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# Guidance for monitoring trace components in landfill gas

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This guidance is based on R&D projects P1-438 *Investigation of the composition, emissions and effect of trace components in landfill gas* and P1-491 *Quantification of trace components in landfill gas*. Tom Parker of Komex project managed these studies with the support of Harwell Scientifics.

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**Statement of Use**

This guidance is one of a series of documents relating to the management of landfill gas. It is intended for use in monitoring the concentration of trace components in raw landfill gas at permitted or licenced landfill sites. It is issued by the Environment Agency and the Scottish Environment Protection Agency (SEPA) as best practice guidance and will be used in the regulation of landfills. It is primarily targeted at regulatory officers, but will also be of use to the waste industry and contractors, consultants and the local authorities. It does not constitute law, but officers may use it during their regulatory and enforcement activities. Any exemption from any of the requirements from other legislation is not implied.

Throughout this document, the term 'regulator' relates jointly to the Environment Agency and the Scottish Environment Protection Agency. SEPA does not necessarily support and is not bound by the terms of reference and recommendations of other documentation mentioned in this guidance, and reserves the right to adopt and interpret legislative requirements and guidance as it sees fit. The term 'Agency' should therefore be interpreted as appropriate.

# Executive summary

The regulator has produced this document to assist staff in assessing the monitoring of trace components in raw landfill gas at permitted or licensed landfill sites. The information on the concentration of trace components obtained through this monitoring is an integral part of demonstrating compliance with Article 1 of the Landfill Directive.

In particular, the data are used:

- in the development of source term values for a site-specific risk assessment of gaseous emissions and the resulting Gas Management Plan;
- in the development of the source term values for gas generation models that estimate the emissions of landfill gas and are used to produce the Pollution Inventory of specified substances released from a permitted site;
- to provide compositional data to the annual review and refinement of the current Gas Management Plan.

The table below summarises the priority trace components to be monitored in landfill gas, with their recommended sampling and analytical methods.

## Priority trace components to be monitored in landfill gas

Significant trace component	CAS Number	Sampling method	Analytical method*
1,1-dichloroethane	75-34-3	Dual solid sorbent	ATD-GC-MS
1,1-dichloroethene	75-35-4	Dual solid sorbent	ATD-GC-MS
1,2-dichloroethene	540-59-0	Dual solid sorbent	ATD-GC-MS
1,3-butadiene	106-99-0	Dual solid sorbent	ATD-GC-MS
1-butanethiol	109-79-5	Dual solid sorbent	ATD-GC-MS
1-pentene	109-67-1	Dual solid sorbent	ATD-GC-MS
1-propanethiol	107-03-9	Dual solid sorbent	ATD-GC-MS
2-butoxy ethanol	111-76-2	Dual solid sorbent	ATD-GC-MS
Arsenic (as As)	7440-38-2	Solid sorbent	ICP-MS/AAS
Benzene	71-43-2	Dual solid sorbent	ATD-GC-MS
Butyric acid	107-92-6	Dual solid sorbent	ATD-GC-MS
Carbon disulphide	75-15-0	Dual solid sorbent	ATD-GC-MS
Chloroethane	75-00-3	Dual solid sorbent	ATD-GC-MS
Chloroethene (vinyl chloride)	75-01-4	Dual solid sorbent	ATD-GC-MS
Dimethyl disulphide	624-92-0	Dual solid sorbent	ATD-GC-MS
Dimethyl sulphide	75-18-3	Dual solid sorbent	ATD-GC-MS
Ethanal (acetaldehyde)	75-07-0	Reactive sorbent	HPLC
Ethanethiol	75-08-1	Dual solid sorbent	ATD-GC-MS
Ethyl butyrate	105-54-4	Dual solid sorbent	ATD-GC-MS
Furan (1,4-epoxy-1,3-butadiene)	110-00-9	Dual solid sorbent	ATD-GC-MS
Hydrogen sulphide	7783-06-4	Direct on-site measurement of raw gas	Hand-held instrument
Methanal (formaldehyde)	50-00-0	Reactive sorbent	HPLC
Methanethiol	74-93-1	Dual solid sorbent	ATD-GC-MS
Tetrachloromethane	56-23-5	Dual solid sorbent	ATD-GC-MS
Trichloroethene	79-01-6	Dual solid sorbent	ATD-GC-MS

The table below lists example additional determinands that may need quantification on a site-specific risk basis. A number of these are detected by the methods used for the priority trace components. Different monitoring methods are recommended for others.

#### Additional components that may be monitored in landfill gas

Monitor using dual solid sorbent and ATD-GC-MS		Monitor by other methods
1,2-dichloroethane	Tetrachloroethene	Mercury (as Hg) <sup>1</sup>
1,1,2,2-tetrachloroethane	Toluene	PCDDs and PCDFs <sup>2</sup>
Dichloromethane	Trimethylbenzene	Carbon monoxide <sup>3</sup>

<sup>1</sup>sample on solid adsorbent and analysis by ICP-MS or CV-AAS

<sup>2</sup>sample on solid sorbent and analysis by GC-HRMS

<sup>3</sup>sample in Gresham tube or Tedlar bag and analyse by laboratory GC

This guidance adopts the methods recommended by Environment Agency R&D Project P1-438, adapted in the light of experience in R&D Project P1-491.

The monitoring of priority trace components should be carried out annually as a minimum frequency, but subject to site-specific circumstances such as significant changes to the gas management system or waste composition. It is essential that:

- the sampling point(s) is selected so that the landfill gas sampled is representative of the gas collected at the site;
- the gas sample is metered to provide an accurate value for the sample volume;
- precautions are taken to avoid moisture or condensate entering the sampling system;
- care is taken to prevent contamination or degradation of the sample during transfer to the laboratory and preparation for analysis;
- any priority trace components that are not positively identified using the recommended methods are reported as being present at below their respective detection limits. Recommended detection limits are provided in Appendix 3.

Once trace gas data have been derived, they must be summarised in a way that allows meaningful interpretation and use as a source term in risk assessment or the Pollution Inventory. The portion of the site for which the trace gas sample is a representative source term should be clearly identified. To aid this process, an example report format suitable for submitting to the regulator is provided in Appendix 4. Data must be assessed for consistency with previously reported data and other sources of information identified. The compositional data reported on the gas should also inform future gas monitoring requirements at that site.



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# Introduction

## 1.1 Purpose of this technical guidance

This guidance is for use in assessing the monitoring of trace components in gas at permitted or licensed landfill sites. The guidance has been produced for monitoring at landfill sites where there are no unusual short-term circumstances such as fire. A standard set of monitoring methods is recommended for collection of data on the concentration of trace components in a valid, transparent and consistent manner.

The information on the concentration of trace components obtained through this monitoring is an integral part of demonstrating compliance with Article 1 of the Landfill Directive. In particular, the data are used:

- in the development of source term values for a site-specific risk assessment of gaseous emissions and the resulting Gas Management Plan;
- in the development of the source term values for gas generation models such as GasSim, which estimate the emissions of landfill gas and are used to produce the Pollution Inventory of specified substances released from a permitted site;
- to provide compositional data to the annual review and refinement of the current Gas Management Plan.

This is one of a series of linked documents that support the overarching document, *Guidance on the management of landfill gas* (Environment Agency, 2004a). The full series comprises:

- Guidance for monitoring trace components in landfill gas
- Guidance on landfill gas flaring
- Guidance for monitoring enclosed landfill gas flares
- Guidance for monitoring landfill gas engine emissions
- Guidance for monitoring landfill gas surface emissions (England and Wales);
- Guidance on gas treatment technologies for landfill gas engines.

The guidance is also likely to be useful to:

- landfill operators who will need to quantify the annual emissions of certain trace components of landfill gas;
- monitoring contractors undertaking work on behalf of operators or the regulator;
- consultants undertaking risk assessments on the impact of emissions from landfills;
- local authorities concerned with landfill gas emissions.

The guidance will be implemented as landfill sites are permitted or re-permitted under the requirements of the Landfill (England and Wales) Regulations 2002.

For closed sites where a waste management licence remains in force, the Agency will require the licence holder to produce a landfill gas Emissions Review. This will be based on the development of a risk screening/conceptual model of gas management for the site. Where this Review identifies unacceptable site-specific risks from landfill gas, an emissions improvement programme should be prepared that incorporates appropriate best practice as described in this guidance. This improvement programme will be undertaken on a risk basis for completion as soon as is reasonably practicable and as identified by a site-specific Emissions Review. The improvements identified in the Emissions Review will be completed at all Agency-regulated landfills by 16 July 2009.

## 1.2 Structure of this document

Section 1 provides information on the context of this guidance and the identification of priority trace components. Section 2 discusses a number of general monitoring issues to be considered before sampling on-site and Section 3 identifies the recommended approach to monitoring for priority trace components. Section 4 describes specific on-site preliminary field measurements and Section 5 details protocols for monitoring specific trace components.



Example report formats, recommended detection limits, and an introduction to analytical methodologies are given in the Appendices. There is also a glossary, a list of acronyms and an explanation of the units of measurement used.

## 1.3 Background

### 1.3.1 Regulatory

Paragraph 4 of Schedule 2 of the Landfill (England and Wales) Regulations 2002 (the 2002 Regulations), which implement the Landfill Directive 1999/31/EC, requires the following gas control measures.

- Appropriate measures must be taken in order to control the accumulation and migration of landfill gas.
- Landfill gas must be collected from all landfills receiving biodegradable waste and the landfill gas must be treated and, to the extent possible, used.
- The collection, treatment and use of landfill gas must be carried on in a manner, which minimises damage to or deterioration of the environment and risk to human health.
- Landfill gas that cannot be used to produce energy must be flared.

The Pollution Prevention and Control Regulations 2000 (PPC Regulations), together with the 2002 Regulations, specify the requirements for technical standards covering aspects of the construction, operation, monitoring, closure and surrender of landfills.

In accordance with Section 28(2) of the PPC Regulations, the operator of a landfill site must produce an annual report on the emission of certain substances from the site. This Pollution Inventory includes several compounds for which the most significant route of emission will be the escape of landfill gas. Quantification of trace component concentrations will help determine the releases in relation to Pollution Inventory reporting thresholds.

The GasSimLite model (<http://www.gassim.co.uk>) can be used by operators to create a ready-formatted Pollution Inventory return for a site. In addition, information on the release of substances that may have a health, environmental or amenity impact will be needed to conduct a risk assessment for a landfill. The full GasSim model (Environment Agency, 2002a) may be used for preliminary assessments. GasSim includes default values for trace components of landfill gas that have been set from concentrations observed in landfill gas at a range of waste sites. Where reliable site-specific data on trace components

are available, these should be used in the assessment. Where detailed risk assessments are considered necessary, site-specific assessments will require actual or projected trace component profiles based on field data.

The regulator's strategy for landfill gas control is based on regulating the outcomes and emissions associated with landfill gas. A fundamental part of this process is the quantification of landfill gas trace components. Detailed guidance on the management of landfill gas is available (Environment Agency, 2004a).

The timely installation of active landfill gas collection systems at modern engineered landfills ensures that only a small proportion of the raw gas will escape to the wider environment. The concentration of the trace components in the raw gas will usually reflect the composition of that portion of the landfill gas that will be emitted to the environment without utilisation or treatment. This guidance deals with the measurement of the concentration of particular components in the raw gas (i.e. the source term) and does not deal with estimating the flux or annual emission of landfill gas from the site.

This guidance does not change the requirement for routine monitoring and reporting of bulk gas composition at landfill sites. Detailed procedures for the monitoring of bulk gases (methane, carbon dioxide, oxygen) are described in *The monitoring of landfill gas* (IWM, 1998).

### 1.3.2 Technical

Microbial action on biodegradable wastes under anaerobic conditions generates methane and carbon dioxide as bulk gases. Small amounts of other gases are also present in landfill gas. These trace components may arise from volatilisation of materials in the waste or can be formed through biochemical reactions associated with the degradation processes. In total, these trace components may make up less than 1 per cent of the volume of the gas emitted from the waste in a landfill. However, the impact of some trace gases on the environment and on human health (e.g. through stress) may be more significant than that of the bulk gases.

Under certain circumstances, the concentration of trace components may be greater than 1 per cent, e.g. if there is a deep-seated fire, carbon monoxide levels may rise temporarily. Sites that have a serious odour problem may also have high levels of trace components in the bulk gas. Details given in this guidance note may need to be adapted to deal with these non-standard situations.



Over 500 substances have been reported in landfill gas (Environment Agency, 2002b). These include:

- higher alkanes and alkenes;
- cycloalkanes and cycloalkenes;
- aromatic, cyclic aromatic and polycyclic aromatic hydrocarbons and derivatives;
- alcohols;
- aldehydes;
- ketones;
- esters;
- organosulphur compounds;
- organohalogens;
- oxygenated compounds.

However, many of these substances are benign or occur at such low concentrations that they will have very little impact on human health, the environment or amenity. Volatile substances contained in the waste (e.g. chlorinated solvents) will release vapour that mixes with the bulk landfill gas. If the waste contains significant amounts of sulphate, hydrogen sulphide will be produced by anaerobic microbial action. Vinyl chloride may also be generated by anaerobic microbial action on polychloroethenes in the waste (Smith and Dragun, 1984).

The Agency has developed a method for ranking the significance of individual substances based on their inherent toxic or odour properties and their reported concentration in landfill gas (Environment Agency, 2002b). A list of priority substances that had the greatest significance when considering the potential health impact of landfill gas and other substances with the greatest significance for the potential odour impact from landfill gas was compiled from this ranking. A suite of sampling and analytical methods that could be used to monitor these significant trace components in typical landfill gas was recommended.

#### **1.4 Priority trace components of landfill gas**

The trace components judged as most significant in terms of their potential impact (health or odour or both) are listed alphabetically in Table 1.1 (from Environment Agency, 2002b and 2004b). This list is derived from existing average concentrations found in UK landfill gas and forms the basis of this monitoring guidance. Trace components that are not identified in Table 1.1 should not initially be disregarded in a site-specific risk assessment.

**Table 1.1** | Priority trace components to be monitored in landfill gas

Significant trace component	CAS Number	Potential impact	Category
1,1-dichloroethane	75-34-3	Health	Halocarbon
1,1-dichloroethene	75-35-4	Health	Halocarbon
1,2-dichloroethene	540-59-0	Health	Halocarbon
1,3-butadiene	106-99-0	Health	Aliphatic hydrocarbon
1-butanethiol	109-79-5	Odour	Organosulphur
1-pentene	109-67-1	Odour	Aliphatic hydrocarbon
1-propanethiol	107-03-9	Odour	Organosulphur
2-butoxy ethanol	111-76-2	Health	Alcohol
Arsenic (as As)	7440-38-2	Health	Inorganic
Benzene	71-43-2	Health	Aromatic hydrocarbon
Butyric acid	107-92-6	Odour	Carboxylic acid
Carbon disulphide	75-15-0	Odour and health	Organosulphur
Chloroethane	75-00-3	Health	Halocarbon
Chloroethene (vinyl chloride)	75-01-4	Health	Halocarbon
Dimethyl disulphide	624-92-0	Odour	Organosulphur
Dimethyl sulphide	75-18-3	Odour	Organosulphur
Ethanal (acetaldehyde)	75-07-0	Odour	Aldehyde
Ethanethiol	75-08-1	Odour	Organosulphur
Ethyl butyrate	105-54-4	Odour	Ester
Furan (1,4-epoxy-1,3-butadiene)	110-00-9	Health	Ether
Hydrogen sulphide	7783-06-4	Health and odour	Inorganic
Methanal (formaldehyde)	50-00-0	Health	Aldehyde
Methanethiol	74-93-1	Odour	Organosulphur
Tetrachloromethane	56-23-5	Health	Halocarbon
Trichloroethene	79-01-6	Health	Halocarbon

CAS = Chemical Abstracts System

**Table 1.2** | Additional components that may be monitored in landfill gas

Trace component	CAS Number	Significance	Category
Mercury (as Hg)	7439-97-6	Health	Inorganic
PCDDs and PCDFs	N/A	Health	Chlorinated aromatic
Carbon monoxide	N/A	Health	Inorganic

PCDD = polychlorinated dibenzo-*p*-dioxin

PCDF = polychlorinated dibenzofuran

Other substances in different categories may need quantification on a site-specific risk basis. Example

additional determinands that will require alternative monitoring techniques are listed in Table 1.2.

**Table 1.3** Recommended methods for monitored priority trace components in landfill gas

Category	Sampling method	Analytical method *
<b>Priority components</b>		
Speciated VOCs <sup>#</sup>	Dual solid sorbent	ATD–GC–MS
Aldehydes	Reactive sorbent	HPLC
Hydrogen sulphide	Direct on-site measurement of raw gas	Hand-held instrument
Arsenic	Solid sorbent	ICP–MS/AAS
<b>Additional components</b>		
Mercury	Solid sorbent	ICP–MS/CV–AAS
PCDDs and PCDFs	Solid sorbent	GC–HRMS
Carbon monoxide	Gresham tube/Tedlar bag	Laboratory GC

VOC = volatile organic compounds

# Table 1.1 compounds except for those listed subsequently.

\* A list of acronyms is given at the end of this guidance and the various methods are outlined in Appendix 2.

The methods recommended in R&D Project P1-438 (Environment Agency, 2002b) and adapted in the light of experience during R&D Project P1-491 (Environment Agency, 2004b) have been adopted for use in this guidance. The techniques were selected to give the best overall cover of all the priority substances with the smallest number of individual monitoring methods. These methods for sampling and analysing the more significant substances in landfill gas are summarised in Table 1.3.

These methods will also quantify certain substances that have similar properties to those nominated in Table 1.1. It is recommended that the detection of an unusually high concentration of a substance not on the list of significant compounds should be investigated.

The significance ranking of substances was based on average concentrations found in UK landfill gas. If, on a site-specific assessment, the concentration is much higher than the UK average, the relative significance of substances at that site may be different from those identified in the tables above.

Examples of substances that may require investigation on a site-specific basis include:

- tetrachloroethene
- 1,2-dichloroethane
- dichloromethane

These were the ranked next highest in the list of significant substances. Other substances include:

- 1,1,2,2-tetrachloroethane
- toluene
- trimethylbenzene

These were identified as important indicator compounds by Redfearn *et al.* (2002). None of these common trace components are on the priority list in Table 1.1, but will be detected by the recommended method for speciated VOCs.

### 1.5 Non-gaseous components of landfill gas

This guidance relates only to gaseous emissions. Landfill gas is normally at a low pressure relative to atmospheric, and flow rates in gas lines are insufficient to suspend substantial quantities of particulate matter or aerosols. Gaseous emissions are therefore unlikely to be a significant source of non-volatile substances such as heavy metals. The exceptions are:

- mercury, which has a significant vapour pressure at ambient conditions and can form volatile derivatives;
- arsenic and antimony, which may form arsine gas (AsH<sub>3</sub>) or stibine gas (SbH<sub>3</sub>) under certain conditions.

If the gas at a site is known to entrain large quantities of dust or aerosol, a separate sample of gas should be drawn through a simple, inert filter to estimate the likely contribution from particulates to the concentrations of compounds found during the analysis of the gas samples.

# Monitoring considerations

The trace components are a very small proportion of landfill gas. They are diluted with a large amount of the bulk gases, methane and carbon dioxide (typically 55–65 per cent and 45–35 per cent by volume, respectively). In practice, air infiltrates into the gas system and some of the oxygen may be utilised by organisms within the fill, leaving nitrogen as a residual component. Thus, some landfill gases may contain 40 per cent nitrogen and up to 5 per cent oxygen.

Where leachate is present, the landfill gas may also be saturated with water at the temperature of the landfill and condensate will form as the gas cools during sampling. If there has been a fire within the landfill, there will be detectable concentrations of carbon monoxide.

## 2.1 Other relevant monitoring data

There will generally be previous information on gas composition. For example:

- the waste composition will highlight the likelihood of unusual trace components being present;
- qualitative screening by gas chromatography (GC) may have been carried out for principal trace components irrespective of their potential significance;
- elemental analysis of total chlorine and total sulphur may have been carried out to assess gas quality for utilisation.

Existing data on trace landfill gas composition should be used to inform the selection of sample points and the analytical suite on a site-specific basis. The consistency of data generated by this guidance should be verified against these existing data. In instances where such 'sanity checks' indicate inconsistency, this should be investigated further.

Historical data may be reported in ppmv (parts by million by volume) concentrations. A conversion factor to the recommended unit of measurement (mass per unit volume) is provided in Appendix 1.

## 2.2 Monitoring frequency

The monitoring of priority trace components should be carried out annually as a minimum frequency. The frequency should be greater when site-specific circumstances alter, e.g. if significant changes to the gas management system or waste composition occur.

## 2.3 Choice of sampling point

The selection of sampling point is an important consideration. It is essential that the gas sample is typical and representative of the source landfill gas. In order to achieve this, the detailed sampling for trace components must be preceded by a check on the composition of the bulk gases.

The area of the landfill for which the sample is spatially representative should be reported with the data.

The sample can only be representative of the particular time of sampling. Some temporal variation in gas composition must be expected from all sites and will be part of the uncertainty in the reported value for trace gases. However, if the gas emissions from a site are known to be unstable in terms of quality and quantity, some estimate of temporal variation in trace component composition of the landfill gas must be made. Gas composition may take some time to stabilise after changes in gas management. As a minimum sampling should not take place within three hours of major changes to the gas flow such as the switching on or off of the gas engines.

Potential sampling points providing samples representative of the main source of gas in an area of the landfill are:

- the main line carrying gas to the engines or site flare
- gas field manifolds
- individual gas wells
- in-waste gas monitoring points.

When the source gas is associated with a particular

leachate and there is no other representative sampling point, it may be necessary to sample the gas from capped leachate wells.

A sample may be unrepresentative of the source gas if, at the sample point, there is evidence that the gas has been:

- diluted with large amounts of air;
- cooled such that large amounts of condensate form (thus partitioning some trace gases into the aqueous phase);
- mixed with emissions from an area where there is combustion within the landfill, e.g. elevated carbon monoxide concentrations;
- drawn from an area known to have large temporal variations in gas composition.

Inappropriate sampling points where the gas is likely to be unrepresentative of the source gas are:

- perimeter gas monitoring points
- spike points
- odour control or gas migration extraction systems drawing significant air
- uncapped leachate wells.

A sample taken from the main gas line to the utilisation plant will generally be representative of the source gas collected at that site. Samples taken from manifolds or individual wellheads will be progressively less representative of the main source term and more representative of a particular part of the site.

Where there is a central utilisation plant, a sampling point in the main gas line will typically provide the only samples needed to characterise the raw gas at the site. If there are several gas lines extracting gas from a number of areas of the site for separate treatment, each of these lines should be sampled to obtain data representative of the whole site.

Allowance must be made for the volume of gas extracted along each pipe when reporting a representative composition of gas for the site where a number of sampling points have been monitored.

When a cell contains atypical waste, it may be necessary to sample from a manifold where the gas is representative of this particular source in order to provide information for a specific risk assessment.

If the methane content of the gas at the chosen sampling point is less than 30 per cent (i.e. more than 50 per cent diluted), it may be unsuitable for assessment and an alternative point more representative of raw, undiluted gas should be found.

Wherever possible, the selected sample point should be one where significant condensation does not form as gas sample is taken. Condensate will selectively

remove some polar substances from the gas and may affect the performance of the monitoring method. If a sampling point prone to condensation cannot be avoided, see Section 5.1 for advice on dealing with condensation.

Carbon monoxide concentrations greater than 25 ppmv (as verified in the laboratory) may indicate the presence of a deep-seated fire within the landfill; the resulting data set could thus be abnormal, as it will temporarily contain other combustion products. Carbon monoxide determined by field measurements using an electrochemical cell are likely to be affected by the presence of hydrogen (typically 100 ppmv hydrogen may appear as 25 ppmv carbon monoxide). Landfill gas from fresh or moderately fresh waste may be rich in hydrogen and this can lead to erroneous interpretation of field-measured carbon monoxide data.

## 2.4 Potential contamination of gas samples

Bulk gases are typically present at percentage concentrations and trace gas components from mg/m<sup>3</sup> to ng/m<sup>3</sup> concentrations. Hence, quantification of trace components is particularly susceptible to contamination during sample collection, transport and analysis.

To minimise potential contamination, all monitoring equipment must be clean and the equipment should be appropriately designed and constructed (IWM, 1998). The samples must be transported in clean, sealed containers with the minimum exposure to other volatile substances prior to analysis. Samples should be analysed as soon as possible after collection.

## 2.5 Normalisation of data

Data will generally be reported as mass per cubic metre of landfill gas. However, the values will be affected by the:

- temperature
- pressure
- moisture content of the gas.

There will be uncertainty in both the temperature and the pressure of the gas at the point of sampling.

To allow inter-comparison, emissions from high temperature sources such as flares are normalised to standard temperature and pressure (STP). However, this adjustment is not warranted for landfill gas measurements under normal UK site conditions because sampling errors are likely to be more

substantial than uncertainty over standard conditions. For instance, temperature uncertainty may be  $\pm 10^{\circ}\text{C}$ , but this is relatively insignificant when expressed as  $\pm 10\text{K}$  on a normal ambient temperature of  $293\text{K}$ .

Similarly, the pressure of the gas sample is likely to be only a few percent different from  $101.3\text{ kPa}$ . Some published reference data, such as exposure limits in *Guidance Note EH40* (HSE, 2002), are normalised to room temperature and pressure, i.e. to a temperature of  $20^{\circ}\text{C}$  or  $293\text{K}$ . Again, the errors arising from not normalising the data on raw gas are insignificant in comparison with the sampling errors (see Section 6).

Since landfill gas is generated in a moist waste, it is assumed that the emitted gas will be saturated with moisture at the slightly lower temperature at the landfill surface.

While recognising that small errors will result, it is recommended that for most sites, trace gas data are reported without normalising to STP and that data are assumed to relate to ambient temperature and pressure at 100 per cent moisture saturation. Should it be necessary to normalise the data to STP or normal room temperature and pressure, suitable conversion factors are given in Appendix 1.

Methane is a marker compound for landfill gas and its concentration may be used as a reference for dilution of the gas both within and outside the waste. It is therefore important to record the methane concentration of the gas in which the trace components are measured. This ensures that, if necessary, the concentrations of gaseous components can be normalised against the methane concentration to take account of air dilution either within the landfill or during ambient air monitoring above the surface of the landfill.

## 2.6 Health and safety issues

The Agency does not regulate health and safety at work. This guidance is issued as advice to those who will be required by the regulator to carry out the work described in this document. Any health and safety issues should be discussed with the Health and Safety Executive (HSE).

A site-specific risk assessment should be undertaken before sampling begins. Health and safety for work on a site is the responsibility of the operator and written protocols for on-site tasks must be agreed with the site manager before work commences. In addition to conforming to site requirements, work must be undertaken in accordance with relevant health and safety legislation.

Landfill gas is flammable and may contain harmful

components. The need for intrinsically safe equipment must therefore be determined by the risk assessment. This must also account for appropriate occupational exposure standards such as those contained in *Guidance Note EH40* (HSE, 2002) or its successor documents.

Sampling must not disturb the normal safe operation of a gas collection system. Liaison with the site manager is thus essential to prevent unexpected surges of gas or introduction of air into the system. The gas vented during sample collection must be dispersed and the exposure of staff to undiluted gas should be minimised. However, the volumes of gas concerned are relatively small compared with those normally emitted from gas management systems, making specific waste disposal arrangements unlikely.



# Monitoring principals

The main purpose of monitoring trace components in landfill gas is to characterise the source term within the gas. Although there are standard methods approved by the European Committee for Standardisation (CEN) and the British Standards Institute (BSI) for measuring some of the relevant determinands in stack emissions, these are not appropriate for monitoring landfill gas.

Landfill gas includes a very wide variety of labile organic compounds in a water-saturated gas, under a slight vacuum. Although the principles outlined in the Agency's Technical Guidance Note M2 on stack monitoring (Environment Agency, 2002c) are followed where possible, this document depends on techniques developed for monitoring occupational health rather than emissions from combustion processes. This approach uses compact, intrinsically safe equipment to draw small volumes over relatively short periods. This lightweight equipment can be handled safely in the exposed, difficult and isolated environment typical of a landfill site.

The methodology for measuring the trace components will be divided into two stages:

- preliminary checks and field measurements that are completed at the site;
- sampling and analysis that requires work at the site and in the laboratory.

## 3.1 Preliminary checks and field measurements

These activities should be completed at the site and only the recorded results will be taken away. Knowledge of the site history and preliminary checks yield important metadata (secondary data) as well as establishing the suitability of the sampling point for the more extensive sampling for laboratory analysis.

In general, hand-held field instruments used to monitor landfill gas have poor selectivity compared with laboratory analysis. They measure the bulk gases such as methane, carbon dioxide and oxygen satisfactorily, but are inappropriate for discriminating the complex mixture of trace components in landfill gas.

The exception is the measurement of hydrogen sulphide, which can be as adequately analysed using certain types of dedicated, real-time analyser. Such instruments are able to detect hydrogen sulphide at levels from 2 ppbv to 50 ppmv, which is comparable with most laboratory-based techniques. Instrument selectivity eliminates interference from sulphur dioxide, carbon dioxide, carbon monoxide and water vapour, although organic sulphur compounds will be reported with the hydrogen sulphide.

Commonly used hand-held landfill gas monitors could also be used to obtain preliminary values for hydrogen sulphide and carbon monoxide. However, the electrochemical cells used in these multi-determinand instruments are vulnerable to positive interference from other components (e.g. hydrogen). Data obtained from these general-purpose field instruments must be regarded only as indicative and to be confirmed by laboratory analysis.

Portable instruments require regular calibration in accordance with the manufacturer's recommendations.

## 3.2 Sample collection and laboratory analysis

In order to quantify most of the priority trace components in landfill gas, the target compounds are selectively adsorbed and concentrated in sample tubes on-site and subsequently desorbed for selective analysis in the laboratory.

In general, a representative sample of the landfill gas is drawn through a tube containing a small volume of the sorbent, which selectively extracts the target analytes. Alternative methods, such as grab sampling at ambient pressure into a Tedlar bag, are used to take a total gas sample from the site for fractionation later in laboratory analytical equipment. This latter approach may be appropriate to investigate simple gases or site-specific issues where the effect of adsorption to the Tedlar bag material, moisture and rate of sample deterioration can be estimated, i.e. in situations where quantification is less important.



However, the use of solid sorbents according to the procedures in this guidance is recommended for routine sampling of the full range of trace components in gas at standard sites.

Although sampling and analysis are separate procedures, each sampling method is devised to match the particular analytical method; together these constitute the **monitoring method**. The following sub-sections summarise the main monitoring methods recommended to quantify the classes of trace components of interest. The Glossary explains the abbreviations used in this section and short descriptions of the analytical methods are given in Appendix 2.

Use of alternative methods for sampling and analysis may be considered on an individual basis, provided that they have been demonstrated fit-for-purpose before being used (i.e. they have been shown to meet the selectivity and detection limits achieved by the recommended methods). Accredited analytical laboratories can provide details of alternative methods of gas analysis that may achieve the detection limits required for quantification of all the priority trace components in the gas at a particular site.

### 3.2.1 *Speciated VOCs*

Speciated VOC substances are pre-concentrated by adsorption onto sequentially packed beds of two sorbents – Tenax TA and Unicarb TM (formerly known as Spherocarb). These sorbents are held in tubes that are suitable for automated thermal desorption (ATD) and have an inert coating (e.g. Sulphinert or Silicosteel) that prevents loss of labile species. Moisture is eliminated by purging with dry nitrogen. The concentrated compounds are thermally desorbed in the laboratory and analysed by gas chromatography–mass spectrometry (GC–MS). The method is an adaptation of techniques used for monitoring occupational health and is a further development of the triple sorbent method that had been used previously to quantify a wide range of trace components in landfill gas (Allen *et al.*, 1997).

This selection of sorbents has also been chosen to sample for butyric acid. Although butyric acid is polar and elutes poorly through the GC column, this method was found to provide superior results compared with separate monitoring and sampling onto other sorbents.

### 3.2.2 *Aldehydes*

Simple aldehydes polymerise when heated, making gas chromatography inappropriate to quantify this

category of components. The recommended method is in situ derivatisation of the aldehydes with dinitrophenylhydrazine (DNPH) and laboratory analysis by high performance liquid chromatography (HPLC) based on the US Environmental Protection Agency (USEPA) Method TO-5 (USEPA, online). This method has been validated for use in environmental monitoring.

### 3.2.3 *Arsenic*

Arsenic is determined by National Institute of Occupational Safety and Health (NIOSH) Method 6001 Issue 2 (NIOSH, 1994) using inductively coupled plasma–mass spectrometry (ICP–MS) for measurement. This method quantifies total inorganic arsenic including arsine. Cold vapour atomic absorption spectroscopy (CV–AAS) is a suitable method of analysis.

### 3.2.4 *Mercury*

Mercury is sampled using a variation of NIOSH Method 6009 Issue 2 (NIOSH, 1994). Before sampling begins, it must be demonstrated that the tubes have low background levels of mercury, i.e. <1 ng of mercury on the tube and ideally 0.1–0.5 ng. The laboratory determination of total gaseous mercury is by ICP–MS. CV–AAS is also a suitable method of analysis.

### 3.2.5 *PCDDs and PCDFs*

PCDDs (polychlorinated dibenzo-*p*-dioxins) and PCDFs (polychlorinated dibenzofurans) are sampled onto an XAD resin sorbent. This method (NIOSH Method 5515 Issue 2) was developed specifically for polycyclic aromatic hydrocarbons (PAHs) (NIOSH, 1994) and is also used by the USEPA for dioxin sampling. Analysis involves Soxhlet/accelerated Soxhlet extraction sequentially by dichloromethane followed by toluene, and high resolution GC–MS analysis of the toluene fraction for PCDDs and PCDFs.

## 3.3 **Accreditation**

Appropriate accredited sources should be used for reference materials and approved methods adopted. The status of the methods recommended in this guidance is summarised in Table 3.1.

**Table 3.1** Recommended monitoring methods

Determinand	Sampling method	Status	Analytical method
Hydrogen sulphide	Gold film portable analyser		Real time
	Gresham tube or Tedlar bag		In the laboratory. After dilution into range of gold film instrument or by GC-MS with no dilution.
Speciated VOCs	ATD tube	Based on ISO 16017-1	GC-MS using suitable capillary column
Aldehydes	DNPH impregnated silica	USEPA TO-11	HPLC with ultra-violet (UV) detection
Total inorganic arsenic	Activated charcoal/cellulose filter	NIOSH 6001	CV-AAS/ICP-MS
Total mercury	Iodinated charcoal	NIOSH 6009	CV-AAS/ICP-MS
PCDDs and PCDFs	XAD resin column	NIOSH 5515 Issue 2	High resolution GC-MS
Carbon monoxide	Gresham tube/Tedlar bag	BS EN 60567:1993	GC

# On-site measurement

This section identifies – in template format – the purpose, recommended approach, requirements, method, results, known interference/causes of error and alternative methods for on-site measurements.

## 4.1 Preliminary checks

### *Purpose*

To establish which sample point to use and to confirm that the gas sample is not temporarily atypical due to perturbations such as a fire.

### *Recommended approach*

Hand-held instruments to make direct measurements of gas using infra-red and electrochemical cell sensors.

### *Requirements*

- Hand-held bulk gas analyser (this must be pre-calibrated)
- Appropriate connectors for gas taps
- Gresham tube(s) or Tedlar bag(s) and pump
- Hand-held manometer

### *Method*

- i. Select a sampling point that is representative of the gas in the area of study and appropriate for reference sampling. The sampling point should have a good quality, serviceable valve.
- ii. Connect the hand-held gas monitor to the valve using plastic tubing and pump a sample through the instrument to measure the bulk gases (methane, carbon dioxide and oxygen).
- iii. Measure the gas composition at a number of candidate locations and select the location that has the highest methane concentration while remaining typical of the area for detailed trace component sampling.
- iv. Record the carbon monoxide concentration reported by the instrument. However, the electrochemical cell used in most general-purpose instruments is subject to positive interference and is indicative at best. If an elevated carbon

monoxide value is recorded (i.e. >25 ppm), take a sample in a Gresham tube or a Tedlar bag and send it for laboratory gas chromatography to determine the actual carbon monoxide concentration.

- v. Measure the vacuum on the gas line using the manometer. If the vacuum is greater than 10 kPa (0.1 bar), a standard sampling pump cannot reliably withdraw gas from the sampling point. Under these circumstances the sample point will not be appropriate for trace gas sampling or a specialised pump will be required.
- vi. Observe the tendency of the gas sample to form a condensate. Conditions that result in formation of a heavy condensate will make sampling onto sorption tubes more difficult and, in extreme cases, will invalidate the sample. A sampling point where little or no condensation forms is preferred for detailed sampling of trace components.

### *Results*

The bulk gas composition (methane, carbon dioxide, oxygen and, by difference, nitrogen) is recorded as percentage by volume.

The concentration of carbon monoxide reported by the field instrument is recorded and the results of any subsequent laboratory analysis (normally in ppmv) linked to this by sample identification.

The following metadata for the location are recorded:

- location of sampling point
- nature of sampling point
- type of waste in sample area
- age of waste in sample area
- vacuum on gas line
- gas flow, if possible
- tendency to form a condensate
- ambient temperature
- temperature of gas.

### *Known interference and causes of error*

When measuring carbon monoxide concentrations, hand-held instruments are subject to positive interference from a range of components that may be

present in landfill gas. Field measurements must be verified by laboratory analysis.

#### *Alternative methods*

Laboratory analysis by GC with a thermal conductivity detector can be used to quantify the bulk gases as an alternative to the field instrument. However, the results may take 1–2 days and the sample gas composition may change during this time.

## **4.2 Field measurement of hydrogen sulphide**

Hydrogen sulphide is the only priority trace component that can be reliably quantified in the field –though only if the readings are below 50 ppmv. If concentrations are higher, then laboratory measurement is required for accurate quantification. Portable instruments may, however, provide orders of magnitude results.

#### *Purpose*

To measure hydrogen sulphide concentrations using a dedicated field instrument.

#### *Recommended approach*

Direct measurement with a hand-held instrument specific for hydrogen sulphide and not affected by commonly encountered substances such as sulphur dioxide, carbon dioxide, carbon monoxide and moisture. This approach is only viable if hydrogen sulphide concentrations are within the usable range of the instrument.

#### *Requirements*

- Hydrogen sulphide analyser, e.g. Jerome 631-X or similar (this must be pre-calibrated)
- Appropriate connectors for gas taps
- Tedlar bag in a lung box

#### *Method*

A gas sample is drawn into the Tedlar bag from the gas sampling point and held at atmospheric pressure. Gas from this bag is drawn into the instrument to provide the measurement.

#### *Results*

Hydrogen sulphide concentration in ppmv.

#### *Known interference and causes of error*

Gold leaf instruments such as the Jerome 631-X are affected by other sulphides, and particularly the organosulphur compounds found in landfill gas. Because these substances may also take longer to

clear from the instrument, exposure to substantial concentrations of an organosulphur compound may give a persistently high reading even after several purge cycles. In most landfill gases, however, hydrogen sulphide is at a concentration many times that of any other sulphur compound and, for practical purposes, the reading on the instrument can be taken as a measure of hydrogen sulphide.

#### *Alternative methods*

Occupational Safety and Health Administration (OSHA) Method ID 141 (OSHA, online) uses silver nitrate impregnated filters to collect the sample followed by laboratory analysis by pulse polarography. NIOSH Method 6013 (NIOSH, 1994) uses a charcoal trap and extraction with peroxide solution for ion chromatography.

Both methods have a detection limit of 10–20 ppm. Other methods are indicated in Table 7.3 of Technical Guidance Note M9 (Environment Agency, 2000). The Jerome instrument has a useable range of 1 ppbv to 50 ppmv, and is well suited to low concentrations of hydrogen sulphide in landfill gas and above ground ambient air measurements.

If preliminary site data indicate that hydrogen sulphide is likely to be present at >50 ppmv of the gas, use alternative portable general-purpose field instrumentation. However, it is important to confirm the results by laboratory analysis of a representative grab sample.

# Sampling and off-site analytical methods

This section identifies – in template format – the purpose, recommended approach, requirements, method, results, known interference/causes of error, and alternative methods for on-site sampling and subsequent analysis of landfill gas for trace components. The taking of blanks is also included.

## 5.1 Sample collection on-site

### Purpose

To collect representative samples for subsequent analysis off-site. Separate samples are required for:

- speciated VOCs
- aldehydes
- inorganic arsenic
- mercury
- PCDDs and PCDFs.

### Recommended approach

Landfill gas is drawn through solid sorbent material, packed in a tube, by means of a pump or a manually operated metering system. The sorbents selectively extract and concentrate the target analytes, allowing those components that are not adsorbed to pass through.

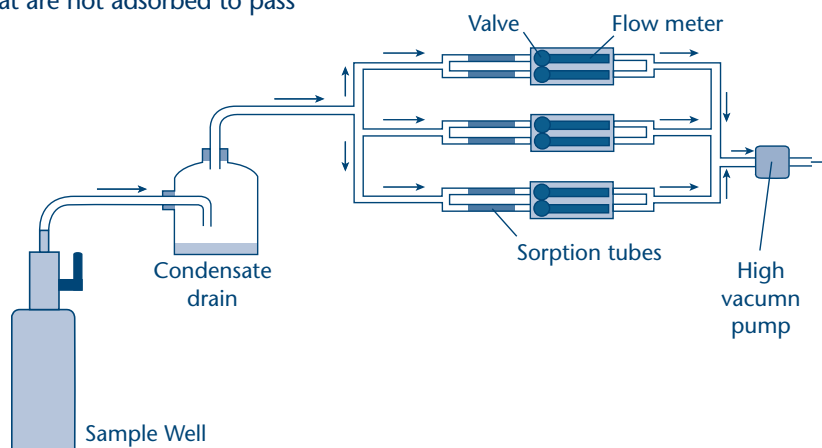


Figure 5.1 | Example sampling assembly

For each determination, duplicate samples are taken and a trip-blank tube (not exposed) is assigned. For speciated VOCs, a 100 ml volume sample is taken unless the trace components are known to be present in low concentrations; in which case, a low volume (100 ml) and a high volume (400 ml) sample will be necessary. For the other methods, a smaller range of analytes is sampled and a single volume sample can be taken (Table 5.1 gives indicative values).

The various samples may be taken simultaneously using a manifold to hold the sorbent tubes and valves to stop flow once the required volume has been drawn. Alternatively, each type of monitoring sample may be drawn separately, although the duplicates should be taken together.

Some sorbent tubes (e.g. for PCDDs) will have been pre-spiked with standards at the laboratory for calibration purposes.

The quantity of sorbent required is proportional to the time sampled, flow rate and the expected concentration of trace components. Too little sorbent may cause the tube to become overloaded, resulting in an underestimate of the total amount of analyte.

Conversely, too much sorbent or too little sample will result in poor limits of detection. It is important to use *a priori* site knowledge and laboratory experience when selecting the most appropriate quantities of sorbent material.

The sorbent recovery efficiency should be known for priority analytes. General advice on sorbent selection for other VOCs is given in ISO 16017-1 (ISO, 2000)

An example sampling assembly is shown in Figure 5.1. As far as is reasonably possible, a minimum of hardware (e.g. valves or connecting tubes) should be used to connect the source of the sample gas to the sorbent tubes. Whatever hardware is used must be constructed from non-sorbing and non-emitting materials.

The exact sampling requirements may vary on a site-specific basis. An example on-site set-up of appropriate equipment is shown in use in Figures 5.2 and 5.3.

#### Universal requirements

- Hand-held bulk gas analyser
- Pumps (e.g. a battery-powered SKC Universal constant flow pump is appropriate for low/medium vacuum; an Air Dimensions Inc. 12V Micro Dia-Vac Model B101 for sampling against high vacuums), or a manually operated metering system
- Condensate drain between the gas tap and the sample tubes
- Gas sample manifolds and connection tubing with low adsorption properties (e.g. Tygon 2275 high purity tubing, plasticiser-free), assembled and leak-tested in the laboratory
- Frame-mounted tube holders (e.g. SKC sorbent tube holders with individual adjustable flows)
- Rotameters on gas lines (e.g. an influx direct reading variable area flowmeter (calibrated) glass

tube and float, stainless steel needle valve)  
20–250 ml/minute for routine sampling

- Moisture trap between the sample tube and rotameters.

#### Requirements for sampling specific trace components

- Uniquely numbered ATD sorption tubes with an inert coating and dual sorbent packing (200 mg each of Tenax TA and Unicarb) for speciated VOCs (see Figure 5.4). Such tubes are commercially available.
- DNPH-coated silica gel sorption tubes for aldehydes (commercially available with a front and back section containing 300 mg and 150 mg of sorbent, respectively)
- Activated charcoal/cellulose filter for arsenic sorption (commercially available with a front and back section containing 100 mg and 50 mg of sorbent, respectively)
- Where necessary iodinated charcoal (Carulite) for mercury sorption (commercially available with a front and back section containing 150 mg and 75 mg of low-background sorbent, respectively, with background levels of mercury consistently less than 1 ng)
- Where necessary amberlite XAD-2 resin packed tube for PCDDs and PCDFs. Simple glass tubes can be self-packed; at least 30 g of sorbent are required to cope with the recommended sampling regime.

Spare tubes should be carried where it is anticipated that condensate formation could result in a sample being abandoned. Table 5.1 gives typical sampling volumes and sampling flow rates for the principal types of sampling tube.

**Table 5.1** | Indicative volumes and flow rates for landfill gas trace component sampling

Determinand	Tube type	Indicative landfill gas sampling volume*	Indicative flow rates (ml/min)
VOC	ATD dual sorbent	0.1 litre (to give high quality quantification with typical variations in trace gas concentrations)**	50
Aldehyde	DNPH silica	1 litre	100
Arsenic	Activated charcoal	5 litres	100
Mercury <sup>#</sup>	Iodinated charcoal	20 litres	100
Dioxin <sup>#</sup>	XAD resin	100 litres	2,000

\* Sample volumes are approximate and are based on the stated capacities of solid sorbents and current experience with UK landfill gas (Environment Agency, 2002b and 2004b).

\*\* The ATD sample volume has a critical bearing on the quality of the results in sampling landfill gas at a site. Where a landfill gas may have a low concentration of trace components, an additional 0.4 litre, high-volume sample may be required.

# Additional components that may be monitored.

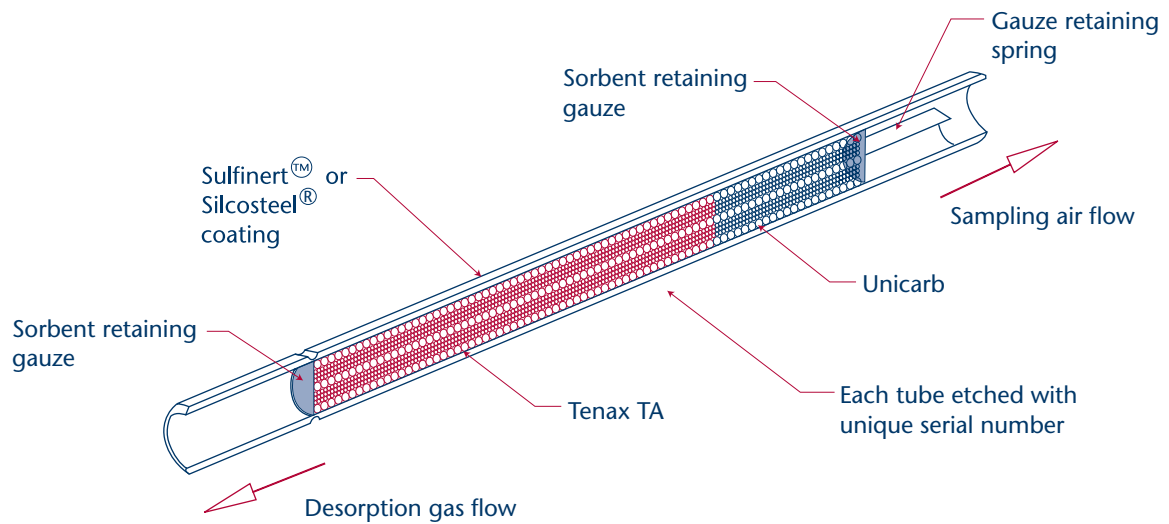




**Figure 5.2** | On-site sampling system connected to a landfill gas well



**Figure 5.3** | Sampling tubes and rotameter assemblies



**Figure 5.4** | ATD packed with dual sorbent



## Method

- i. Use the hand-held gas analyser to re-confirm that the bulk gas composition is suitable for monitoring trace gases.
- ii. Use a hand-held manometer to check that the vacuum on the gas line is less than 10 kPa (0.1 bar) relative to atmospheric pressure. Neither standard battery-powered pumps nor manually operated metering systems can draw reliably at vacuums greater than this. Specialised pumps are required in this instance. If the selected sampling point has a vacuum greater than this, the gas valves or pumps must be adjusted and allowed to re-stabilise before sampling begins. Note the pressure reading. If heavy condensation is observed, consider using insulation or heating to maintain the gas temperature through the lines and tube.
- iii. Set up the sample apparatus with the appropriate packed sorbents, pumps, splitters and tubing. Connect it to the sample point with Tygon tubing (see typical layout in Figure 5.1).
- iv. Leak test the system using the pump to generate a 5 kPa (50 mbar) vacuum and ensuring that the system will hold this for 5 minutes. If this is not achieved, check all connectors and repeat.
- v. Re-check that the pressure is within the acceptable range.
- vi. If pumps are to be used to draw the gas, start these and open the master valve. If all flows are within 30 per cent of expected values, tune the flows and begin sampling. If flows are outside of 30 per cent of expected values, adjust the valves as rapidly as possible. Note the flow rate and sampling time.
- vii. At the end of the sampling sequence, close the master valve and shut off the pumps. Remove the sample tubes from the manifolds and seal them using long-term storage caps. Fit metal screw-type caps with combined PTFE ferrules on the ATD tubes and attach suitable caps to the other types of tube (ISO, 2000).
- viii. Place the tubes in individual zip-lock polythene bags or similar clean, non-emitting containers. Label each bag with the unique number of the tube and relevant sampling details. Do not use solvent-based inks and adhesive labels on the sorbent tubes. Immediately place the samples in appropriate containers for transportation to the laboratory. Such containers are metal cans containing about a third of their volume of scavenging charcoal.

- ix. Recheck the bulk gas composition using the hand-held instrument.

## Results

Volumes of gas samples are calculated from the flow rate and duration of sampling.

## Known interference and causes of error

- Sorption of components on the sample connection tubing – this can be minimised by conditioning the tubing with analytical grade nitrogen and re-use of tubing at the sample points on a particular site.
  - Condensate accumulation (see Figure 5.5) may remove polar components from the gas phase. The preliminary tests should have identified whether this would be a problem at the sampling location, thus allowing avoidance or preventative action to be taken. Formation of condensate in the line can be minimised by:
    - keeping the connection tubing as short as possible;
    - only extracting gas for the short time required in sampling;
    - maintaining the temperature of the gas using insulation or gentle warming.
- Because some substances will desorb thermally from the sorbent, the tube should not be heated above the ambient conditions. It is not practical to use driers because these may selectively remove some components of the gas. Mixing the sample with a dry inert gas during sampling will reduce the condensation, but it is difficult to meter gases accurately in these circumstances and this approach could introduce significant errors. If condensation has formed close to the inlet to the sample tube, water is likely to have interfered with the sorption and the sample is therefore invalid.
- Rotameter errors due to water collecting on the bob – this can be minimised by avoiding condensate formation and/or placing a drying tube between the samples and the rotameters (note that in this position it will not interfere with adsorption of the sample).
  - Rapid fluctuations of gas flow. The preliminary tests should have indicated that this is a problem and the sampling period adjusted to minimise the risk.
  - Tubing faults, particularly breaks and leaks can be minimised by care during sample changes and prior testing for weakness and leaks.

## Blanks

To provide adequate quality assurance/quality control (QA/QC), the following blanks and checks are required.

- To ensure the tubes are not contaminated and have not been affected by environmental factors during the journey, one trip-blank per method per site is transported, unopened, from the beginning to the end of the sampling programme and subsequently analysed. If the blank for a particular trip is higher than routinely found, re-sampling may be required.
- Before the start of sampling programme, the sampling rig (including tubing) is assembled to collect analytical grade nitrogen at typical conditions. The sorption tube is then checked for VOCs to ensure off-gassing from the tubing will not interfere with results during monitoring. Assuming this is satisfactory, then this tubing type is used in the sampling campaign. Fresh tubing from the batch is tested is used at individual sites to prevent contamination being carried over from location to location.



**Figure 5.5** | Condensate in connection tubing during sampling

## Alternative methods

- Portable mass spectrometers with time-of-flight analysis can measure and quantify the organic components. However, these may require significant calibration and referencing for analysis of a complex mixture such as landfill gas.
- Individually packed tubes can be used instead of dual sorbent tubes. These allow greater optimisation for individual compounds, but are

more complicated to set up, have double the analytical costs and require multiple blanks.

- Column packings that require solvent desorption are unacceptable for general use because commonly used desorbents such as carbon disulphide are on the list of priority substances to be monitored in landfill gas.
- Canister or Tedlar bag grab samples, which are quickly concentrated onto an adsorbent, may be used for VOC analysis. If a Tedlar bag sample is not concentrated post-sampling, the analytical method is unlikely to achieve the required detection limit for the priority trace components. During transport to the laboratory in Tedlar bags, some compounds may adsorb irreversibly to these containers and others may decompose. Tedlar bags are only accredited by the USEPA for a small number of the trace components of concern in landfill gas. If these sample collection methods are used, additional blanks must be used to allow sampling losses to be estimated.

## 5.2 Sample handling and storage

Sorbent tubes should be analysed as soon as possible after sampling and preferably within a week. While awaiting analysis, they must be kept in a clean environment, away from laboratory vapours, within the transfer container. If a longer delay is necessary, store the samples under clean refrigerated conditions to minimise migration of analytes within the sorbent tube. This is particularly important with dual sorbent tubes where there is differential sorption on the two types of packing. Re-tighten the screw-type seals as soon as the tubes reach the minimum storage temperature.

Tubes stored under refrigerated conditions must be allowed to re-equilibrate at room temperature before the seals are removed for analysis. This will prevent water from the laboratory atmosphere condensing inside the cold tube and interfering with the subsequent analysis.

## 5.3 Laboratory analysis

### Purpose

To quantify the components adsorbed in the sample tubes.

Each of the analytical methods is dealt with separately below. A recommended minimum detection limit for each trace component is given in Appendix 3. The laboratory undertaking these analyses should have the appropriate United Kingdom Accreditation Service

(UKAS) accreditation, although the regulator recognises that this is not yet available (March 2004).

### 5.3.1 Speciated VOCs by GC–MS

#### *Recommended approach*

Before analysis, pass 2 litres of pure nitrogen through the ATD tube in the same direction as the original sample. This dry nitrogen purge will considerably increase the peak shape and response of the trace components in GC–MS by removing moisture from the tubes.

The sample is thermally desorbed from the solid sorbent and focused on a suitable cold trap. The sample extract is desorbed a second time onto the capillary column of the gas chromatograph, where compounds are separated and identified by mass spectrometry.

#### *Requirements*

ATD unit interfaced to a gas chromatograph–mass spectrometer.

#### *Method*

- i. Fit the ATD unit with a back-flushable focussing trap containing two or more sorbents in series and covering the same retention range as the Tenax and Unicarb (formally Sphero carb) sampling tube. Focussing traps packed with Tenax (front) and Unicarb (back) are suitable. Equivalent sorbent combinations may also be used provided it has been demonstrated that active sites on the sorbent do not cause degradation of priority compounds during the analytical thermal desorption process.
- ii. Minimise the inlet and outlet splits to maximise the sensitivity of the system. Install a thick film capillary column suitable for VOCs in the gas chromatograph and operate the mass spectrometer in scan mode.
- iii. Calibrate the system with standards containing as many of the target compounds as possible, loaded onto the sorbent tube from the gas or liquid phase as described in ISO 16017-1 (ISO, 2000). These standards should be loaded at a number of different concentrations to obtain multi-level calibration for each compound of interest.
- iv. Identify target compounds (the priority odorous and health VOCs) by their mass spectra and retention time. Where other significant peaks correspond to basic analytes in standard analytical suites (e.g. C1–C5 alkanes and BTEX), these should be assigned. Judgement should be used to assess whether identification (with the aid of mass

spectral libraries) of any other significant peaks present is justified.

#### *Results*

Express in  $\mu\text{g}/\text{m}^3$  of gas as sampled.

#### *Known interference and causes of error*

The assignment and quantification can only be assured if the instrument is calibrated with the nominated compound in the full gas mixture. Although calibration is normally with a representative range of gases, it is impractical to include all the target compounds and the report should specify which compounds have been used as calibration standards.

Significant peaks not included in the standard list should be identified with the aid of mass spectral libraries. There may be ambiguity in assigning peaks to compounds not on the priority list.

The results are normally expressed with precautionary statements regarding assignment and quantification.

Sample adsorption capacity of the ATD sorbents is affected by variables such as moisture and temperature. Normal recommended 'safe' sampling volumes may thus be too high for landfill gas, leading to breakthrough and under-reporting of concentrations for some substances. If the ATD sorbents are overloaded, the weakly adsorbed compounds that would normally be held on the Tenax beads will leak through onto the stronger adsorbent. These will subsequently not desorb and thus will be under-reported.

The relatively low sample volume (0.1 litre) of samples recommended for typical operation in this method minimises the risk of breakthrough and/or overloading of sorbent during sample collection. Migration of analytes within the sample tube can be prevented by minimising storage times between sampling and analysis, and by using refrigerated storage conditions.

The GC–MS system may also become overloaded with high levels of VOCs such that the mass quantification becomes non-linear for a target compound or leads to the signal for the target compound being swamped by a non-target compound. The risk of this is minimised by following the recommended sampling volumes for typical landfill gas.

Butadiene is retained less well than other priority substances on the dual sorbent column. It will thus have a poor detection limit compared with other species and may suffer interference from other butenes and butanes. Hence, the reported values

should be seen as semi-quantitative and a more specific investigation may be required if high concentrations are indicated.

#### *Alternative methods*

- Time-of-flight mass spectroscopy on full sample.
- Use of dual detectors can extend the GC technique. For instance, splitting the gas chromatogram output to pass through both a mass spectrometer and flame ionisation detector allows identification of the peak by MS and quantification by flame ionisation detection (FID). However, significant problems with the identification of analytes are likely to arise when using FID to analyse such complex chromatograms.

### **5.3.2 Aldehydes as their DNPH derivative**

#### *Recommended approach*

Carbonyl compounds in the gas are captured by reaction with the DNPH coating on a silica gel. This solid phase holds the resulting mixture of derivitised aldehydes during sampling. These products are subsequently desorbed and the derivatives, which now have a strong UV chromophore, are analysed by HPLC to distinguish the different carbonyl compounds. This method is described in NIOSH Method 2539 (NIOSH, 1994).

#### *Requirements*

HPLC with UV detector

#### *Method*

Desorb the sample tubes with acetonitrile and make up to volume. The sample extracts should be analysed using a chromatogram capable of gradient elution. Typically, separation is achieved with an octadecyl phase column under reversed-phase conditions. The carbonyl derivatives are detected at 365 nm, following the USEPA Method TO-5 (USEPA, online).

The analytes are identified on the basis of retention time and are quantified against pre-derivitised standard solutions.

#### *Results*

Express in  $\mu\text{g}/\text{m}^3$  of gas as sampled.

#### *Known interference and causes of error*

High ozone concentrations will affect the sample, but these are unlikely in landfill gas.

Other aldehydes and ketones (particularly acetone) will be adsorbed by these tubes and may result in

overloading of the tubes well below the expected capacity for the priority aldehydes.

#### *Alternative methods*

- An alternative is NIOSH Method 2541 (NIOSH, 1994). Sampling is carried out with XAD-2 treated with 2-(hydroxymethyl) piperidine. The solvent extract is analysed by GC-MS.

### **5.5.3 Inorganic arsenic by ICP-MS**

#### *Recommended approach*

The inorganic arsenic adsorbed on the activated charcoal/cellulose filter tube is extracted with nitric acid and quantified by ICP-MS.

#### *Requirements*

Ultrasonic bath, ICP-MS

#### *Method*

The contents of the activated charcoal/cellulose filter tube are extracted using 0.01M nitric acid in an ultrasonic bath for 1 hour. The resulting solutions are measured for arsenic using ICP-MS, calibrated using the method of standard additions. Internal standards are added to monitor and correct for instrumental drift. USEPA Method 6020 CLP-M (Version 3.4 Special Analytical Services) outlines analysis by ICP-MS and includes detailed instructions in the use of internal standards (USEPA online). The determination of total arsenic is by NIOSH Method 6001 Issue 2 (NIOSH, 1994).

#### *Results*

Results from the measurement are expressed as total ng As per tube and then converted to  $\mu\text{g}/\text{m}^3$  of gas as sampled.

#### *Known interference and causes of error*

A potential polyatomic interference at  $^{75}\text{As}$  is caused by  $^{40}\text{Ar}^{35}\text{Cl}$ .

#### *Alternative methods*

- The OSHA method (OSHA, online) uses a mixed cellulose ester filter that is digested in nitric acid with a nickel stabiliser and analysed by atomic absorption spectroscopy (AAS) with a heated graphite furnace atomiser.
- NIOSH Method 5022 (NIOSH, 1994) uses a polytetrafluoroethylene (PTFE) backed filter membrane and extraction with borate-carbonate buffer for separation by ion chromatography and processing through an arsine generator connected to a mass spectrometer. This method can quantify organic arsenic compounds.

### 5.3.4 Mercury by ICP–MS

#### Recommended approach

The mercury adsorbed on the iodinated charcoal tube is extracted with hot sulphuric acid, hydrogen peroxide and nitric acid, and quantified by ICP–MS.

#### Requirements

Microwave digestion system, ICP–MS

#### Method

The contents of the iodinated charcoal tube are transferred to a microwave vessel. A mixture of sulphuric acid, hydrogen peroxide and nitric acid is added and the samples are extracted under high temperature and pressure in a microwave system. The resulting solutions are measured for mercury using ICP–MS, calibrated using the method of standard additions. Internal standards are added to monitor and correct for instrumental drift. USEPA Method 6020 CLP-M (Version 3.4 SAS) outlines analysis by ICP–MS and includes detailed instructions on the use of internal standards (USEPA online).

#### Results

Results from the measurement are expressed as total ng Hg per tube and then converted to  $\mu\text{g}/\text{m}^3$  of gas as sampled.

#### Known interference and causes of error

None known.

#### Alternative methods

- NIOSH Method 6009 (NIOSH, 1994) samples onto a Hopcalite sorbent tube, which is extracted into nitric acid and hydrochloric acid at room temperature. The resulting solutions are measured by CV–AAS. This method determines elemental mercury.
- OSHA Method ID-145 (OSHA, online) describes an ester filter that is extracted in nitric and sulphuric acids followed by the addition of potassium permanganate and hydroxylamine hydrochloride. The resulting extracts are measured by CV–AAS.

### 5.3.5 PCDDs and PCDFs

#### Recommended approach

The PCDDs and PCDFs are adsorbed onto Amberlite XAD-2 resin (an XAD resin trap). The resin is extracted with solvent and the extract analysed by gas chromatography with detection by high resolution mass spectrometry (GC–HRMS).

#### Requirements

Established extraction and clean up technique

Gas chromatograph with high-resolution mass spectrometer.

#### Method

The dried XAD resin is spiked with a selection of  $^{13}\text{C}$  labelled dioxin/furan isomers before being solvent extracted (Soxhlet or accelerant solvent extraction). The extract is concentrated before undergoing column clean-up. The concentrated extract is analysed by GC–HRMS alongside standards and blanks with a typical minimum resolution of 10,000. Calibration is achieved using a relative response standard containing known amounts of native and  $^{13}\text{C}$  dioxin/furan isomers. This sample preparation and measurement should be carried out in accordance with BS EN 1948 Parts 2 and 3 (BSI, 1997).

Identification of individual isomers is achieved by a combination of GC retention times and mass spectra. Identities of isomers significantly above the limit of detection are confirmed by isotope ratio.

#### Results

Express in  $\mu\text{g}/\text{m}^3$  of gas as sampled.

The amount present should be calculated as an I-TEQ (International Toxicity Equivalent Factor) value according to the NATO/CCMS scheme, which takes into account the relative toxicities of the various isomers.

#### Known interference and causes of error

None known.

#### Alternative methods

None



# Errors and uncertainty

## 6.1 Overview

The guidance adopts a pragmatic approach that uses a limited number of techniques to measure the more significant trace compounds that may be present in landfill gas. Monitoring a complex, variable mixture by field sampling will involve some compromises over specificity and detection limits. However, the guidance provided here will permit screening of all the substances of concern in a typical landfill gas to a level that is sufficient for the purposes stated in Section 1.

This guidance is intended to give an estimate of a broad range of priority substances over a range of environmental conditions. If subsequent risk assessment demonstrates that a sub-set of these trace components is potentially of concern, targeted monitoring methods should be used to quantify individual substances.

The errors and uncertainty in implementing this guidance can be divided into two broad categories:

- those relating to sampling
- those relating to analysis.

Of these, sampling errors are normally the main cause of uncertainty.

## 6.2 Sampling errors

The uncertainty in taking a sample that is representative of the source term gas falls into three categories:

- spatial uncertainty
- temporal variability
- sampling point errors.

The guidance recommends taking a sample from the main gas flow from the landfill because this is most representative of the gas collected from the area under consideration. If the collection system is ineffective, then bulk gas containing trace components may be emitted from atypical zones of the site.

Where the gas is extracted through several lines or the sampling cannot be undertaken on the main line for physical reasons (e.g. too much vacuum), then several samples will have been taken and analysed. The overall composition of gas for the site will be estimated by apportioning these data to the different zones. There is inevitably additional uncertainty in the estimating relative flows and differential loss from these different sources.

Hence, if the composition of the source gas is derived from several samples or if the site's gas collection efficiency is much lower than that stated in *Guidance on the management of landfill gas* (Environment Agency, 2004a), these factors should be noted as a potential source of error.

The analysed sample can only be truly representative of the gas composition at the time of sampling (generally an annual event). The composition of the gas collected will vary over time as changes occur in the overall gas management and the condition of waste. The degree of temporal variability for a particular site will be revealed as records of trace gas analysis build up.

Additional trace gas composition monitoring should be undertaken if there are major changes in the source term gas such as substantial changes in the volume of gas collected, the bulk gas composition or the leachate head. The data from the latest sampling on trace components should be compared with any earlier data and the significance of any differences noted on the reporting form.

The gas in a pipeline network will not be perfectly mixed. Sample points in landfill gas pipelines are generally installed in the wall of the pipe and thus a sample will be drawn from a stratified layer near this boundary. It is not practical to undertake isokinetic sampling as recommended for the monitoring of emissions from stacks. However, some of precautions adopted in stack monitoring can be followed such as avoiding sampling at bends or dips in the pipe, or close to process zones. It is recommended that, wherever possible, samples are not taken immediately downstream of knock-out pots where gases may have partitioned into water and entrained droplets.

Controlling and measuring the volume of a field sample is a potential source of error. The pipework in the sampling train must be leak-free to prevent air rather than gas being metered through the sorption tube. The rotameter must be calibrated and moisture-free to minimise errors from measuring the sample volume drawn through the sorption tubes.

Additional uncertainty may be introduced in particularly complex mixtures where there could be unpredictable competition and interference during the sorption process. Inconsistencies in the data from the two sampling volumes may highlight these effects. This uncertainty is minimised by using the lowest sample volume consistent with achieving the necessary detection limit and by selecting the widest possible range of calibration gases.

### **6.3 Analytical errors**

The errors in analysing the sample can generally be estimated in the laboratory. Calibration standard mixtures and pre-spiked tubes allow an estimate to be made of quantification and recovery by each method. These analytical errors should be reported with the results.





# Data reporting

## 7.1 Standard reports

Knowledge of trace gas composition at a specific landfill site should be used to inform the Gas Management Plan. Once trace gas data have been derived, they must be summarised in a way that allows meaningful interpretation and use as a source term in risk assessment or the Pollution Inventory. The portion of the site for which the trace gas sample is a representative source term should be clearly identified. An example report format, suitable for submitting to the regulator, is provided in Appendix 4.

Substances that are positively identified should be reported in the units specified in Appendix 4 (typically in  $\mu\text{g}/\text{m}^3$  without normalising for moisture, temperature and pressure). Any priority trace components that are not positively identified must be reported as being present at below their respective detection limits.

Data must be assessed for consistency with previously reported data and other sources of information as identified in Section 2.1. The report should highlight instances where variation from normal procedure has been necessary and should inform future monitoring requirements.

## 7.2 Inter-comparison of data

The methods in this guidance may be used to characterise the gas that is the input to a landfill gas engine or flare. However, VOC emissions from the engine or flare should be monitored in line with Technical Guidance Note M2 (Environment Agency, 2002c) and the specific guidance on flares and engine emissions. These use the standard methods developed for stack monitoring and so may not necessarily be directly comparable with the source term monitoring methods for trace components used here. Estimates of mass balance and destruction efficiency during combustion of landfill gas should take account of these potential differences.

## Appendix 1:

# Conversion factors

(a) Conversion of reported mg per m<sup>3</sup> @ STP into ppmv:

$$mg.m^{-3} = ppmv \times \frac{Mw}{22.4}$$

Where:

Mw = molecular weight

STP is a temperature of 273K and pressure of 101.3 kPa.

To convert the concentration as measured at a temperature (T) in degrees K to the normalised concentration at 273K, multiply by the factor T/273.

To convert the concentration as measured at a pressure (P) in kPa to the normalised concentration at 101.3 kPa, multiply by the factor 101.3/P.

Both temperature and pressure relate to the point at which the sample volume was metered.

(b) Conversion of reported mg per m<sup>3</sup> @ normal room temperature and pressure into ppmv:

$$mg.m^{-3} = ppmv \times \frac{Mw}{22.06}$$

Where:

Mw = molecular weight

Normal room temperature and pressure are 293K and 101.3 kPa.

To convert the concentration as measured at a temperature (T) in degrees K to the normalised concentration at 293K, multiply by the factor T/293.

To convert the concentration as measured at a pressure (P) in kPa to the normalised concentration at 101.3 kPa, multiply by the factor 101.3/P.

Both temperature and pressure relate to the point at which the sample volume was metered.



## Appendix 2:

# Introduction to analytical methods

The main analytical methods are outlined below. More detailed descriptions are given in Technical Guidance Note M9 (Environment Agency, 2000).

### CV-AAS

Cold vapour atomic absorption spectroscopy involves the reduction of mercury to its zero oxidation state. A gas-liquid separator is used to release a stream of mercury vapour into an argon carrier gas flowing to an absorbance cell for measurement. The absorbance is measured at known wavelengths and the extent of absorbance is concentration dependant.

### GC-MS

In gas chromatography, a mixture is separated in the vapour phase through adsorption, solubility or chemical bonding. The carrier gas is the mobile phase and the stationary phase is typically a solid particle onto which differential sorption takes place. The separated fractions can be detected by mass spectrometry, which is an analytical technique based on the formation of ions by a variety of methods, e.g. electron impact fragmentation.

### HPLC

High performance liquid chromatography is a high pressure variation of conventional packed-column liquid chromatography. The main application is the analysis of less volatile compounds in liquid samples. Separation is achieved through differential sorption from a mobile liquid phase onto small particles of a solid phase material. The separated fractions can be detected by a variety of methods, e.g. ultra-violet/visible absorption.

### ICP-MS

Inductively coupled plasma mass spectrometry is a multi-element technique for the determination of ultra-trace levels of analytes in a variety of sample matrices. The argon ICP generates singly charged positive ions from the aspirated sample. These ions are separated on their mass to charge ratio by a quadrupole mass spectrometer and detected.

### In situ derivatisation (as in the sampling of aldehydes with DNPH tubes)

This typically involves the simultaneous collection and reaction of the analyte to a non-reactive stable derivative, which can be detected easily using standard analytical techniques.

## Appendix 3:

# Recommended minimum detection limits

Trace component	Recommended detection limit	Units
1,1-dichloroethane	60	$\mu\text{g}/\text{m}^3$
1,1-dichloroethene	90	$\mu\text{g}/\text{m}^3$
1,2-dichloroethene	70	$\mu\text{g}/\text{m}^3$
1,3-butadiene	70	$\mu\text{g}/\text{m}^3$
1-butanethiol	300	$\mu\text{g}/\text{m}^3$
1-pentene	160	$\mu\text{g}/\text{m}^3$
1-propanethiol	200	$\mu\text{g}/\text{m}^3$
2-butoxyl ethanol	200	$\mu\text{g}/\text{m}^3$
Arsenic (as As)	0.04	$\mu\text{g}/\text{m}^3$
Benzene	30	$\mu\text{g}/\text{m}^3$
Butyric acid	400	$\mu\text{g}/\text{m}^3$
Carbon disulphide	100	$\mu\text{g}/\text{m}^3$
Carbon monoxide	1	ppmv
Chloroethane	120	$\mu\text{g}/\text{m}^3$
Chloroethene (vinyl chloride)	300	$\mu\text{g}/\text{m}^3$
Dimethyl disulphide	100	$\mu\text{g}/\text{m}^3$
Dimethyl sulphide	110	$\mu\text{g}/\text{m}^3$
Ethanal (acetaldehyde)	12	$\mu\text{g}/\text{m}^3$
Ethanethiol	300	$\mu\text{g}/\text{m}^3$
Ethyl butyrate	90	$\mu\text{g}/\text{m}^3$
Furan (1,4-epoxy-1,3-butadiene)	70	$\mu\text{g}/\text{m}^3$
Hydrogen sulphide	150	$\mu\text{g}/\text{m}^3$
Mercury	0.5	$\mu\text{g}/\text{m}^3$
Methanal (formaldehyde)	12	$\mu\text{g}/\text{m}^3$
Methanethiol	1,000	$\mu\text{g}/\text{m}^3$
PCDDs and PCDFs	0.1	$\text{ng}/\text{m}^3$ I-TEQ
Tetrachloromethane	70	$\mu\text{g}/\text{m}^3$
Trichloroethene	40	$\mu\text{g}/\text{m}^3$



## Appendix 4:

# Example report format

### A. Site information

Sample point details	Enter details	Sample point details	Enter details
Date		Site	
Ambient temperature		Atmospheric pressure	
Monitoring organisation(s)		Analytical laboratory	
Location of sampling point		Area of influence of collection system sampled	
Type of sample point		Temperature of gas	
Vacuum on sample point		Type of waste	
		Age of waste (if known)	
Status of gas system		Other	

### B. Preliminary checks and field measurements

Parameter	Concentration	Units	Comments
Methane		%	
Carbon dioxide		%	
Oxygen		%	
Nitrogen		%	
Hydrogen sulphide (field value)		ppmv	
Carbon monoxide (field value)		ppmv	

### C. Laboratory analysis results

Trace component	CAS Number	Concentration in landfill gas sample	Units	Recommended method (Y/N)*	UKAS (Y/N)
1,1-dichloroethane	75-34-3		µg/m <sup>3</sup>		
1,1-dichloroethene	75-35-4		µg/m <sup>3</sup>		
1,2-dichloroethene	540-59-0		µg/m <sup>3</sup>		
1,3-butadiene	106-99-0		µg/m <sup>3</sup>		
1-butanethiol	109-79-5		µg/m <sup>3</sup>		
1-pentene	109-67-1		µg/m <sup>3</sup>		
1-propanethiol	107-03-9		µg/m <sup>3</sup>		
2-butoxyl ethanol	111-76-2		µg/m <sup>3</sup>		
Arsenic (as As)	7440-38-2		µg/m <sup>3</sup>		
Benzene	71-43-2		µg/m <sup>3</sup>		
Butyric acid	107-92-6		µg/m <sup>3</sup>		
Carbon disulphide	75-15-0		µg/m <sup>3</sup>		
Chloroethane	75-00-3		µg/m <sup>3</sup>		
Chloroethene (vinyl chloride)	75-01-4		µg/m <sup>3</sup>		
Dimethyl disulphide	624-92-0		µg/m <sup>3</sup>		
Dimethyl sulphide	75-18-3		µg/m <sup>3</sup>		
Ethanal (acetaldehyde)	75-07-0		µg/m <sup>3</sup>		
Ethanethiol	75-08-1		µg/m <sup>3</sup>		
Ethyl butyrate	105-54-4		µg/m <sup>3</sup>		
Furan (1,4-epoxy-1,3-butadiene)	110-00-9		µg/m <sup>3</sup>		
Hydrogen sulphide	7783-06-4		µg/m <sup>3</sup>		
Methanal (formaldehyde)	50-00-0		µg/m <sup>3</sup>		
Methanethiol	74-93-1		µg/m <sup>3</sup>		
Tetrachloromethane	56-23-5		µg/m <sup>3</sup>		
Trichloroethene	79-01-6		µg/m <sup>3</sup>		
<i>Additional site-specific</i>					
Mercury (as Hg)	7439-97-6		µg/m <sup>3</sup>		
PCDDs and PCDFs	N/A		ng/m <sup>3</sup> I-TEQ		
Carbon monoxide	N/A		ppmv		
[Others]					

\* State method and provide justification if not by recommended method.

# Glossary

## **Adsorption**

The uptake of a substance from the mobile phase to a surface.

## **ATD tubes**

Automated thermal desorption tubes used for sampling from the gas phase.

## **Bulk gas**

Gases drawn from the landfill at percentage concentrations.

## **Chromophore**

A chemical group that strongly absorbs light at a particular wavelength.

## **Condensate**

The condensed water and associated soluble compounds derived from the landfill gas stream as the gas cools.

## **Desorption**

The release of a substance from a surface to the mobile phase.

## **DNPB**

Dinitrophenylhydrazine – reacts with aldehydes and ketones to form a derivative that absorbs UV and visible light.

## **Fractionation**

The separation of a mixture of chemically related or otherwise similar components into constituent fractions with different properties.

## **GC**

Gas chromatography. The process whereby components in a gas mixture are separated by volatilising the sample into a carrier gas stream, which is then passed through a liquid or solid stationary phase. The components of the mixture interact differentially with the stationary phase and appear separately in the effluent where they are detected and measured.

## **Gresham Tube**

A proprietary design of sampling equipment that can be used to collect gas samples. It comprises an empty metal tube, valves and hand pump.

## **Labile**

Easily degraded by chemical reaction

## **Landfill gas**

All the gases generated from landfilled waste.

## **Manometer**

A simple device for measuring gas pressure relative to atmospheric pressure.

## **Metadata**

Secondary data or supplementary information relevant to the interpretation of primary data. Includes supplementary parameters such as physical data.

## **Monitoring**

A continuous or regular periodic check to determine the ongoing nature of the potential hazard, conditions along environmental pathways and the environmental impacts of landfill operations to ensure the landfill is performing according to design. The general definition of monitoring includes measurements undertaken for compliance purposes and those undertaken to assess landfill performance.

## **Non-polar compounds**

Compounds lacking significant dielectric constant (see also polar compounds).

## **Occupational Exposure Limits**

OELs are concentrations of hazardous substances in the air, averaged over a specified period of time (referred to as a time-weighted average). There are two types of occupational exposure limit – Maximum Exposure Limits and Occupational Exposure Standards

## **PAH**

Polycyclic aromatic hydrocarbons – a group of chemical compounds where the atoms form more than one delocalised aromatic ring structure.

## **Polar compounds**

Compounds with a significant dielectric constant (permanent dipole moment) (see also non-polar compounds).

## **Polarography**

A technique for analysing ions in solution.

## **Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans**

Polychlorinated dioxins and polychlorinated furans are a wide group of heterocyclic organic compounds. PCDDs and PCDFs are a group of 210 similar chlorinated aromatic compounds of which 17 are recognised as highly toxic. The group is referred to colloquially as dioxins and furans.

## **Raw gas**

The immediate gaseous product from microbial degradation within the landfill.



**Rotameter**

An instrument for measuring gas flow.

**Speciation**

Identification of individual components.

**STP**

Standard temperature and pressure. Used to normalise gas data to 273K (i.e. 0°C), and 101.3 kPa (i.e. one atmosphere)

**Tedlar bag**

A bag constructed of inert material (polyvinyl fluoride) for taking gaseous grab samples.

**Trace component**

A landfill gas component typically encountered at a ppm concentration and constituting less than 1 per cent by volume.

**XAD**

A proprietary ion exchanger comprising beads of cross-linked polystyrene.

# Acronyms

<b>AAS</b>	Atomic absorption spectroscopy	<b>STP</b>	Standard temperature and pressure
<b>ATD</b>	Automated thermal desorption	<b>UKAS</b>	United Kingdom Accreditation Service
<b>BSI</b>	British Standards Institution	<b>USEPA</b>	United States Environmental Protection Agency
<b>BTEX</b>	Benzene, toluene, ethyl benzene and xylene	<b>UV</b>	Ultra-violet
<b>CAS</b>	Chemical Abstracts System	<b>VOC</b>	Volatile organic compound
<b>CV-AAS</b>	Cold vapour atomic absorption spectroscopy		
<b>DNPH</b>	Dinitrophenylhydrazine		
<b>FID</b>	Flame ionisation detection		
<b>GC</b>	Gas chromatography		
<b>GC-FID</b>	Gas chromatography with flame ionisation detection		
<b>GC-HRMS</b>	Gas Chromatography with detection by high resolution mass spectrometry	<b>I-TEQ</b>	International Toxicity Equivalent – a normalised expression of concentration for PCDDs and PCDFs
<b>GC-MS</b>	Gas Chromatography with detection by mass spectrometry	<b>ppbv</b>	parts per billion by volume – an expression of concentration. 1 ppb is a thousandth of a ppm.
<b>HPLC</b>	High performance liquid chromatography	<b>ppmv</b>	parts per million by volume – an expression of concentration. 10,000 ppm v/v equates to 1 per cent gas at STP by volume.
<b>HSE</b>	Health and Safety Executive	<b>µg/m<sup>3</sup></b>	Micrograms of gaseous substance in one cubic metre of total gas. The temperature, pressure and percentage moisture saturation of the total gas must be stated to permit inter-comparison from different sources.
<b>ICP-MS</b>	Inductively coupled plasma mass spectrometry		
<b>ISO</b>	International Standards Organisation		
<b>MS</b>	Mass spectrometry		
<b>NATO/CCMS</b>	North Atlantic Treaty Organisation's Committee on the Challenges of Modern Society		
<b>NIOSH</b>	National Institute of Occupational Safety and Health		
<b>OSHA</b>	Occupational Safety and Health Administration		
<b>PAH</b>	Polycyclic aromatic hydrocarbon		
<b>PCDD</b>	Polychlorinated dibenzo- <i>p</i> -dioxin		
<b>PCDF</b>	Polychlorinated dibenzo furan		
<b>PPC</b>	Pollution Prevention and Control		
<b>PTFE</b>	Polytetrafluoroethylene		
<b>QA</b>	Quality assurance		
<b>QC</b>	Quality control		

## Units of measurement

<b>I-TEQ</b>	International Toxicity Equivalent – a normalised expression of concentration for PCDDs and PCDFs
<b>ppbv</b>	parts per billion by volume – an expression of concentration. 1 ppb is a thousandth of a ppm.
<b>ppmv</b>	parts per million by volume – an expression of concentration. 10,000 ppm v/v equates to 1 per cent gas at STP by volume.
<b>µg/m<sup>3</sup></b>	Micrograms of gaseous substance in one cubic metre of total gas. The temperature, pressure and percentage moisture saturation of the total gas must be stated to permit inter-comparison from different sources.

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