

TDTS 3

National and international standard methods relating to speciated monitoring of vapour-phase organic chemicals in air

Introduction

There are a growing number of nationally and internationally approved standard methods relating to monitoring speciated volatile organic compounds (VOCs) in air. They are generated by relevant government agencies (US EPA, UK HSE, *etc.*), international standards agencies such as ISO and CEN, or consensus-based standards organisations such as ASTM.

Key issues to consider when reviewing and selecting appropriate standards are:

- Method scope e.g. ambient, indoor, workplace, materials emissions test chambers
- · Sampling and analytical requirements
- Method format
- 'Recipe'
- General guidance (e.g. appropriate choice of sorbents, selection of suitable GC column)
- Validation protocol
- Method limits list of target analytes (if applicable), concentration range, detection limits, analyte volatility range, etc.

Generally speaking, methods written in 'recipe' format are restrictive both with respect to the analytical technology available at the time they were published, and the cost of use, *e.g.* requiring calibration for the entire target analyte set in situations where only two or three specific compounds are of interest.

A summary listing of key national and international standards is presented here – please contact the relevant organisation directly for information about how to obtain copies of standards.

US Environmental Protection Agency (EPA)

Website: http://www.epa.gov

Air Toxics Information (TO-1, TO-2, TO-17 etc.): http://www.epa.gov/ttn/amtic/airtox.html

T0-1: Method for the determination of volatile organic compounds in ambient air using Tenax adsorption and gas chromatography/mass spectrometry.

T0-2: Method for the determination of volatile organic compounds in ambient air by carbon molecular sieve adsorption and gas chromatography/mass spectrometry.

T0-14: The determination of volatile organic compounds (VOCs) in ambient air using SUMMA passivated canister sampling and gas chromatographic analysis.

T0-15: The determination of volatile organic compounds (VOCs) in air collected in SUMMA canisters and analysed by gas chromatography/mass spectrometry

T0-17: Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes.

Method 18: Measurement of gaseous organic compound emissions by gas chromatography.

EPA/600-8-91/215: Technical assistance document for sampling and analysis of ozone precursors.

Method 24 (thermal desorption variant: work in progress): Solvents in inks, paints and coatings.

Method 25A: Determination of total gaseous organic concentration using a flame ionization analyzer.

Method 311 (thermal desorption variant: work in progress): Analysis of hazardous air pollutant compounds in paints and coatings by direct injection into a gas chromatograph.

N.B. US EPA methods for the analysis of VOCs in water and soil by purge-and-trap – e.g. 502.1, 602, 524 and 624 – also specify analysis by thermal desorption and gas chromatography. www.markes.com

European Committee for Standardization (CEN)

Website: http://esearch.cen.eu/esearch/

Standard methods generated by CEN typically specify performance criteria against which the suitability of an analytical method can be assessed. CEN is associated with the International Standards Organisation (ISO), and copies of CEN standards may be obtained from National Standards Organisations worldwide.

Note that CEN and ISO standards may now each be reissued as the other without extensive review, under the so-called 'Vienna Agreement'.

EN 482: Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents.

EN 689: Guidelines for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy.

EN 838: Workplace atmospheres – Diffusive samplers for the determination of gases and vapours – Requirements and test methods.

EN 1076: Workplace atmospheres – Requirements and test methods for pumped sorbent tubes for the determination of gases and vapours.

EN 1232: Workplace atmospheres – Pumps for personal sampling of chemical agents – Requirements and test methods.

EN 13528: Ambient Air Quality – Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Part 1: General requirements.

Part 2: Specific requirements and test methods. Part 3: Guide to selection, use and maintenance.

EN 14412: Indoor Air Quality – Diffusive samplers for the determination of concentrations of gases and vapours. Guide for selection, use and maintenance.

ENV 13419: Building products – Determination of the emission of volatile organic compounds.

Part 1: Emission test chamber method (superseded by EN ISO 16000-9).

Part 2: Emission test cell method (superseded by EN ISO 16000-10).

Part 3: Procedure for sampling, storage and preparation of test specimens (superseded by EN ISO 16000-11). Part 4: Not approved by CEN. See ISO 16000-6.

EN ISO 16000: Indoor Air Part 9: Emission test chamber. Part 10: Emission test cell method. Part 11: Procedure for sampling, storage of samples and preparation of test specimens.

EN 13999: Adhesives – Short term method for measuring the emission properties of low-solvent or solvent-free adhesives after application. Part 1: General procedure.

Part 2: Determination of volatile organic compounds.

EN 14662: Ambient air quality – Standard method for the measurement of benzene concentrations. Part 1: Pumped sampling followed by thermal desorption and gas chromatography method. Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.

EN ISO 16017: Air quality – Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/ capillary gas chromatography. Part 1: Pumped sampling.

Part 2: Diffusive sampling.

prEN 15052: Resilient, textile and laminate floor coverings – Evaluation and requirements of volatile organic compounds (VOC) emissions.

EN 71-11: Safety of toys – Part 11: Organic chemical compounds – Methods of analysis. See Annex A2 Thermal Desorption – GC/MS-method.

TC 351 Working Draft: Construction products: Assessment of emissions of regulated dangerous substances from construction products – Determination of emissions into indoor air.

prEN 13649: Stationary source emissions – Determination of the mass concentration of individual gaseous organic compounds.

The International Standards Organization (ISO)

Website: http://www.iso.org/iso/home/standards.htm

(EN) ISO 16017: Air quality – Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/ capillary gas chromatography.

Part 1: Pumped sampling.

Part 2: Diffusive sampling.

ISO 16000: Indoor Air

Part 1: General aspects of sampling strategy.

Part 5: Sampling strategy for VOCs.

Part 6: Determination of VOCs in indoor and chamber air by active sampling on Tenax TA, thermal desorption & gas chromatography MSD/FID.

Part 9: Emission test chamber.

Part 10: Emission test cell method.

Part 11: Procedure for sampling, storage of samples and preparation of test specimens.

ISO DIS 16000:

Part 24: Performance test for evaluating the reduction of volatile organic compounds and carbonyl compounds without formaldehyde concentrations by sorptive building materials.

Part 25: Determination of the emission of semi-volatile organic compounds by building products – Microchamber method.

ISO CD 12219-1: Road vehicles

Part 1: Whole vehicle test chamber. Specification and method for the determination of volatile compounds in car interiors.

ISO 16107: Workplace atmospheres – Protocol for evaluating the performance of diffusive samplers.

ISO/FDIS 15009: Soil Quality

GC determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons – Purge and trap method with thermal desorption.

The American Society for Testing and Materials (ASTM)

Website: http://www.astm.org/Standard/index.shtml

D5116-05: Standard guide for small-scale environmental chamber determinations of organic emissions from indoor materials/products.

D5466-95: Standard test method for determination of volatile organic chemicals in atmospheres (canister sampling methodology).

D6177-97: Standard practice for determining emission profiles of volatile organic chemicals emitted from bedding sets.

D6196-03: Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air.

D6246-01: Standard practice for evaluating the performance of diffusive samplers.

D6330-98: Standard practice for the determination of volatile organic compound (excluding formaldehyde) emissions from wood-based panels using small environmental chambers under defined test conditions.

D6345-98: Standard guide for selection of methods for active, integrative sampling of volatile organic compounds in air.

D6399-99a: Standard guide for selecting instruments and methods for measuring air quality in aircraft cabins.

D6670-01: Standard practice for full-scale chamber determination of volatile organic emissions from indoor materials/products.

D6803-02: Standard practice for testing and sampling of volatile organic compounds (including carbonyl compounds) emitted from paint using small environmental chambers.

D7143-05: Emission cells for the determination of VOCs from indoor materials/products.

D7339: Test method for determination of volatile organic compounds emitted from carpet using a specific sorbent tube and thermal desorption/gas chromatography.

F1982-99: Standard Test Methods for analysing organic contaminants on silicon wafer surfaces by thermal desorption gas chromatography.

WK proposed: Standard practice for: Micro-scale test chambers for screening vapor-phase organic emissions from materials/products.

UK Health and Safety Executive

Website: http://www.hse.gov.uk/pubns/mdhs/

The following methods have been validated by the UK Health & Safety Laboratory.

MDHS 2: Acrylonitrile in air. Laboratory method using porous polymer adsorption tubes and thermal desorption with gas chromatographic analysis (March 1981).

MDHS 3: Generation of test atmospheres of organic vapors by the syringe injection technique. Portable apparatus for laboratory and field use (March 1981).

MDHS 4: Generation of test atmospheres of organic vapors by the permeation tube method. Apparatus for laboratory use (April 1981).

MDHS 22: Benzene in air. Laboratory method using porous polymer adsorbent tubes, thermal desorption and gas chromatography (March 1983).

MDHS 23: Glycol ether and glycol acetate vapors in air. Laboratory method using Tenax[™] sorbent tubes, thermal desorption and gas chromatography (revised March 1988).

MDHS 27: Protocol for assessing the performance of a diffusive sampler (June 1987).

MDHS 33: Adsorbent tube standards. Preparation by the syringe technique loading (December 1987).

MDHS 33/2: Sorbent tube standards. Preparation by the syringe injection technique (February 1997).

N.B. This procedure describes the preparation of sorbent tube standards to be used for calibration, determination of desorption efficiency and quality control in connection with sorbent tube/gas chromatographic methods for the determination of the time-weighted average concentrations of volatile organic compounds in workplace air. This method is suitable for a wide variety of volatile organic compounds.

MDHS 40: Toluene in air. Laboratory method using pumped porous polymer adsorbent tubes, thermal desorption and gas chromatography (June 1984).

MDHS 43: Styrene in air. Laboratory method using porous polymer diffusive samplers, thermal desorption and gas chromatography (March 1985).

MDHS 50: Benzene in air. Laboratory method using porous polymer diffusion samplers, thermal desorption and gas chromatography (October 1985).

MDHS 53/2: 1,3-Butadiene in air. Laboratory method using pumped samplers, thermal desorption and gas chromatography (revision in press).

MDHS 54: Protocol for assessing the performance of a pumped sampler for gases and vapors (August 1986).

MDHS 55: Acrylonitrile in air. Laboratory method using porous polymer diffusion samplers, thermal desorption and gas chromatography (June 1986).

MDHS 60: Mixed hydrocarbons (C_3 to C_{10}) in air. Laboratory method using pumped porous polymer and carbon sorbent tubes, thermal desorption and gas chromatography (December 1987).

MDHS 63/2: 1,3-Butadiene in air. Laboratory method using diffusive samplers, thermal desorption and gas chromatography (revision in press).

MDHS 66: Mixed hydrocarbons (C_5 to C_{10}) in air. Laboratory method using porous polymer diffusion samplers, thermal desorption and gas chromatography (November 1989).

MDHS 70: General methods for sampling airborne gasses and vapors (October 1990).

N.B. This method deals with the collection and analysis of gases and vapours commonly found in the workplace environment. It is limited to descriptions of sampling methods for subsequent laboratory analysis. It does not, therefore, include any discussions of direct reading instruments, colorimetric indicators, tape samplers, and other 'on the spot' testing devices.

MDHS 71: Analytical quality in workplace air monitoring (March 1991).

N.B. This MDHS is intended to provide guidance to laboratories on the practical application of internal quality control procedures within the laboratory, although it also includes some information on external quality assessment. It is not intended to be exhaustive, nor does it set down detailed requirements for the operation of quality control schemes in particular laboratories.

MDHS 72: Volatile organic compounds in air. Laboratory method using pumped solid sorbent tubes, thermal desorption and gas chromatography (February 1992).

N.B. This method is suitable for the measurement of the airborne concentrations of individual compounds and of components of volatile organic mixtures. It recommends a number of different sorbents for use in the sample tube, which are appropriate for different ranges of volatile organic compounds. Breakthrough volumes and safe sampling volumes are given for a range of components and sorbents.

MDHS 80: Volatile organic compounds in air. Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography (August 1995).

N.B. This method is suitable for the measurement of the airborne concentrations of individual compounds and of components of volatile organic mixtures. It recommends a number of different sorbents for use in the sample tube, which are appropriate for different ranges of volatile organic compounds. Uptake rates are given for a range of components and sorbents.

MDHS 89: Dimethyl sulphate and diethyl sulphate in air. Laboratory method using thermal desorption, gas chromatography-mass spectrometry (March 1998).

US National Institute for Occupational Safety and Health (NIOSH)

Website: http://www.cdc.gov/niosh/pubs/default.html

E. Kennedy *et al.*, Protocol for the evaluation of passive monitors: Diffusive sampling: an alternative approach to workplace air monitoring, eds: Berlin *et al.*, CEC Publication No. 10555EN, Brussels/Luxembourg (1987).

Method 2549: Volatile organic compounds – (screening) using multibed sorbent tubes, thermal desorption, gas chromatography and mass spectrometry.

Method pending (work in progress): Volatile organic compounds – (quantitative) using multibed sorbent tubes, thermal desorption and gas chromatography.

DHHS (NIOSH) Publ. No. 95-117: Guidelines for air sampling and analytical method development and evaluation.

UK Health and Safety Laboratory (HSL)

Website: http://www.hsl.gov.uk/home-page.aspx

HSL produce a series of Laboratory Notes for monitoring VOCs in breath as an indication of occupational exposure:

Breath Xylene Breath Ethyl acetate Breath 4-Methyl-2-pentanone Breath Perchloroethylene Breath Toluene Breath Butanone Breath Dichloromethane

These are available free of charge from Markes – please email enquiries@markes.com

Deutsches Institut für Bautechnik (DIBt)

Website: http://www.dibt.de/index_eng.html

Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB) – German contribution to the European discussion on the CPD.

Health-related Evaluation Procedure for Volatile Organic Compounds Emissions (VOC and SVOC) from Building Products (March 2008)

California Department of Public Health, Division of Environmental and Occupational Disease Control (DEODC)

Website:

http://www.cdph.ca.gov/programs/deodc/Pages/default.aspx

Standard practice for the testing of volatile organic emissions from various sources using small-scale environmental chambers (Ref. California Specification Section 01350 of the Collaborative for High Performance Schools (CHPS)) (July 2004).

Agence nationale de securite sanitare de l'alimentation, de l'environnement et du travail (ANSES) (previously AFSSET)

Website: http://www.anses.fr/

Relatif à une procédure d'évaluation des risques sanitaires concernant les composés organiques volatils (COV) et le formaldéhyde émis par les produits de construction (Saisine Afsset No. 2004/011).

Gemeinschaft Umweltfreundlicher Teppichboden (GUT)

Website: www.pro-dis.info/about_gut.html?&L=%C2%B01

GUT test method for the screening of VOC-emissions from textile floor coverings.

Verein Deutscher Ingenieure (VDI)

Website: http://www.vdi.de/

VDI 3864 (Draft German standard): Gaseous air pollution measurement. Gas chromatographic determination of volatile halogenated hydrocarbons. Sampling by adsorption, analysis by thermal desorption/gas chromatography.

VDI 4300 Part 1: Indoor air-pollution measurement. General aspects of measurement strategy.

 $\it N.B.$ This standard is based on Report ECA 6, and is being used as the basis of a draft ISO standard by ISO/TC 146/SC 6/WG 1.

2083-17 Draft: Cleanroom technology – Compatibility with required clean lines: class and surface clean lines.

Japanese Standards Association (JSA)

Website: http://www.jsa.or.jp/default_english.asp

The following list of methods relating to indoor air is reproduced with kind permission of Prof. Tanabe, Waseda University, Tokyo.

JIS A 1901, 2003: Determination of the emission of volatile organic compounds and aldehydes for building products – Small chamber method (Ref: ISO 16000-9 and -11).

JIS A 1902 (Parts 1 to 4), 2006: Building products – Procedures for sampling and storage of samples and preparation of test specimens.

JIS A 1903, 2008: Determination of the emissions of VOCs for building products – Passive method.

JIS A 1904, 2008: Determination of the emissions of SVOC for building products – Micro-chamber method.

JIS A 1906, 2008: Performance test of sorptive building materials of reducing indoor air pollution with small chamber – Measurement of adsorption flux with supplying constant concentration of contaminant air of VOC and aldehydes without formaldehyde.

JIS A 1912, 2008: Determination of the emissions of VOCs and aldehydes (except formaldehyde) for building materials and related products – Large chamber method.

JIS A 1960, 2005: Indoor air – General aspects of sampling strategy (Ref.: ISO 16000-1).

JIS A 1964, 2005: Indoor air – Measurement strategy for VOCs (Ref.: ISO-16000-5).

JIS A 1965, 2005: Indoor air – Determination of VOCs in indoor air and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and GC using MS/FID (Ref.: ISO 16000-6.2).

JIS A 1966, 2005: Indoor, ambient and workplace air – Sampling and analysis of VOCs by sorbent tube/thermal desorption/capillary GC – Part 1: Pumped sampling (Ref.: ISO 16017-1).

JIS A 1967, 2005: Indoor, ambient and workplace air – Sampling and analysis of VOCs by sorbent tube/thermal desorption/capillary GC – Part 2: Diffusive sampling (Ref.: ISO 16017-2).

JIS C 9913, 2008: Measuring method of volatile organic compounds and carbonyl compounds emissions for electronic equipment – Chamber method.

JIS X 6936, 2005: Information technology – Office equipment – Measurement of ozone, volatile organic compounds and dust emissions rate from copiers, printers and multi-function devices (Ref.: Blue Angle RAL).

UK Environment Agency

Website: http://publications.environment-agency.gov.uk/

Technical Guidance Note 04: Guidance for monitoring trace components in landfill gas.

Technical Guidance Note M2: Monitoring of stack emissions to air.

Sector Guidance Note IPPC S4.01: Guidance for the large volume organic chemicals sector.

Sector Guidance Note IPPC S4.02: Guidance for the speciality organic chemicals sector.

Horizontal Guidance Document H4 – Odour: How to comply with your environmental permit.

The following documents were prepared in collaboration with the Energy Institute (formerly the Institute of Petroleum), and are available from them.

Website: <u>http://www2.energyinstpubs.org.uk/cgibin/open.cgi?page=index</u>

ISBN 085293 405 X, April 2004: Protocol for the determination of the speciation of hydrocarbon emissions from oil refineries.

IP 442: Analysis of fuel- and oil-derived hydrocarbons in diesel particulate on filters – Gas chromatography method.

European Collaborative Action on Urban Air, Indoor Environment and Human Exposure (ECA) (formerly ECA-IAQ)

Website:

http://ihcp.jrc.ec.europa.eu/our_activities/publichealth/indoor_air_quality/eca

These reports do not have the status of CEN or ISO standards, but are widely quoted.

Methods

ECA 6: Strategy for sampling chemical substances in indoor air.

ECA 8: Guideline for the characterization of VOCs emitted from indoor materials and products using small test chambers.

ECA 13: Determination of VOCs emitted from indoor materials and products.

ECA 14: Sampling strategies for volatile organic compounds in indoor air.

ECA 16: Determination of VOCs emitted from indoor materials and products.

ECA 18: Evaluation of VOC emissions from building products – Solid flooring materials.

ECA 19: Total volatile organic compounds (TVOCs) in indoor air quality investigations.

ECA 24: Harmonisation of indoor material emissions labelling systems in the EU – Inventory of existing schemes.

US Institute of Environmental Sciences and Technology (IEST) (formerly IES)

Website:

http://www.iest.org/RecommendedPractices/IESTRDCC0 11/tabid/9658/Default.aspx

IEST-RP-CC031: Method for characterizing outgassed cleanroom materials and components:

Part 1: Determination of organic emissions from cleanroom construction materials by direct thermal desorption and GC-MS analysis.

Part 2: Desorption, trapping and thermal desorption– GC–MS analysis of organic contaminants on the surface of silicon wafers.

Netherlands Standardization Institute (NEN)

Website: http://www.nen.nl/web/Normshop.htm

NVN 2792 – Ambient Air Quality: Determination of vinyl chloride concentration using adsorption onto PoraPak followed by thermal desorption/gas chromatography analysis.

NVN 2774 – Ambient Air Quality: Determination of the concentration of phenols by adsorption onto Tenax followed by thermal desorption/gas chromatography analysis.

NVN 2796 – Ambient Air Quality: Determination of acrylonitrile concentration using adsorption onto PoraPak followed by thermal desorption/gas chromatography analysis.

NVN 2797 – Ambient Air Quality: Determination of the concentration of volatile esters by adsorption onto a sorbent tube followed by thermal desorption/gas chromatography analysis.

NVN 2968 – Workplace Air Quality: Determination of the concentration of ketone by pumped sampling onto a sorbent tube followed by thermal desorption/gas chromatography analysis.

Verband der Automobilindustrie (VDA)

Website:

http://www.vda.de/en/publikationen/publikationen_downloads/

VDA 276-1: Measuring emissions from car trim components using a 1 m^3 chamber at $65 \degree \text{C}$.

VDA 278: Thermal desorption analysis of organic emissions for the characterization of non-metallic materials for automobiles.

Other international standards

Australian Standard – 2986 (1987): Workplace atmospheres – Organic vapours – Sampling by solid adsorption techniques.

International Organization of Legal Metrology (OIML) P 2 (draft): Guide to air sampling devices for toxic chemical pollutants at hazardous waste sites.

Nordtest Methods: NT Build 358: Building materials: Emission of volatile compounds. Chamber method.

Nordtest Methods: NT Build 438: Building materials: Emission of volatile compounds. Field and Laboratory Emission Cell (FLEC).

American National Standards Institute ANSI/ISEA 104-1998 (draft): American national standard for air sampling devices – Diffusive type for gases and vapors in working environments.

Korean Association for Clean Air, Testing Method: Environmentally-friendly building materials – Regulations on small chambers.