

Australian Standard™

**Workplace air quality—Sampling and
analysis of volatile organic compounds
by solvent desorption/gas
chromatography**

Part 1: Pumped sampling method



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This Australian Standard was prepared by Committee CH-031, Methods for the Examination of Workplace Atmospheres. It was approved on behalf of the Council of Standards Australia on 3 November 2003 and published on 24 December 2003.

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STANDARDS AUSTRALIA

RECONFIRMATION

OF

AS 2986.1—2003

**Workplace air quality—Sampling and analysis of volatile organic compounds by
solvent desorption/gas chromatography
Part 1: Pumped sampling method**

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Technical Committee CH-031 has reviewed the content of this publication and in accordance with Standards Australia procedures for reconfirmation, it has been determined that the publication is still valid and does not require change.

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Coal Services
National Association of Testing Authorities Australia
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NOTES

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PREFACE

This Standard was prepared by the Standards Australia Committee CH-031, Methods for Examination of Workplace Atmospheres to supersede, in part, AS 2986—1987, *Workplace atmospheres—Organic vapours—Sampling by solid absorption techniques*.

This Standard is identical with and has been reproduced from ISO 16200-1:2001, *Workplace air quality—Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography*, Part 1: *Pumped sampling method*.

The objective of this Standard is to provide a method for sampling, using a personal pump and analysis of organic compounds by gas chromatography in workplace atmospheres.

As this Standard is reproduced from an International Standard, the following applies:

- (a) Its number appears on the cover and title page while the International Standard number appears only on the cover.
- (b) In the source text, ‘this part of ISO 16200’ should read ‘this Australian Standard’.
- (c) A full point should be substituted for a comma when referring to a decimal marker.

None of the documents referenced in this Standard have been adopted as Australian Standards.

This Standard is Part 1 of the following series:

AS

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|--------|--|
| 2986 | Workplace air quality—Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography |
| 2986.1 | Part 1: Pumped sampling method |
| 2986.2 | Part 2: Diffusive sampling method |

The Committee acknowledges advice from NATA (National Association of Testing Authorities) that, in Australia, some clauses in this Standard, which are given as advisory, are mandatory requirements for laboratories seeking NATA accreditation. Specifically:

- (i) Clause 4.4: Traceability of calibration blend solutions to national or international Standards is a NATA requirement.
- (ii) Clause 6: Preparation of field blanks is a NATA requirement.
- (iii) Clause 10: Estimations of uncertainty are required by NATA to be prepared in accordance with the principles of ISO GUM.*

The term ‘informative’ has been used in this Standard to define the application of the annex to which it applies. An ‘informative’ annex is only for information and guidance.

* ‘Guide to the Expression of Uncertainty in Measurement’ issued by BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML, Geneva, 1993.

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NOTES

AUSTRALIAN STANDARD

Workplace air quality—Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography

Part 1:

Pumped sampling method

1 Scope

This part of ISO 16200 gives general guidance for the sampling and analysis of volatile organic compounds (VOCs) in air by solvent desorption/gas chromatography using pumped sampling.

This part of ISO 16200 is applicable to a wide range of VOCs, including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. A number of sorbents are recommended for the sampling of these VOCs, each sorbent having a different range of applicability. However, activated coconut shell charcoal is frequently used. Very polar compounds may require derivatization; very low boiling compounds will only be partially retained by the sorbents and can only be estimated qualitatively. Semi-volatile compounds will be fully retained by the sorbents, but may only be partially recovered.

The upper limit of the useful range is set by the sorptive capacity of the sorbent used and by the linear dynamic range of the gas chromatograph column and detector or by the sample-splitting capability of the analytical instrumentation used. The lower limit of the useful range depends on the noise level of the detector and on blank levels of analyte and/or interfering artefacts on the sorbent tubes or in the desorption solvent. Artefacts are typically subnanogram for activated charcoal, but higher levels of aromatic hydrocarbons have been noted in some batches.

The concentration range for which this part of ISO 16200 is valid for the measurement of airborne vapours of VOCs is dependent on the volume sampled. For example, for a 10-litre sample of air, the range is approximately 1 mg/m³ to 1000 mg/m³ individual organic compound. For a 1-litre sample of air, the range is approximately 10 mg/m³ to 10 000 mg/m³ individual organic compound, and *pro rata*.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 16200. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 16200 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

EN 1232, *Workplace atmospheres — Pumps for personal sampling of chemical agents — Requirements and test methods*

EN 1540, *Workplace atmospheres — Terminology*

3 Principle

A measured volume of sample air is drawn through one (or more) sorbent tubes in series; an appropriate sorbent (or sorbents) being selected for the compound or mixture to be sampled. Provided suitable sorbents are chosen, volatile organic components are retained by the sorbent tube and thus are removed from the flowing air stream. The collected vapour is desorbed by a solvent, typically carbon disulfide, and the solution is analysed with a gas chromatograph equipped with a flame ionization detector, mass spectrometer or other selective detector.

4 Reagents and materials

During the analysis, use only reagents of analytical reagent grade.

4.1 Volatile organic compounds

A wide range of VOCs are required as reagents for calibration purposes.

4.2 Desorption solvent

The desorption or elution solvent, commonly carbon disulfide, should be of chromatographic quality. It shall be free from compounds co-eluting with the substances of interest. Tables 1 and 2 give recommended desorption solvents for particular vapours (see 7.5).

Where necessary (see Note 2), a desorption solvent modifier should be added at a sufficient concentration to result in a homogeneous solution in desorbed samples. Dimethylformamide may be suitable for this purpose.

NOTE 1 Carbon disulfide is normally recommended for the desorption of non-polar compounds from activated carbon. For polar compounds and mixtures of polar and non-polar compounds there is no ideal universal desorption solvent. Dichloromethane, methanol, higher alcohols, dimethylformamide and acetonitrile have been used as eluents, either singly or mixed with each other or carbon disulfide. OSHA methods 07 and 100 [1] and the NIOSH methods 1301, 1400, 1401, 1402, 1403 for ketones and alcohols [2] give examples of suitable desorption solvents other than pure carbon disulfide.

NOTE 2 The use of carbon disulfide desorption solvent can result in problems when polar analytes are collected from humid atmospheres. Polar analytes may be soluble in a water phase which forms following desorption with carbon disulfide when sufficient water is collected with the sample.

4.3 Sorbents

4.3.1 Activated charcoal

Tubes prepacked by the manufacturer with preconditioned charcoal are available and do not require further conditioning. Alternatively, tubes may be prepared by the user. A particle size of 0,35 mm to 0,85 mm is recommended. Before packing the tubes, the charcoal shall be heated in an inert atmosphere, e.g. high-purity nitrogen, at approximately 600 °C for 1 h. To prevent recontamination of the charcoal, it shall be kept in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes.

The sorptive capacity and desorption efficiency of different batches of activated charcoal may vary. Commercial tubes, if used, should be purchased from the same batch and in sufficient number to provide consistent performance for a definite period of time.

NOTE Activated charcoal is usually processed from coconut shells. For some applications, petroleum-based charcoal is preferred (see Tables 1 and 2). Some manufacturers recommend synthetic carbons as alternatives to charcoal of biological origin.

4.3.2 Other sorbents

Sorbents other than charcoal may be used for certain applications (see Tables 1 and 2).

NOTE A description of sorbent types is given in annex A. Equivalent sorbents may be used.

4.4 Calibration standards

Calibration blend solutions are required in order to compare the concentrations of desorbed solutions (7.3) with those calibration standards in the gas chromatographic analysis. Such solutions should be prepared in a way that is traceable to national standards.

An internal standard is optional. If used, it should not interfere with the compounds of interest and it should not be removed from the elution solvent by the sorbent. In the context of this method, the purpose of the internal standard is to correct for small variations in the injection volume. The use of an internal standard as a surrogate to correct for desorption efficiency (e.g. *n*-propyl acetate in the analysis of *n*-butyl acetate) is not recommended. Desorption efficiency should be determined directly with the compounds of interest (7.5).

Storage times for calibration solutions vary according to application. Typically, carbon disulfide dilutions should be prepared fresh weekly, or more frequently if evidence is noted of decomposition or evaporation.

NOTE In the analysis of complex mixtures, calibration blends of the pure compounds may be prepared before dilution with the elution solvent. Examples of three calibration blends are listed here. These have been used in the analysis of mixed solvents in paints, thinners, adhesives, cleaning fluids and miscellaneous commercial products. The components are arranged to give resolved peaks on both BP-1 and BP-10 phases¹⁾. Other blends may be more appropriate on different columns or in other applications. In the examples below, calibration blends 1-3 are stable for at least one year when stored in dark glass bottles with PTFE-lined screw-caps at less than 4 °C.

- a) Blend 1 consists of: *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-undecane, *n*-dodecane, benzene, toluene, *o*-xylene, *p*-xylene, *n*-propylbenzene, isopropylbenzene, *o*-ethyltoluene, *m*-ethyltoluene, *p*-ethyltoluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, *n*-propyl acetate, *n*-butyl acetate, isobutyl acetate, butoxyethyl acetate.
- b) Blend 2 consists of: isopropanol, isobutanol, *n*-butanol, 1-methoxy-2-propanol, butoxyethanol, toluene, ethylbenzene, 1,2,3-trimethylbenzene, ethyl acetate, ethoxyethyl acetate.
- c) Blend 3 consists of: acetone, 2-butanone, 4-methylpentan-2-one, cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, isopropyl acetate, *n*-nonane, toluene.

4.4.1 Solution containing approximately 10 mg/ml of each liquid component

Weigh 1 g of the substance or substances of interest into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with desorption solvent (4.2), stopper and shake to mix.

4.4.2 Solutions containing approximately 1 mg/ml of liquid components

Introduce 50 ml of desorption solvent into a 100 ml volumetric flask. Add 10 ml of solution 4.4.1. Make up to 100 ml with desorption solvent, stopper and shake to mix.

4.4.3 Solution containing approximately 100 µg/ml of each liquid component.

Weigh 10 mg of the substance or substances of interest into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with desorption solvent (4.2), stopper and shake to mix.

4.4.4 Solution containing approximately 10 µg/ml of liquid components

Introduce 50 ml of desorption solvent into a 100 ml volumetric flask. Add 10 ml of solution 4.4.3. Make up to 100 ml with desorption solvent, stopper and shake to mix.

1) BP-1 and BP-10 are examples of suitable products available commercially. This information is given for the convenience of users of this part of ISO 16200 and does not constitute endorsement by ISO of these products. Equivalent products may be used if they can be shown to lead to the same results. Annex B gives a non-exclusive list of products that are believed to be equivalent.

4.4.5 Solution containing approximately 1 mg/ml of gas components

For gases, e.g. ethylene oxide, a high-level calibration solution may be prepared as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a precision 1-ml gas-tight syringe (5.8) with 1 ml of the pure gas and close the valve of the syringe. Using a septum vial of suitable capacity, add 2 ml desorption solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the desorption solvent. Open the valve and withdraw the plunger slightly to allow the desorption solvent to enter the syringe. The action of the gas dissolving in the desorption solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP occupies 22,4 litres.

4.4.6 Solution containing approximately 10 µg/ml of gas components

For gases, e.g. ethylene oxide, a low-level calibration solution may be prepared as follows. Obtain pure gas at atmospheric pressure by filling a small plastic (or other inert material) gas bag from a gas cylinder. Fill a precision 10-µl gas-tight syringe (5.8) with 10 µl of the pure gas and close the valve of the syringe. Using a septum vial of suitable capacity, add 2 ml desorption solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the desorption solvent. Open the valve and withdraw the plunger slightly to allow the desorption solvent to enter the syringe. The action of the gas dissolving in the desorption solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP occupies 22,4 litres.

4.5 Calibration blend atmosphere (for 4.6 and annex B)

Prepare standard atmospheres of known concentrations of the compound(s) of interest by a recognized method. Methods described in ISO 6141, ISO 6145 and ISO 6349 are suitable. If the procedure is not applied under conditions that allow the establishment of full traceability of the generated concentrations to primary standards, confirm the delivered concentrations using an independent procedure.

4.6 Standards for desorption efficiency (for 7.5)

Prepare loaded sorbent tubes by passing an accurately known volume of the standard atmosphere through the sorbent tube, e.g. by means of a pump or mass flow controller. The volume of atmosphere sampled shall not exceed the breakthrough volume of the analyte-sorbent combination (annex B). After loading, the tube is disconnected and sealed.

If the generation of standard atmospheres is not practicable, the standards may be prepared by a liquid spiking procedure, provided that the accuracy of the spiking technique is established by using procedures giving spiking levels traceable to primary standards of mass and/or volume, or is confirmed by an independent procedure.

Load the sorbent tubes by injecting aliquots of standard solutions (4.4) of accurately known mass or volume onto clean sorbent tubes as follows: a sorbent tube is fitted to a T-piece of which one end is fitted with a septum, or injection facility of a gas chromatograph, through which inert purge gas is passed at 100 ml/min. Inject a 1 µl to 4 µl aliquot through the septum and purge for 5 min. Disconnect the tube and seal.

5 Apparatus

Ordinary laboratory apparatus and the following.

5.1 Sorbent tube

A sampling tube, typically consisting of a glass tube with both ends flame-sealed, 70 mm long with an outside diameter of 6 mm and an inside diameter of 4 mm, containing two sections of sorbent. In the case of charcoal, the sorbing section contains 100 mg of charcoal and the back-up section, 50 mg. The sections are separated and their contents are held in place with an inert material, e.g. glass wool plugs (preferably silanized).

Glass tubes shall be held in protective holders to prevent breakage.

The desorption efficiency (D) for each batch of tubes shall be checked by one of the methods described in 4.6. If D is lower than 0,75 (75 %), the tubes shall not be used (but see below).

Tubes meeting these requirements are commercially available; however, they may also be made by the user. Metal tubes may also be used with appropriate end caps. Self-packed samplers should not be used unless they can be shown to have reproducible and constant sorption properties.

Where mixtures of non-polar analytes are desorbed with pure carbon disulfide, the mutual concentration effect on D is generally negligible. If the composition of a mixture of polar and non-polar analytes is known approximately, D values should be established with a similar mixture. It may not be possible to achieve greater than 75 % D for all components of such a mixture with a single desorption solvent. Provided that it can be established that the D is consistent and that no better solvent has been found, then a compromise is acceptable, although where possible, the taking of a second sample and optimizing desorption conditions for both polar and non-polar analytes is preferred.

NOTE 1 Instead of commercial two-section tubes, two single section tubes in series may be used. This arrangement has the advantage that it is not necessary to store tubes at subambient temperatures after sampling, to prevent migration of the sorbed compounds from one section to the other.

NOTE 2 Polyurethane plugs may be used in place of silanized glass wool; however, they are known to sorb certain pesticides [3] for which this part of ISO 16200 is inapplicable.

NOTE 3 When it is desirable to sample highly volatile compounds for extended periods, or at a high volume flowrate, a larger sampling device may be used, provided the proportions of the tube and its charcoal contents are scaled similarly to the base dimensions, to provide nominally the same linear flowrate and contact time with the charcoal bed.

5.2 End caps, made to fit snugly over the sorbent tubes (5.1) to prevent leakage or contamination and made of inert material such as polyethylene.

5.3 Sampling pump, fulfilling the requirements of EN 1232 or equivalent.

The sampling pump should be in accordance with local safety regulations.

5.4 Tubing, plastic or rubber, about 90 cm long of appropriate diameter to ensure a leak-proof fit to both pump and sample tube or tube holder, if used. Clips shall be provided to hold the sorbent tube and connecting tubing to the wearer's lapel area.

It is not recommended to use tubes with any tubing upstream of the sorbent, as sample losses may occur.

5.5 Gas chromatograph, fitted with a flame ionization, photo-ionization detector, mass spectrometric or other suitable detector, capable of detecting an injection of 0,5 ng toluene with a signal-to-noise ratio of at least 5 to 1.

A gas chromatograph column capable of separating the analytes of interest from other components. Examples of suitable choices are 50 m × 0,22 mm fused silica columns with BP-1 or BP-10 stationary phase. A typical film thickness is in the range 0,5 µm to 2,0 µm. Typical operating conditions for these columns might be temperature programming from 50 °C to 200 °C at 5 °C/min with a helium carrier gas flowrate of 0,7-0,8 ml/min. Annex B gives a list of equivalent phases.

5.6 Autosampler

These are commercially available with liquid-chilled sample trays, suitable for the analysis of volatile solvents.

5.7 Precision volumetric flasks, of accurately known volumes, to be used for the preparation of calibration blend solutions (4.4).

5.8 Precision gas-tight syringes, of accurately known volumes of 1,0 ml and 10 µl, readable to 0,1 ml and 1,0 µl, respectively.

5.9 Flow meter, soap bubble type, or other suitable device for calibrating the flowrate of sampling pumps. The flow meter readout should be traceably calibrated or checked to a primary flow standard.