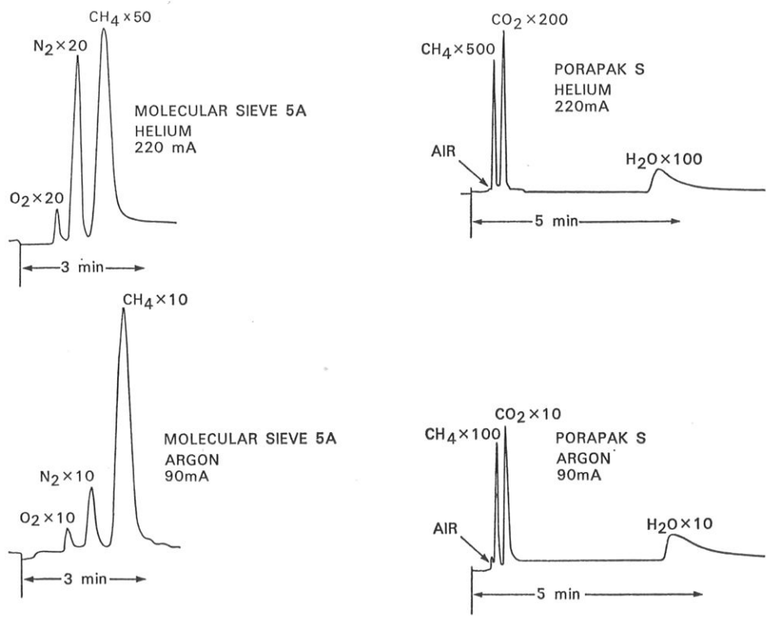

Figure 3 Typical chromatograms (WRC Stevenage Laboratory)

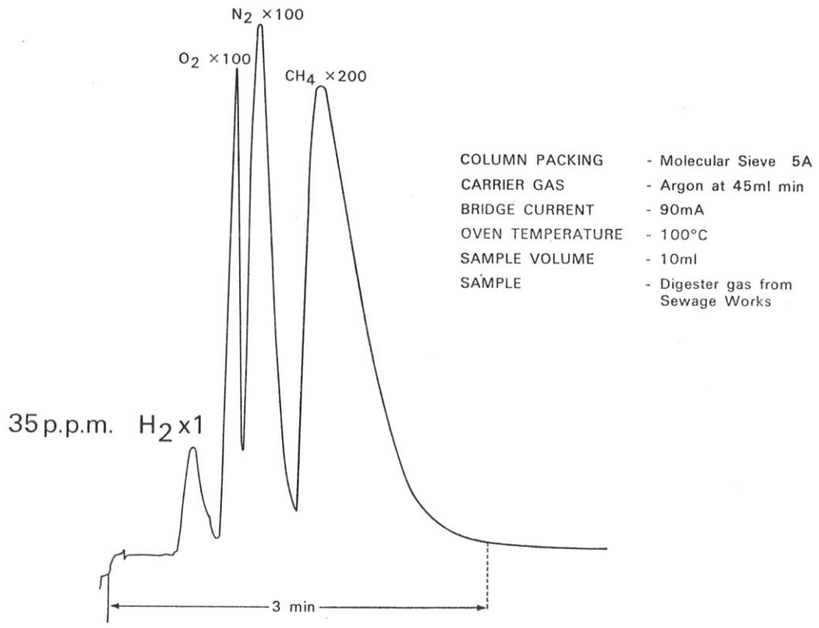

Figure 4 Chromatogram showing determination of trace concentration of hydrogen in digester gas (WRC)

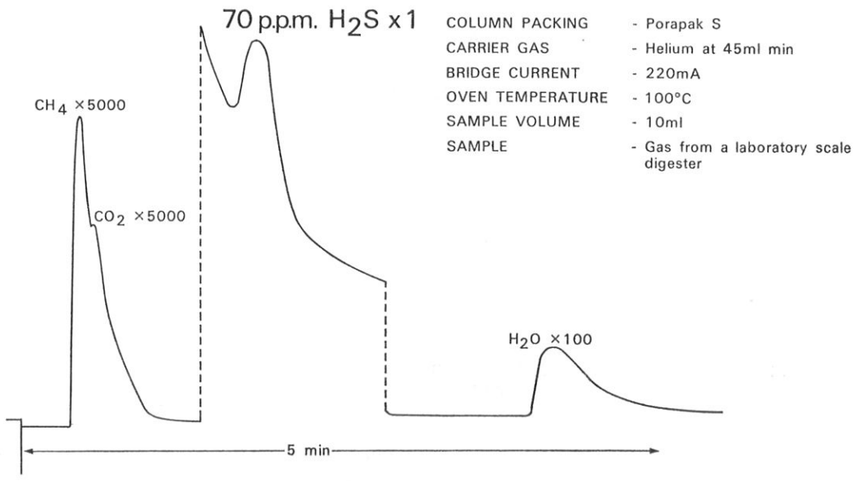

Figure 5 Chromatogram showing determination of trace concentration of hydrogen sulphide

Method B Volumetric Method
(Orsat Technique)

B1 Performance Characteristics of the method

(For further information on the determination and definition of performance characteristics see a publication in this series).

B1.1	Substances determined	Carbon dioxide, oxygen and residual gases.
B1.2	Type of sample	Gas produced by anaerobic digestion of organic sludges and digestion plant purge gas.
B1.3	Basis of method	Measurement of the decrease in sample volume after absorption of carbon dioxide in potassium hydroxide and oxygen in pyrogallol*. Residual gases (methane plus nitrogen) are estimated by difference from the known volume of gas originally taken.
B1.4	Range of application	Up to 40 $\%^{v}/_{v}$.
B1.5	Standard deviation (within batch)	These were determined from ten replicate analyses in each case† (ie 9 degrees of freedom).

Carbon dioxide		Oxygen	
Concn $\%^{v}/_{v}$	S.D. $\%^{v}/_{v}$	Concn $\%^{v}/_{v}$	S.D. $\%^{v}/_{v}$
28·8	2·05	20·6	0·38
4·3	0·14	4·45	0·135

B1.6	Limit of detection	About 0·1 $\%^{v}/_{v}$ (judged from the sensitivity of the analytical method).
B1.7	Bias	Not studied (see Section B1.10).
B1.8	Interferences	Other acid gases eg hydrogen sulphide are also absorbed.
B1.9	Time required for analysis	10 minutes per sample (operator time is the same as total time).

* Chromous chloride may be used as an alternative.

† Data provided by the Water Research Centre.

B2 Principle

A measured volume of sample is drawn into the apparatus (see Figure 6) and is then transferred back and forth between the first absorption pipette and the measuring burette until the carbon dioxide is completely absorbed. The decrease in volume of the sample, at constant pressure, provides the measure of the concentration of carbon dioxide in the sample. The procedure is repeated using a second absorption vessel to determine the concentration of oxygen. The unabsorbed residue of a sample of gas from a digester is assumed to be a mixture of methane and nitrogen.

B3 Interferences

Any acid gas present in the sample, eg hydrogen sulphide, will be absorbed by the solution of potassium hydroxide and be reported by the analyst as carbon dioxide.

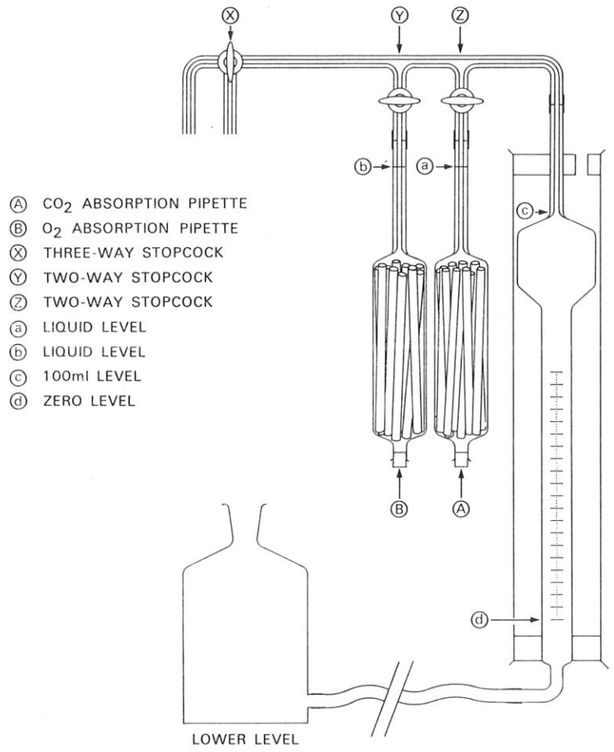

Figure 6 General layout of orsat apparatus (front view)

B4 Hazards

B4.1 Digester and purge gases may contain high concentrations of methane and therefore great care should be taken to ensure that explosive mixtures of methane-enriched gas with air are not allowed to form in confined areas around the digestion plant and in the laboratory. A NO SMOKING, NO NAKED LIGHTS policy should always be operated.

B4.2 The Orsat apparatus will not withstand pressures much above that of the atmosphere and sampling of gas at elevated pressures must be carried out via an inflatable bladder. The gas to be sampled is allowed to inflate the bladder which is isolated from the high pressure sampling point before connecting it to the Orsat apparatus (full details are given in section B6).

B4.3 The 40 $\%^{M}/_{V}$ potassium hydroxide solution and the pyrogallol solution used as absorbents are highly caustic materials and must be handled with caution; safety glasses must be worn. Any spillages should be flushed away with water. If the solution comes into contact with the skin thoroughly wash the affected areas with water. In the case of the solution entering the eyes, irrigate with water and obtain medical advice.

B4.4 The confining liquid is acidic and should be handled with care (section B5.3).

B4.5 The preferred confining liquid in the apparatus for reference testing is mercury and proper precautions should be taken regarding handling and disposal which must not be to the drain.

Distilled or deionized water should be used to prepare solutions of the reagents.

B5 Reagents

B5.1 **Carbon dioxide absorbent**

40 $\%^{M}/_{V}$ aqueous solution of potassium hydroxide. The absorbing power is about 40 ml of carbon dioxide per millilitre of solution.

B5.2 **Oxygen absorbents**

B5.2.1 *Alkaline pyrogallol solution* (this is the preferred absorbent)

Three volumes of a 40 $\%^{M}/_{V}$ aqueous solution of pyrogallol with five volumes of a 36 $\%^{M}/_{V}$ aqueous solution of potassium hydroxide prepared from the solution described in section B5.1. The absorbing power is about 14 ml of oxygen per millilitre of solution. When preparing this solution avoid contact with air as far as possible.

B5.2.2 *Acid chromous chloride*

This solution may be used as an alternative to alkaline pyrogallol solution. Wash 8 g of zinc granules (1·7–2·8 mm) with hydrochloric acid (2M approximately). Add 250 g of pure mercury, cover with 5 ml of hydrochloric acid (2M approximately) and heat for one hour on a boiling water bath in an efficient fume cupboard. Allow to cool, wash the amalgam with sulphuric acid (1M approximately) and then with water.

Transfer the amalgam to a 400 ml reagent bottle, add 100 g of chromic chloride hexahydrate, 260 ml of water and 40 ml of hydrochloric acid (d_{20} 1·18). Stopper the bottle with a rubber bung carrying a bunsen valve (Figure 7) and shake the bottle until the

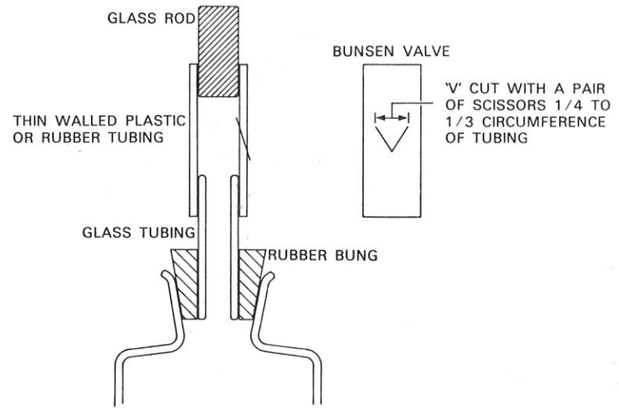

Figure 7 Typical bunsen valve

contents assume the characteristic blue colour of chromous solution. The absorbing power is about 25 ml of oxygen per millilitre of solution.

B5.3 **Confining liquid**

200 g sodium sulphate plus 30 ml concentrated sulphuric acid made up to 1 litre with distilled water containing a few drops of aqueous methyl orange or other suitable indicator. For reference analysis mercury is the preferred confining liquid.

B6 Apparatus

An Orsat-type gas analysis apparatus incorporating two absorption pipettes, a levelling bottle and a water-jacketed 100 ml burette calibrated for at least 40 ml of its capacity at 0·2 ml graduations should be used.

A general diagram of the apparatus is shown in figure 6 and a detailed diagram of one of the absorption pipettes is shown in Figure 8. The use of Shepherd type absorption pipettes with fritted glass distributors (Figure 9) is also permitted. The stopcocks are liable to become jammed if left in contact with sodium hydroxide for a long period. They should be washed with water after completion of the analysis.

Inactivation of the reagents in the apparatus by absorption of oxygen or carbon dioxide from the atmosphere can be minimized by fitting an ordinary rubber balloon to the outlet tube of each absorption vessel or by use of a liquid paraffin seal (2–3 ml) on the exposed vessel.

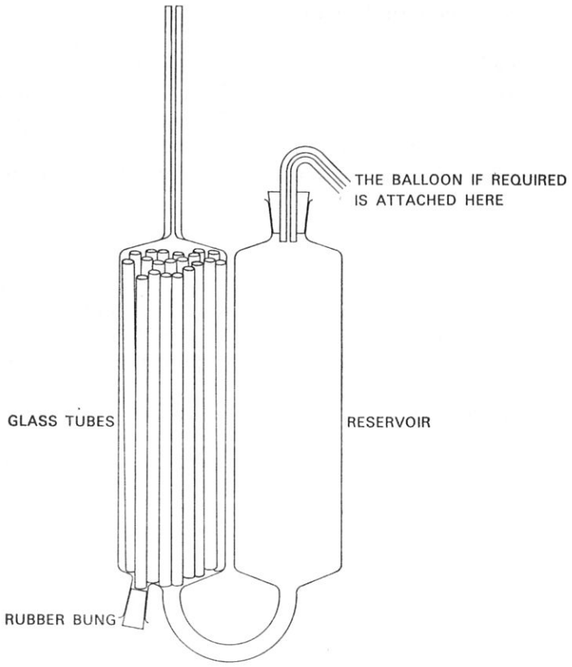

Figure 8 Traditional type of absorption pipette (side view)

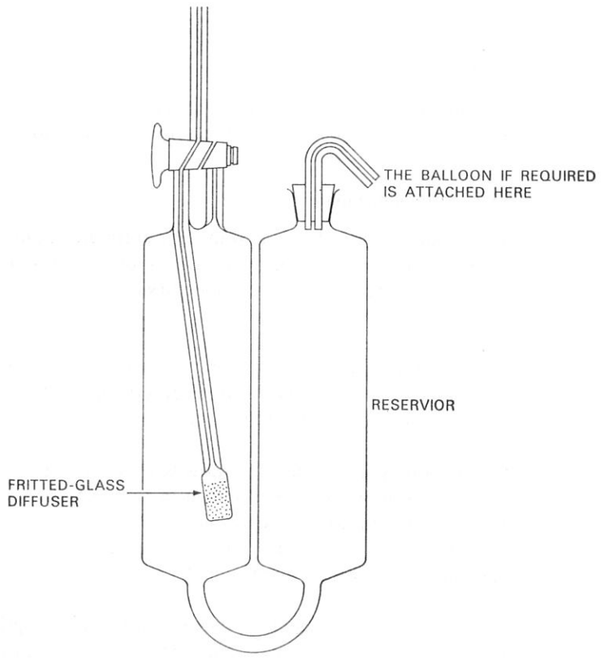

Figure 9 Shepherd type of absorption pipette (side view)

B7 Sampling

For gases at or near atmospheric pressure the apparatus can be taken to the source of gas and samples drawn directly into its measuring burette. An intermediate container is not normally required; alternatively glass sampling tubes, glass bottles or suitable proprietary sampling equipment may be used. Glass sampling tubes are also available with centrally-located ports provided with septa for syringe transfer of samples and are especially useful for gas chromatographic analysis. Gases under high pressure should be transferred to the apparatus by partially inflating a gas-tight, collapsible container eg a football bladder or plastic bag, which permits the sample to be introduced to the apparatus at or near atmospheric pressure. Rubber bladders should be internally washed with approximately 2M hydrochloric acid, then thoroughly washed with water before use. Avoid delay between sampling and analysis if at all possible.

When sampling, either sweep about 10–15 volumes of gas through the sampling equipment before taking the actual sample or if using collapsible containers inflate and expel 3 or 4 times before obtaining the required sample. Special care is necessary to prevent air gaining access to the sample.

Sampling can also be effected by displacement which is particularly useful if the gas supply is limited. Use a gas collection apparatus as in figure 2 with mercury or an acidified salt solution (suggested composition as B5.3). As the latter solution dissolves gases to some extent it is advisable to saturate it with sample gas before use. Fill the glass tube with the confining liquid and after sweeping air from the sampling line with about 10–15 volumes of the gas, turn the three-way stopcock and fill the tube with the gas sample removing as much of the liquid from the tube as is practicable.

B8 Analytical Procedure

In this section the identification of lettered parts will be facilitated by reference to Figure 4.

Step	Analytical procedure	Notes
B8.1	Preparation of the apparatus for use	
B8.1.1	Assemble the apparatus according to the manufacturer's instructions (figure 6).	
B8.1.2	Fill the levelling bottle with the confining liquid (note a).	(a) The levelling bottle should be in the lower position, and stopcocks 'X', 'Y' and 'Z' should be open.
B8.1.3	Pour about 200 ml of carbon dioxide absorbent into vessel A and draw the solution up to reference mark 'a' on the absorption pipette by manipulating the levelling bottle and the stopcocks. This should leave a column of about 15 mm of solution in the absorption pipette reservoir (figure 8).	
B8.1.4	Fit a rubber balloon over the reservoir outlet or introduce sufficient liquid paraffin to provide a seal (notes b and c).	(b) This prevents entry of atmospheric carbon dioxide or oxygen. (c) 2–3 ml liquid paraffin are normally sufficient.
B8.1.5	Repeat steps B8.1.3 and B8.1.4 but introduce oxygen absorbent into absorption pipette B and bring up to mark 'b'.	
B8.1.6	Fill the burette to the 100 ml mark 'c' with confining liquid by raising levelling bottle and opening stopcocks (note d).	(d) Stopcocks 'Y' and 'Z' should be closed.
B8.1.7	Test the apparatus for leaks by closing stopcock 'X' and lowering the levelling bottle and observing whether the levels of liquid in the burette or absorption pipettes change.	

Step	Analytical procedure	Notes
B8.1.8	As carbon dioxide and oxygen must be removed from the gases within the apparatus before valid results can be obtained the procedure under section B8.2 must be carried out initially using air or sludge gas and the results discarded.	
B8.2	Introducing the sample	
B82.1.	Connect the sample supply to stopcock 'X' and purge the connecting line and stopcock with sample. Carefully open stopcock 'X' to the apparatus and draw in not less than 100 ml of sample. Close stopcock 'X' and disconnect sample supply.	
B8.2.2	Raise the levelling bottle (reservoir) so that the confining liquid meniscus in the burette is on the zero mark; pinch the connecting tube with the fingers, or use a screw clip, to keep the meniscus at this mark, then momentarily open to zero mark and close stopcock 'X' to atmosphere. Keep pinching the connecting tube and line up the liquid level in the reservoir with that in the gas burette, this reading will be the zero for the gas volume to be analysed and should correspond to the zero mark 'd' of the burette.	(e) Burette now contains 100 ml sample at atmospheric pressure; stopcock 'X' must remain closed for duration of the analysis.
B8.2.3	Open stopcock 'Z' and by raising and lowering the levelling bottle, transfer the sample back and forth several times between the absorption pipette and the gas burette (note f).	(f) This may prove difficult if an unstretched balloon was fitted to the absorption pipette.
B8.2.4	Return the carbon dioxide absorbent to mark 'a' and close stopcock 'Z'.	
B8.2.5	Hold the levelling bottle so that the surface of the liquid in bottle is level with the surface of the liquid in the burette and note the meniscus reading.	
B8.2.6	Repeat the procedure until readings are constant indicating that no further carbon dioxide is being absorbed. Note this final constant reading record as V_1.	
B8.2.7	Open stopcock Y and repeat the absorption procedure by passing the sample into the oxygen absorption pipette until the volume of the sample remains constant. Record as V_2 (notes g and h).	(g) When oxygen alone is to be determined, the procedure specified must still be adhered to, as alkaline pyrogallol will also absorb carbon dioxide. (h) Renew the reagent in the absorption vessels when absorption becomes slow. Normally carbon dioxide should be absorbed in three passes and oxygen in seven passes.
	Calculation of Results The percentage by volume of each gas is as follows (assuming 100 ml sample taken) (note j). $\%C0_2 = V_1$ $\%\ 0_2 = V_2 - V_1$ $\%$ Residual gases $= 100 - V_2$	(j) Gases are sampled and analysed whilst fully saturated with water vapour. The results should be expressed as percentage by volume saturated gas.
B8.2.8	After completing each set of analyses allow the absorbant levels to fall well below the stopcock.	

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Appendix

Table 1 Typical operating conditions for gas chromatographs at various laboratories

	Water Research Centre (Stevenage)	Beckton Sewage Treatment Works (TWA)	Finham Regional Laboratory (STWA)	Manchester (Davyhulme) Sewage Treatment Works (NWWA)		
				Routine determinations	Purge gases	Traces of sludge gas in air
Type of detector	Katharometer	Katharometer	Katharometer	Katharometer	Katharometer	flame ionization
Katharometer bridge current	90 mA		10 mA	—	—	—
Carrier gas	Argon at 45 ml/min	Hydrogen at 50 ml/min	Helium at 47 ml/min	Helium at 30 ml/min	Helium at 60 ml/min	Nitrogen at 60 ml/min
Carrier gas inlet pressure	103 kN/m² (15 psi)	150 kN/m² (22 psi)	34 kN/m² (5 psi)			
Oven temperature	100°C	ambient	ambient	50°C	Temperature programmed at 90 deg C/min up to 350°C	50°C
Column	both 4 mm id × 1·5 long	(a) 3 mm id × 4·9 m long (b) 3 mm id × 0·6 m long	both 4 mm id × 1·2 m long	(a) 6 mm id × 1·5 m long (b) 3 mm id × 1·5 m long		
Stationery phases	(a) 80–100 mesh Molecular sieve 5A (b) 80–100 mesh Porapak S	(a) 30–60 mesh Molecular sieve 5A (b) 30–60 mesh Silica gel	(a) 40–60 mesh Molecular sieve 5A (b) 80–100 mesh Porapak Q	Porosil A	Molecular sieve 5A	Porosil A
Sample volume	about 0·15 ml	usually 1 ml	usually 1 ml	1 ml–10 ml	1 ml–10 ml	1 ml–10 ml

Table 2 Per cent by volume of water vapour in saturated air at atmospheric pressure (760 mm Hg)

Temperature (°C)	0	1	2	3	4	5	6	7	8	9
0	0·60	0·65	0·70	0·75	0·80	0·86	0·92	0·99	1·06	1·13
10	1·21	1·29	1·38	1·48	1·58	1·68	1·79	1·91	2·03	2·17
20	2·30	2·45	2·61	2·77	2·94	3·12	3·31	3·51	3·73	3·95
30	4·18	4·43	4·69	4·96	5·25	5·54	5·86	6·19	6·53	6·90

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