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# Guidance for monitoring trace components in landfill gas

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# Foreword

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

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This second edition of LFTGN04 was the result of a collaborative review involving the Environment Agency, SEPA and representatives of the landfill gas industry forming a sub-group of the Environment Agency and Environmental Services Association Landfill Regulation Group. The authors would like to thank all parties who contributed to this review.

**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, 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.

[Writer of foreword] [Writer's job title]

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# EXECUTIVE SUMMARY

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

In particular, the data is used:

- to develop source term values for a site-specific risk assessment of gaseous emissions and the resulting Gas Management Plan;
- in developing 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 monitor in landfill gas, with their recommended sampling and analytical methods.

Trace component	CAS number	Sampling method	Analytical method
1,1-dichloroethane	75-34-3	Dual solid sorbent	ATD-GC-MS
1,2-dichloroethane	107-06-2	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-butoxyethanol	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
Dichloromethane	75-09-2	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	Portable instrument
Methanal (formaldehyde)	50-00-0	Reactive sorbent	HPLC
Methanethiol	74-93-1	Dual solid sorbent	ATD-GC-MS
Styrene	100-42-5	Dual solid sorbent	ATD-GC-MS
Tetrachloromethane	56-23-5	Dual solid sorbent	ATD-GC-MS
Toluene	108-88-3	Dual solid sorbent	ATD-GC-MS
Trichloroethene	79-01-6	Dual solid sorbent	ATD-GC-MS

\*\* Additional specific monitoring required if chloroethene concentration exceeds 78 mg/m<sup>3</sup> during routine analysis.

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
1,1,2,2-tetrachloroethane	Tetrachloroethene	Mercury (as Hg) <sup>1</sup>
Carbon monoxide <sup>3</sup>	Trimethylbenzene	PCDDs, PCDFs <sup>2</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

### Method

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.

Carry out the monitoring of priority trace components out annually as a minimum, but you can do this more frequently subject to site-specific circumstances such as significant changes to the gas management system, high concentrations of particular trace compounds or waste composition. It is essential you:

- select the sampling point(s) so the gas sampled is representative of the gas collected at the site, or is representative of a particular area of the site under investigation;
- meter the gas sample to provide an accurate value for the sample volume;
- take precautions to avoid moisture or condensate entering the sampling system;
- take care to prevent contamination or degradation of the sample during transfer to the laboratory and preparation for analysis;
- report any priority trace components that are not positively identified, using the recommended methods as being present at below their respective detection limits. (See [Appendix 3](#) for the recommended detection limits);
- report any other trace components other than the priority components that are detected.

Once you have derived the trace gas data, you must summarise it in a way that allows meaningful interpretation and use as a source term in risk assessment or the Pollution Inventory.

You must clearly identify the portion of the site for which the trace gas sample is a representative source term. To aid this process, use the example report format suitable for submitting to the regulator in [Appendix 4](#). You must assess the data 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.

# 1 Introduction

## 1.1 Purpose of this technical guidance

This guidance is for use in assessing the monitoring of trace components in gas at permitted 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 collecting data on the concentration of trace components in a valid, transparent and consistent manner.

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 developing source term values for a site-specific risk assessment of gaseous emissions and the resulting Gas Management Plan;
- in developing 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, 2010a).

The full series comprises:

- Guidance for monitoring trace components in landfill gas
- 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 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 landfill emissions;
- local authorities concerned with landfill gas emissions.

For closed sites, where a waste management licence became an Environmental Permit, we will require the permit holder to produce a landfill gas emissions review. This should be based on developing a risk screening/conceptual model of gas management for the site. Where this review identifies unacceptable site-specific risks from landfill gas, the permit holder prepares an emissions improvement programme 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.

## 1.2 Structure of this document

Section 1: provides information on the context of this guidance and identifies priority trace components.

Section 2: discusses a number of general monitoring issues to be considered before sampling on-site.

Section 3: identifies our 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.

See the [appendices](#) for example report formats, recommended detection limits, and an introduction to analytical methodologies. 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

The Landfill Directive 1999/31/EC specifies the technical standards covering aspects of the construction, operation, monitoring, closure and surrender of landfills. The Directive is applied in England and Wales through Schedule 10 of The Environmental Permitting (England and Wales) 2007 Regulations.

Landfill Directive 1999/31/EC, requires the following gas control measures:

- take appropriate measures in order to control the accumulation and migration of landfill gas;
- collect landfill gas from all landfills receiving biodegradable waste. The 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;
- flare landfill gas that cannot be used to produce energy.

In accordance with Article 12 of the Landfill Directive, 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. Quantifying trace component concentrations will help determine the releases in relation to Pollution Inventory reporting thresholds.

#### **GasSim model**

The GasSimLite model (<http://www.gassim.co.uk>) has been widely used by operators to create a ready-formatted Pollution Inventory return for a site. However this is based on an older version of the GasSim model. Cross checking GasSimLite against the latest version of GasSim 2 shows a better estimate of the Pollution Inventory returns using GasSim 2. Use the GasSim 2 PI module for the annual PI reporting.

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 GasSim2 model (Environment Agency, 2002a) may be used for preliminary assessments. GasSim2 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 we consider detailed risk assessments are necessary, site-specific assessments will require actual or projected trace component profiles based on field data.

#### **Strategy**

Our strategy for landfill gas control is based on regulating the outcomes and emissions associated with landfill gas. A fundamental part of this process is quantifying landfill gas trace components. Detailed guidance on managing landfill gas is available (Environment Agency, 2010a).

The timely installation of active landfill gas collection systems at modern engineered landfills ensures only a small proportion of the raw gas escapes 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 use or treatment. This guidance deals with measuring the concentration of particular components in the raw gas (that is, 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.

### 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 one 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 (such as, through stress) may be more significant than that of the bulk gases.

Under certain circumstances, the concentration of trace components may be greater than one per cent, for example, 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 gases (Environment Agency, 2002b). These include:

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

However, many of these substances are benign or occur at such low concentrations they will have very little impact on human health, the environment or amenity. Volatile substances contained in the waste (such as 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).

#### Ranking system

We have 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). We compiled a list of priority substances with 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 from this ranking. We recommended a suite of sampling and analytical methods that can be used to monitor these significant trace components in typical landfill gas as a result.

Since we issued the first version of this guidance, several new practices have begun to divert biodegradable wastes away from landfills, instead favouring waste segregation and treatment. The changing composition of wastes going to landfill has the potential to significantly change the gas generated in landfills.

Some landfills are now accepting wastes which contain significantly higher proportions of inorganic or non-cellulosic material. This type of waste produces lower total volumes of gaseous emissions than traditional municipal solid wastes (MSW).

#### Data

The data we used to originally identify the priority trace components of landfill gas was heavily influenced by analytical data from older co-disposal landfills. This guidance includes recommendations based on recent on-site gas samples. There are also specific amendments to the priority list. They are:

- 1,2-dichloroethane
- chloroethene (vinyl chloride)
- Styrene

### **1.3.3 Guidance for inorganic landfills**

Recent research has been undertaken into eight non-inert landfill cells receiving mostly 'inorganic' or 'low biodegradable carbon' waste. It has identified potential chemical and microbial reactions that may generate gaseous products in landfills low in biodegradable carbon (Environment Agency, 2007; Environment Agency, 2005).

Biological activity in sites containing a high proportion of inorganic material is potentially much lower than a site containing predominantly municipal waste. Large quantities of landfill gas are not expected to be generated from such sites; therefore assumptions of predominantly anaerobic conditions and a reducing environment are less certain in landfill sites with a high inorganic waste content.

Detailed gas sampling was undertaken using a range of analytical techniques to obtain the maximum coverage of potential trace gases. The composition of the gas generated from the waste was found to be highly variable in nature over short distances (metres).

#### **Observations**

In many cases, the pore gas sampled was derived from the air trapped during waste placement and nitrogen concentrations exceeding the ambient 79% were often observed. Hydrogen concentrations of up to a few percent were also observed in the cells. In general, odorous compounds and VOCs were found to be present at lower concentrations than are frequently observed at MSW sites. In one or two instances, high levels of VOCs were present. These were attributed to the absence of large volumes of gas generation, thereby limiting dilution.

Many chemical processes, for example, the corrosion of metals producing hydrogen and the generation of organo-metallic (notably lead and nickel) and organo-silicon compounds, may occur in inorganic landfills, resulting in landfill gas with significantly different compositions to general landfills (Environment Agency, 2007; Parker et al., 2006).

Due to the variation in trace gas composition observed and the relative absence of bulk gas generation, predominantly inorganic landfills may require site-specific gas risk assessments to determine the appropriate management procedures and monitoring techniques to use.

## 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. This list was heavily influenced by old co-disposal sites. The research behind this list suggested that odorous components of landfill gas may be isomers or related chemicals. It also indicated that toxic compounds not on the priority list may also be present.

Table 1.1 Priority trace components to be monitored in landfill gas

Trace component	CAS number	Potential impact	Category
1,1-dichloroethane	75-34-3	Health	Halocarbon
1,2-dichloroethane	107-06-2	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-butoxyethanol	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
Styrene	100-42-5	Health	Aromatic hydrocarbon
Tetrachloromethane	56-23-5	Health	Halocarbon
Toluene	108-88-3	Health	Aromatic hydrocarbon
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	630-08-0	Health	Inorganic

PCDD = polychlorinated dibenzo-p-dioxin

PCDF = polychlorinated dibenzofuran

Other substances in different categories may need additional determinands that will require alternative quantification on a site-specific risk basis.

Example monitoring techniques are listed in Table 1.3 below.

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 or Tedlar Bag and GCMS	Hand held instrument Laboratory GC
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

<sup>#</sup> 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.

We have adopted the methods recommended in R&D Project P1-438 (Environment Agency, 2002b) and adapted in light of experience during R&D Project P1-491 (Environment Agency, 2004b) for use in this guidance. The techniques were selected to give the best overall cover of all 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 with similar properties to those nominated in Table 1.1. We recommend that any 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.

#### Substances requiring investigation

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). Some of these common trace components are not on the priority list in Table 1.1, but will be detected by the recommended method for speciated VOCs.

All sampling and analysis of trace components must be carried out by MCERTS or UKAS certified individuals, equipment and laboratories. For determinands where no MCERTS/UKAS approved method exists, you must state the method of analysis along with a justification for using it.

### **Chloroethene (vinyl chloride)**

Use of chloroethene is almost exclusively limited to the plastics industry. Chloroethene can also form anaerobically through the de-chlorination of some halogenated organic solvents, such as tetrachloroethene (perchloroethylene or PCE) and trichloroethene (trichloroethylene or TCE). Chloroethene is a known human carcinogen, and is readily absorbed by inhalation. Therefore, chloroethene remains on the priority list of trace compounds.

The existing suite of analytical techniques for monitoring trace compounds is necessarily a compromise due to practical limitations. As a result, routine trace gas analysis may underestimate the concentration of chloroethene present in a sample. Therefore, if you obtain chloroethene concentrations near or above the risk-based threshold concentration (78 mg/m<sup>3</sup>) using our recommended general sampling method, you may need to carry out chloroethene-specific analysis on the sample.

Our recommended sampling method is dual solid sorption followed by ATD-GC-MS.

## **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.

# 2 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 used 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.

Use existing data on trace landfill gas composition to select sample points and the analytical suite on a site-specific basis. Verify the consistency of data generated by this guidance against these existing data. In instances where such 'sanity checks' indicate inconsistency, investigate this 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

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

## 2.3 Choosing a sampling point

Selecting a sampling point is an important consideration. It is essential 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 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.

### **Unrepresentative sample**

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, such as 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 in significant quantities of 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.

Make allowance 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.

### **Atypical waste**

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. Where there are very high concentrations of trace components, such that any fugitive release could pose a risk to workers' health and safety, additional trace gas monitoring should be taken to identify areas of the site and wells where there are high levels of trace components. The area of the landfill for which the sample is spatially representative should be reported with the data.

If the methane content of the gas at the chosen sampling point is **less than 30 per cent** (that is, 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 the 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**

Carbon monoxide concentrations **greater than 25 ppmv** (as verified in the laboratory) may indicate 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 and hydrogen sulphide. 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. Any field measurement of carbon monoxide **greater than 100 ppmv** should be investigated and confirmed by laboratory analysis.

## 2.4 Potential contamination of gas samples

Bulk gases are typically present at percentage concentrations and trace gas components from  $\text{mg/m}^3$  to  $\text{ng/m}^3$  concentrations. Hence, quantifying 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). Ensure the samples are transported in clean, sealed containers with minimum exposure to other volatile substances prior to analysis. Analyse samples 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 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  $293\text{K}$ .

### Pressure

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, that is 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 the emitted gas will be saturated with moisture at the slightly lower temperature at the landfill surface.

While recognising that small errors will result, we recommend 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

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

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

**Risk assessment**

Undertake a site-specific risk assessment 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. Use the risk assessment to determine the need for intrinsically safe or ATEX equipment. This must also account for appropriate occupational exposure standards, such as those contained in Guidance Note EH40/2005 (HSE) or its successor documents.

Sampling must not disturb the normal safe operation of a gas collection system. Talking with the site manager is essential to prevent unexpected surges of gas or introducing 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.

# 3 Monitoring principles

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 our Technical Guidance Note M2 on stack monitoring (Environment Agency) 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 is divided into two stages:

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

## 3.1 Preliminary checks and field measurements

Complete these activities at the site, taking away only the recorded results. Having knowledge of the site history and preliminary checks yield important metadata (secondary data). This will also help 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 measuring hydrogen sulphide, which can be adequately analysed using certain types of dedicated, real-time analyser. Depending on the instrument, such instruments are able to detect hydrogen sulphide at levels from 2 ppbv to 10,000 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 can 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 (such as hydrogen). Data obtained from these general-purpose field instruments must be regarded only as indicative and 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, for example in situations where quantification is less important.

However, we recommend using solid sorbents according to the procedures in this guidance 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](#).

### **Alternative methods**

You may consider using alternative sampling and analysis methods on an individual basis, provided they have been demonstrated fit-for-purpose before being used (that is, they have been shown to meet the selectivity and detection limits achieved by the recommended methods). Accredited analytical laboratories can provide details of alternative gas analysis methods that may achieve the detection limits required for quantifying 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 suitable for automated thermal desorption (ATD) and have an inert coating (such as, 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 previously used 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 provides 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. Our 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 the tubes have low background levels of mercury, that is **less than 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 or similar dedicated H <sub>2</sub> S portable meter  Tedlar bag		Real time  In the laboratory. After dilution into range of gold film instrument or by GC-MS with no dilution. Make analysis within 24 hours of sampling to minimise oxidation.
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

# 4 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**

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

### **Recommended approach**

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

### **Requirements**

- a hand-held bulk gas analyser (this must be pre-calibrated);
- appropriate connectors for gas taps;
- Gresham tube(s) or Tedlar bag(s) and pump.

### **Method**

- i. Select a sampling point that is representative of the gas in the study area 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 with 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 you record an elevated carbon monoxide value (>100 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. If the vacuum is greater than 10 kPa (0.1 bar), a standard sampling pump can't 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 a heavy condensate forming 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 preferable for detailed sampling of trace components.

### **Results**

Record the bulk gas composition (methane, carbon dioxide, oxygen and, by difference, nitrogen) as percentage by volume.

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

Record the following metadata for the location:

- 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 (only if the data needs to be normalised).

#### **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 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 10,000 ppmv (1 per cent v/v). If concentrations are higher, then laboratory measurement is required for accurate quantification. Portable instruments may, however, provide orders of magnitude results.

#### **Purpose**

The purpose is to measure hydrogen sulphide concentrations using a dedicated field instrument.

#### **Recommended approach**

Use 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**

- a Hydrogen sulphide analyser (this must be pre-calibrated);
- appropriate connectors for gas taps;
- Tedlar bag in a lung box.

#### **Method**

Draw a gas sample into the Tedlar bag from the gas sampling point and hold at atmospheric pressure. Draw gas from this bag into the instrument to provide the measurement.

#### **Results**

The result is the 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 samples 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 hydrogen sulphide concentrations in landfill gas and above ground ambient air measurements.

If preliminary site data indicates hydrogen sulphide is likely to be present at greater than 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.

# 5 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.

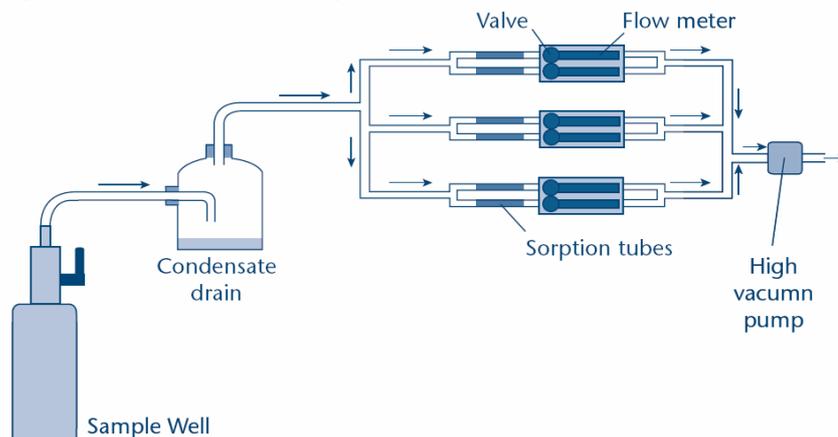
For each determination, take duplicate samples and assign a trip-blank tube (not exposed). For speciated VOCs, take a 100 ml volume sample, unless the trace components are known to be present in low concentrations; in which case, a low volume (100 ml) and a high volume (400 ml) sample will be necessary. For the other methods, sample a smaller range of analytes and take a single volume sample ([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 (such as 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.

Figure 5.1 Example sampling assembly



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).

See [Figure 5.1](#) for an example sampling assembly. Use a minimum of hardware (such as valves or connecting tubes) to connect the source of the sample gas to the sorbent tubes, as far as is reasonably possible. Whatever hardware you use 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 [Figure 5.2](#) and [Figure 5.3](#).

#### **Universal requirements**

- a hand-held bulk gas analyser;
- pumps (a battery-powered or a manually operated metering system);
- a condensate drain between the gas tap and the sample tubes;
- gas sample manifolds and connection tubing with low adsorption properties (such as Tygon 2275 high purity tubing, plasticiser-free), assembled and leak-tested in the laboratory;
- frame-mounted tube holders (SKC sorbent tube holders with individual adjustable flows);
- rotameters on gas lines (an influx direct reading variable area flowmeter (calibrated) glass tube and float, stainless steel needle valve) 20–250 ml/minute for routine sampling;
- a 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);
- an 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.

Carry spare tubes where you anticipate 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	2000

\* 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; you may require an additional 0.4 litre, high-volume sample.

<sup>#</sup> Additional components you may monitor.

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



Figure 5.3 Sampling tubes and rotameter assemblies

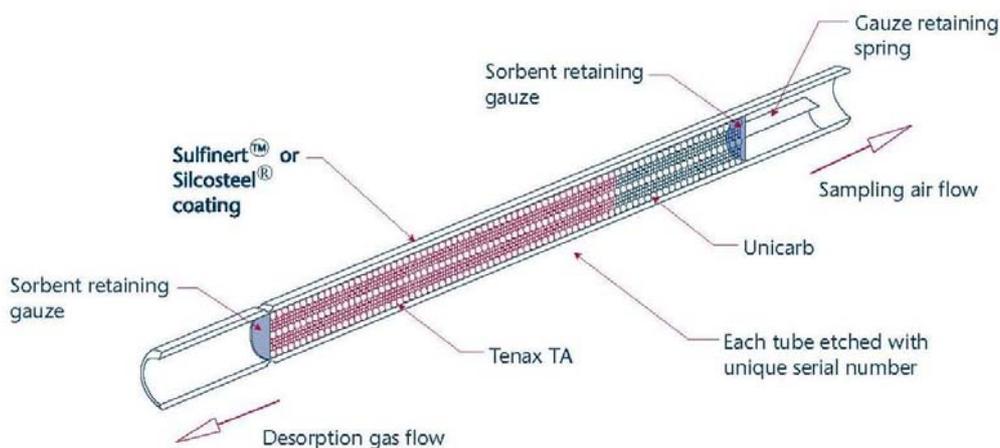
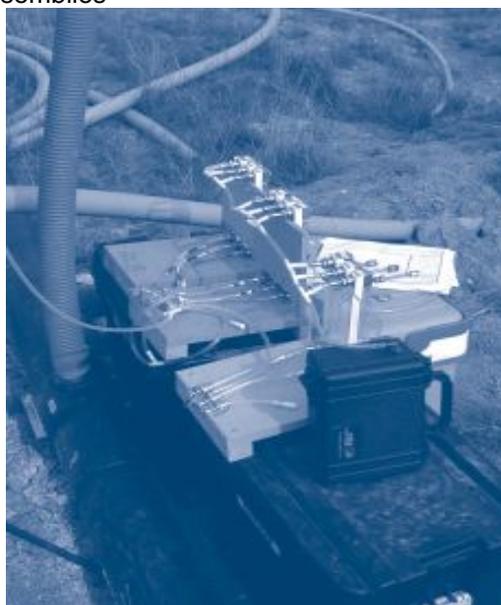


Figure 5.4 ATD packed with dual sorbent

## Method

- i. Use the hand-held gas analyser to reconfirm the bulk gas composition is suitable for monitoring trace gases.
- ii. Check 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 you note heavy condensation, 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 five minutes. If this is not achieved, check all connectors and repeat.
- v. Recheck 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. Seal the sample tubes 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 handheld 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 – you can minimise this 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 of 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), you require the following blanks and checks:

- 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, 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.
- You can use individually packed tubes 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.
- You may use Canister or Tedlar bag grab samples, which are quickly concentrated onto an adsorbent, 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, 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

Analyse sorbent tubes 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.

We chose the sampling methodologies below to provide the best cover of the priority substances using a minimum number of methods. 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.

If your monitoring identifies significant quantities of hazardous substances other than those on the priority list, you should adopt the most appropriate methods for quantifying the substances in question.

### 5.3.1 Speciated VOCs by GC–MS

#### Recommended approach

Before analysis, pass two 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 SpheroCarb) 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 all the target compounds 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. Also, assign any other significant peaks corresponding to basic analytes in standard analytical suites (for example, C1–C5 alkanes and BTEX). Use your judgement to decide whether to identify (with the aid of mass spectral libraries) any other significant peaks present.

## Results

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

### Known interference and causes of error

Due to the high likelihood of peaks overlapping in the chromatogram, identification and quantification of each target compound can only be carried out using ions specifically selected for that compound. For this reason it is important that the calibration accompanying each batch of samples contains all of the target compounds. Due to the nature of some of the target compounds, there is likely to be a higher degree of uncertainty than normal associated with their quantification. However these uncertainties are likely to be small compared with the errors produced from quantifying one compound using the response obtained for another.

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

The results should be 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 identifying 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 **one 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

There are 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

An established extraction and clean up technique

You need a 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

There are none known.

#### Alternative methods

None

# 6 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, this guidance will permit screening of all 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 a sub-set of these trace components is potentially of concern, use targeted monitoring methods 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 can't be undertaken on the main line for physical reasons (such as 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 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, 2010a), note these factors 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. Compare the data from the latest sampling on trace components with any earlier data and note the significance of any differences 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 the precautions adopted in stack monitoring can be followed, such as avoiding sampling at bends or dips in the pipe, or close to process zones. We recommend that wherever possible, do not take samples 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. Minimise this uncertainty 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. Report these analytical errors with the results.

# 7 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](#).

Report any substances that are positively identified 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 must highlight instances where variation from normal procedure has been necessary and should inform future monitoring requirements.

## 7.2 Inter-comparison of data

You may use the methods in this guidance to characterise the gas that is the input to a landfill gas engine or flare. However, monitor VOC emissions from the engine or flare 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 must take account of these potential differences.

# Appendix 1: Conversion factors

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

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

**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.

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

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:

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

**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.

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

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 is given in Technical Guidance Note M9 (Environment Agency, 2000).

## **CV-AAS**

Cold vapour atomic absorption spectroscopy involves reducing 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, for example, 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, for example, ultraviolet/visible absorption.

## **ICP-MS**

Inductively coupled plasma mass spectrometry is a multi-element technique for determining 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 quadruple 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	$\mu\text{g}/\text{m}^3$
1,2-dichloroethane	70	$\mu\text{g}/\text{m}^3$
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-butoxyethanol	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
Styrene	40	$\mu\text{g}/\text{m}^3$
Tetrachloromethane	70	$\mu\text{g}/\text{m}^3$
Toluene	60	$\mu\text{g}/\text{m}^3$
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 (if required)	
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		$\mu\text{g}/\text{m}^3$		
1,2-dichloroethane	107-06-2		$\mu\text{g}/\text{m}^3$		
1,1-dichloroethene	75-35-4		$\mu\text{g}/\text{m}^3$		
1,2-dichloroethene	540-59-0		$\mu\text{g}/\text{m}^3$		
1,3-butadiene	106-99-0		$\mu\text{g}/\text{m}^3$		
1-butanethiol	109-79-5		$\mu\text{g}/\text{m}^3$		
1-pentene	109-67-1		$\mu\text{g}/\text{m}^3$		
1-propanethiol	107-03-9		$\mu\text{g}/\text{m}^3$		
2-butoxyethanol	111-76-2		$\mu\text{g}/\text{m}^3$		
Arsenic (as As)	7440-38-2		$\mu\text{g}/\text{m}^3$		
Benzene	71-43-2		$\mu\text{g}/\text{m}^3$		
Butyric acid	107-92-6		$\mu\text{g}/\text{m}^3$		
Carbon disulphide	75-15-0		$\mu\text{g}/\text{m}^3$		
Chloroethane	75-00-3		$\mu\text{g}/\text{m}^3$		
Chloroethene (vinyl chloride)	75-01-4		$\mu\text{g}/\text{m}^3$		
Dimethyl disulphide	624-92-0		$\mu\text{g}/\text{m}^3$		
Dimethyl sulphide	75-18-3		$\mu\text{g}/\text{m}^3$		
Ethanal (acetaldehyde)	75-07-0		$\mu\text{g}/\text{m}^3$		
Ethanethiol	75-08-1		$\mu\text{g}/\text{m}^3$		
Ethyl butyrate	105-54-4		$\mu\text{g}/\text{m}^3$		
Furan (1,4-epoxy-1,3-butadiene)	110-00-9		$\mu\text{g}/\text{m}^3$		
Hydrogen sulphide	7783-06-4		$\mu\text{g}/\text{m}^3$		
Methanal (formaldehyde)	50-00-0		$\mu\text{g}/\text{m}^3$		
Methanethiol	74-93-1		$\mu\text{g}/\text{m}^3$		
Styrene	100-42-5		$\mu\text{g}/\text{m}^3$		
Tetrachloromethane	56-23-5		$\mu\text{g}/\text{m}^3$		
Toluene	108-88-3		$\mu\text{g}/\text{m}^3$		
Trichloroethene	79-01-6		$\mu\text{g}/\text{m}^3$		
<b>Additional site-specific</b>					
Mercury (as Hg)	7439-97-6		$\mu\text{g}/\text{m}^3$		
PCDDs and PCDFs	N/A		$\text{Ng}/\text{m}^3$ I-TEQ		
Carbon monoxide	N/A		ppmv		

Figure A4.1 Priority list compounds

# Glossary

**Adsorption**

This is 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**

These are gases drawn from the landfill at percentage concentrations.

**Chromophore**

This is 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**

This is the release of a substance from a surface to the mobile phase.

**DNPH**

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

**Fractionation**

This is 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**

This is 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**

This is a simple device for measuring gas pressure relative to atmospheric pressure.

**Metadata**

This is the secondary data or supplementary information relevant to the interpretation of primary data. It 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**

This is 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**

This is the immediate gaseous product from microbial degradation within the landfill.

**Rotameter**

This is an instrument for measuring gas flow.

**Speciation**

This is the identification of individual components.

**STP**

This is the abbreviation for Standard Temperature and Pressure. Used to normalise gas data to 273K ( 0°C), and 101.3 kPa ( one atmosphere)

**Tedlar bag**

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

**Trace component**

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

**XAD**

This is a proprietary ion exchanger comprising beads of cross-linked polystyrene.

# Acronyms

<b>AAS</b>	Atomic absorption spectroscopy
<b>ATD</b>	Automated thermal desorption
<b>BSI</b>	British Standards Institution
<b>BTEX</b>	Benzene, toluene, ethyl benzene and xylene
<b>CAS</b>	Chemical Abstracts System
<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>GC–MS</b>	Gas Chromatography with detection by mass spectrometry
<b>HPLC</b>	High performance liquid chromatography
<b>HSE</b>	Health and Safety Executive
<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-p-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
<b>STP</b>	Standard temperature and pressure
<b>UKAS</b>	United Kingdom Accreditation Service
<b>USEPA</b>	United States Environmental Protection Agency
<b>UV</b>	Ultra-violet
<b>VOC</b>	Volatile organic compound
<b>STP</b>	Standard temperature and pressure

# Units of measurement

## I-TEQ

International Toxicity Equivalent – a normalised expression of concentration for PCDDs and PCDFs

## ppbv

parts per billion by volume – an expression of concentration. 1 ppb is a thousandth of a ppm.

## ppmv

parts per million by volume – an expression of concentration. 10,000 ppm v/v equates to 1 per cent gas at STP by volume.

## $\mu\text{g}/\text{m}^3$

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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