DRAFT INTERNATIONAL STANDARD

ISO/DIS 16000-3

ISO/TC **146**/SC **6**

Secretariat: **DIN**

Voting begins on:
2021-03-17

Voting terminates on:
2021-06-09

Indoor air —

Part 3:
Determination of formaldehyde and other carbonyl compounds in indoor and test chamber air — Active sampling method

ICS: 13.040.20

This document is circulated as received from the committee secretariat.

Reference number
ISO/DIS 16000-3:2021(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword ..... **iv**
Introduction ..... **v**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **2**
4 Principle **2**
5 Limitations and interferences **2**
5.1 General 2
5.2 Ozone interference 3
6 Safety measures **3**
7 Apparatus **4**
7.1 Sampling 4
7.2 Sample preparation 5
7.3 Sample analysis 5
8 Reagents and materials **7**
9 Preparation of reagents and cartridges **8**
9.1 Purification of 2,4-dinitrophenylhydrazine 8
9.2 Preparation of DNPH formaldehyde derivative 8
9.3 Preparation of DNPH formaldehyde standards 9
9.4 Preparation of DNPH coated silica gel cartridges 9
9.4.1 General 9
9.4.2 DNPH coating solution 9
9.4.3 Coating of silica gel cartridges 9
10 Procedure **10**
10.1 Sample collection 10
10.2 Process blanks 12
10.3 Sample analysis 12
10.3.1 Sample preparation 12
10.3.2 Sample desorption 12
10.3.3 HPLC calibration 13
10.3.4 HPLC analysis for formaldehyde 16
10.3.5 HPLC analysis of other aldehydes and ketones 18
11 Calculations **20**
12 Performance criteria and quality assurance **21**
12.1 General 21
12.2 Standard operating procedures (SOPs) 21
12.3 HPLC system performance 22
12.4 Sample loss 22
12.5 Measurement plan 22
13 Precision and uncertainty **23**
14 Test report **23**
Annex A (informative) **Precision and uncertainty** **24**
Annex B (informative) **Melting points of DNPH carbonyl derivatives** **26**
Bibliography **27**

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 6, *Indoor air*.

This third edition cancels and replaces the second edition (ISO 16000-3:2011), which has been technically revised.

The main changes compared to the previous edition are as follows:

— clarification of the suitability of the method for acrolein measurements

A list of all parts in the ISO 16000 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This part of ISO 16000 is intended to be used for characterizing indoor air following the sampling strategy specified in ISO 16000-2. It is applicable to formaldehyde and other carbonyl compounds. It has been tested for 14 aldehydes and ketones. Formaldehyde is the simplest carbonyl compound, with one carbon, one oxygen and two hydrogen atoms. In its monomolecular state, it is a colourless, pungent, reactive gas. It has been used in the production of urea-formaldehyde resins, adhesives, and insulating foams. Emissions from particle (chip) board and wall insulation are the major sources of formaldehyde in indoor air.

Formaldehyde is collected by passing air through a reactive medium that converts the compound to a derivative of lower vapour pressure that is more efficiently retained by the sampler and can be easily analysed. This part of ISO 16000 determines formaldehyde and other carbonyl compounds by reaction with 2,4 dinitrophenylhydrazine coated on to a sorbent to convert them to their corresponding hydrazones, which can be recovered and measured with high sensitivity, precision, and accuracy. Other carbonyl compounds that may be emitted into air from solvents, adhesives, cosmetics, and other sources can also be determined using this part of ISO 16000.

The sampling procedure is based on US EPA method TO-11A[12].

Formaldehyde and certain other carbonyl compounds have a high toxic potential[15].

ISO 16017[7][8] and ISO 12219[2]–[6] also focus on volatile organic compound (VOC) measurements.

Indoor air —

Part 3: Determination of formaldehyde and other carbonyl compounds in indoor and test chamber air — Active sampling method

WARNING — Persons using this part of ISO 16000 should be familiar with normal laboratory practice. This part of ISO 16000 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This part of ISO 16000 specifies a determination of formaldehyde (HCHO) and other carbonyl compounds (aldehydes and ketones)[1)] in air. The method is specific to formaldehyde but, with modification, at least 12 other aromatic as well as saturated and unsaturated aliphatic carbonyl compounds can be detected and quantified. It is suitable for determination of formaldehyde and other carbonyl compounds in the approximate concentration range 1 µg/m^3 to 1 mg/m^3. The sampling method gives a time-weighted average (TWA) sample. It can be used for long-term (1 h to 24 h) or short-term (5 min to 60 min) sampling of air for formaldehyde.

This part of ISO 16000 specifies a sampling and analysis procedure for formaldehyde and other carbonyl compounds that involves collection from air on to adsorbent cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) and subsequent analysis of the hydrazones formed by high performance liquid chromatography (HPLC) with detection by ultraviolet absorption[12],[16]. The method is not suitable for longer chained or unsaturated carbonyl compounds.

This part of ISO 16000 applies to the determination of:

acetaldehyde	2,5-dimethylbenzaldehyde	*m*-tolualdehyde
acetone	formaldehyde	*o*-tolualdehyde
benzaldehyde	isovaleraldehyde	*p*-tolualdehyde
butyraldehyde	propionaldehyde	valeraldehyde
capronaldehyde		

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

1) Instead of systematic IUPAC nomenclature, traditional names are used in this part of ISO 16000. Some equivalent names are: acetaldehyde: ethanal / acetone: 2-propanone / butyraldehyde: butanal / capronaldehyde: hexanal / formaldehyde: methanal / isovaleraldehyde: 3-methylbutanal / propionaldehyde: propanal / *m*-tolualdehyde: 3-methylbenzaldehyde / *o*-tolualdehyde: 2-methylbenzaldehyde / *p*-tolualdehyde: 4-methylbenzaldehyde / valeraldehyde: pentanal.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

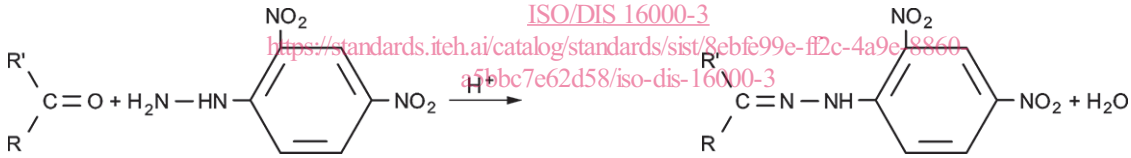
— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The method specified in this part of ISO 16000 involves drawing air through a cartridge containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) reagent. The principle of the method is based on the specific reaction of a carbonyl group with DNPH in the presence of an acid to form stable derivatives according to the reaction shown in Figure 1. The DNPH derivatives are analysed for the parent aldehydes and ketones utilizing high performance liquid chromatography (HPLC) with UV detection or diode array detection. The detection has been extended to other carbonyl compounds that can be determined as outlined in 9.3.5.

This part of ISO 16000 instructs the user on how to prepare sampling cartridges from commercially available chromatographic grade silica gel cartridges by the application of acidified DNPH to each cartridge. Alternatively, pre-coated DNPH silica gel cartridges are available and are recommended since they are generally more uniform in manufacture and possess lower blank levels. However, if commercial cartridges are used, they shall be demonstrated to meet the performance criteria of this part of ISO 16000. Another advantage of commercial cartridges is that they are available with larger particle size silica gel that results in a lower pressure drop across the cartridge. These low pressure drop cartridges may be more suitable for sampling air using battery-powered personal sampling pumps.



Carbonyl compound (aldehyde or ketone) | 2,4-Dinitrophenylhydrazine (DNPH) | DNPH deriative

Key

R, R' H, alkyl group, aromatic group

Figure 1 — Reaction of carbonyl compounds to form 2,4-dinitrophenylhydrazones

5 Limitations and interferences

5.1 General

The sampling flow rate specified in this part of ISO 16000 has been validated for sampling rates up to 1,5 l/min. This flow rate limitation is principally due to the high pressure drop (>8 kPa at 1,0 l/min) across the user-prepared silica gel cartridges, which have particle sizes of 55 µm to 105 µm. These cartridges are not generally compatible with battery-powered pumps used in personal sampling equipment (e.g. those used by industrial hygienists).

The solid-sorbent sampling procedure is specific for sampling and analysis of formaldehyde. Interferences in this method are caused by certain isomeric aldehydes or ketones that may be unresolved by the HPLC system when analysing for other aldehydes and ketones. Any organic compounds that have the same retention times and significant absorbance at 360 nm as the DNPH derivative of formaldehyde

interfere. Such interferences can often be overcome by altering the separation conditions (e.g. using alternative HPLC columns or mobile phase compositions).

Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The DNPH shall be purified by multiple recrystallizations in UV-grade acetonitrile (ACN). Recrystallization is accomplished, at 40 °C to 60 °C, by slow evaporation of the solvent to maximize crystal size. Impurity levels of carbonyl compounds in the DNPH are determined prior to use by HPLC and should be less than 0,15 µg per cartridge.

Exposure of the DNPH coated sampling cartridges to direct sunlight may produce artefacts and should be avoided[17].

Acrolein and crotonaldehyde may not be accurately quantified by the method. Inaccurate results for these compounds may result from the formation of multiple derivative peaks and the instability of the peak ratios[18].

Nitrogen dioxide reacts with DNPH. High concentrations of NO2 (e.g. for gas cooking stoves) may cause problems as the retention time of the DNPH derivative may be similar to that of the DNPH formaldehyde derivative, depending on the HPLC column and the parameters[13][14][19].

5.2 Ozone interference

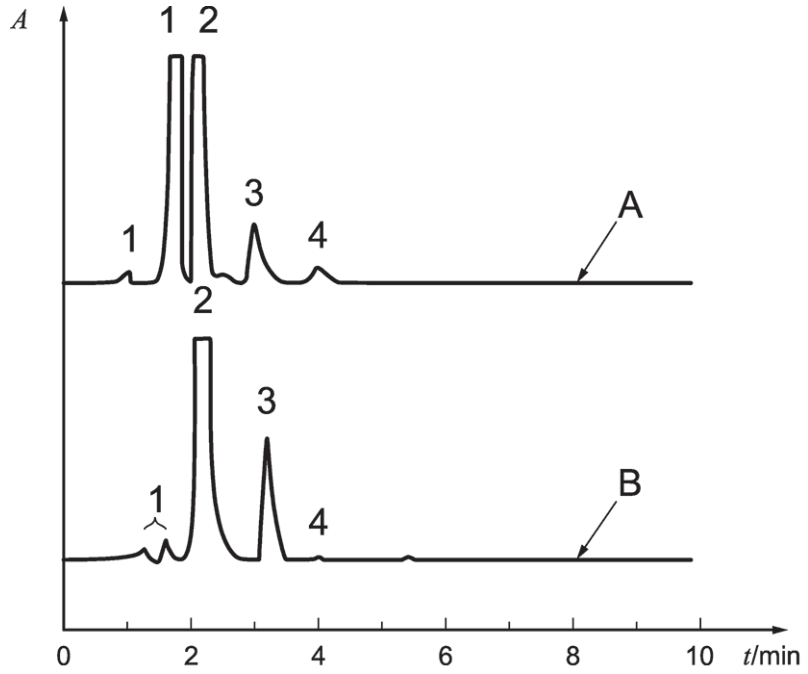
If there is suspicion that abnormally high levels of ozone are present in the area being sampled (e.g. from office copiers), special care should be exercised. Ozone has been shown to interfere negatively by reacting with both DNPH and its derivatives (hydrazones) in the cartridge[20]. The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from ozone has been observed even at concentrations of formaldehyde and ozone typical of clean ambient air (2 µg/m^3 and 80 µg/m^3, respectively)[19]. The presence of ozone in the sample is readily inferred upon analysis by the appearance of new compounds with retention times shorter than that of the hydrazone of formaldehyde. Figure 2 shows chromatograms of samples of a formaldehyde-spiked air stream with and without ozone.

The most direct solution to ozone interference is to remove the ozone before the sampled air reaches the cartridge. This can be accomplished by the use of an ozone denuder or scrubber placed in front of the cartridge. Both ozone denuders and scrubber cartridges are commercially available. A denuder may be constructed of 1 m of copper tubing of outside diameter 0,64 cm and of inside diameter 0,46 cm, that is filled with a saturated solution of potassium iodide in water, allowed to stand for a few minutes (e.g. 5 min), drained and dried with a stream of clean air or nitrogen for about 1 h. The capacity of the ozone denuder as specified is about 200 µg/m^3 h. Test aldehydes (formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde and *p*-tolualdehyde) that were dynamically spiked into an ambient sample air stream passed through the ozone denuder with practically no losses[21]. Commercial ozone scrubbers made from a cartridge filled with 300 mg to 500 mg of granular potassium iodide have also been found to be effective in removing ozone[22].

6 Safety measures

— 2,4-Dinitrophenylhydrazine is explosive in the dry state and shall be handled with extreme care. It is also toxic (in the rat, LD50 = 654 mg/kg), has been shown to be mutagenic in some tests, and is irritating to the eyes and skin.

— Perchloric acid at concentrations less than 68 % mass fraction is stable and non-oxidizing at room temperature. However, it is readily dehydrated at temperatures above 160 °C and can cause explosions on contact with alcohols, wood, cellulose, and other oxidizable materials. It should be stored in a cool, dry place and used only in a chemical fume hood with caution.



Key

A	relative absorbance	1	unknown
t	time	2	DNPH
A	with ozone	3	formaldehyde
B	without ozone	4	acetaldehyde

Figure 2 — Cartridge samples of formaldehyde in an air stream with and without ozone

7 Apparatus

Usual laboratory apparatus and in particular the following.

7.1 Sampling

7.1.1 Sampling cartridge packed with silica gel and coated with DNPH in accordance with Clause 8, or as available commercially.

The cartridge shall contain a minimum quantity of 350 mg of silica gel with a minimum DNPH loading of 0,29 % mass fraction. The ratio of the silica gel bed diameter to bed length shall not exceed 1:1. The capacity of the cartridge for formaldehyde shall be at least 75 µg and the collection efficiency at least 95 % at a sampling rate of 1,5 l/min. Sampling cartridges with very low blank levels and high performance are commercially available.

NOTE A pressure drop through the user-prepared sample cartridge of about 19 kPa at a sampling rate of 1,5 l/min has been observed. Some commercially available pre-coated cartridges exhibit lower pressure-drops, which permit the use of battery-operated personal sampling pumps.

7.1.2 Air sampling pump capable of accurately and precisely sampling at a flow rate of 0,1 l/min to 1,5 l/min.

7.1.3 Flow controller mass flow meters and mass flow controllers, or other suitable device for metering and setting air flow rates of 0,50 l/min to 1,20 l/min through the sample cartridge.

7.1.4 Flow calibrator such as a rotameter, soap-bubble meter or wet test meter.

7.2 Sample preparation

7.2.1 Cartridge containers e.g. borosilicate glass culture tubes (20 mm x 125 mm) with polypropylene screw caps, or other suitable containers, to transport coated cartridges.

7.2.2 Polyethylene gloves to handle silica gel cartridges.

7.2.3 Transportation containers friction-top metal cans (e.g. of volume 4 l) or other suitable containers, with polyethylene air-bubble packing or other suitable padding, to hold and cushion the sealed cartridge containers.

NOTE At heat sealable foil-lined plastic pouch of the type included with some commercial pre-coated DNPH-cartridges can be used for storing a DNPH-coated cartridge after sampling, if appropriate.

7.2.4 Support for coating cartridges.

A syringe rack made from an aluminium plate (0,16 cm x 36 cm x 53 cm) with adjustable legs on four corners. A matrix (5 x 9) of circular holes of diameter slightly larger than the diameter of the 10 ml syringes, symmetrically drilled from the centre of the plate, to enable batch processing of 45 cartridges for cleaning, coating and/or sample elution (see Figure 3).

7.2.5 Cartridge drying manifold such as a support with gas connectors and with multiple standard male syringe connectors (see Figure 3).

NOTE The apparatus specified in 6.2.4 and 6.2.5 is needed only if users choose to make their own DNPH-coated cartridges.

7.3 Sample analysis

7.3.1 HPLC system, consisting of

a) a mobile phase reservoir with an outgassing device (e.g. membrane under reduced pressure);

b) a high-pressure pump;

c) an injection valve (automatic sampler with a 25 µl or other convenient loop volume);

d) a C-18 reverse phase (RP) column (e.g. 25 cm ´ 4,6 mm inside diameter, 5 µm particle size);

e) a UV detector or diode array detector operating at 360 nm;

f) a data system or strip chart recorder.

The DNPH-formaldehyde derivative is determined using isocratic reverse phase HPLC, equipped with an ultraviolet (UV) absorption detector operated at 360 nm. A blank cartridge is likewise desorbed and analysed. Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions.

NOTE 1 Most commercial HPLC analytical systems are adequate for this application.

NOTE 2 A column oven can be used to assure constant column operating temperature and improve reproducibility.

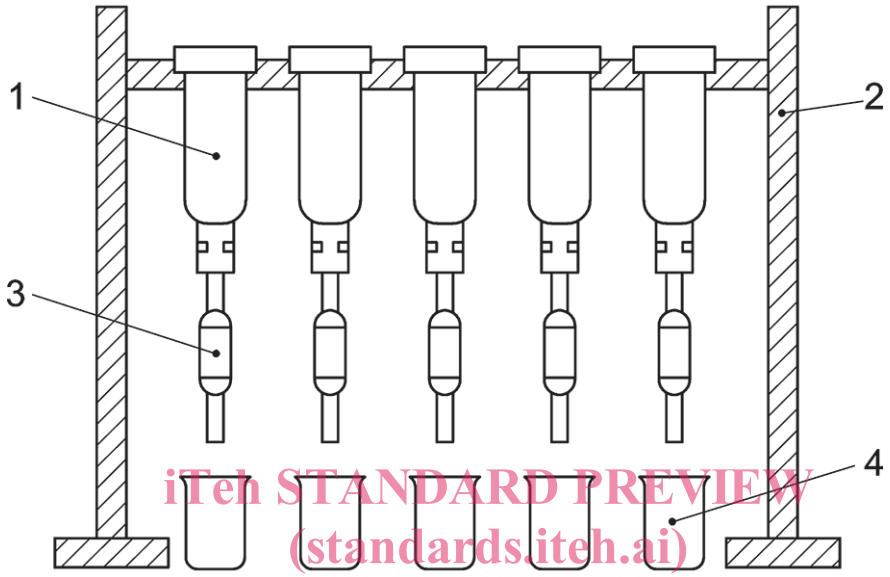
7.3.2 Syringes and pipettes.

7.3.2.1 HPLC injection syringes with capacity at least four times the loop volume (see 6.3.1).

7.3.2.2 Syringes volume 10 ml, used to prepare DNPH-coated cartridges (polypropylene syringes are adequate).

7.3.2.3 Syringe fittings and plugs to connect cartridges to the sampling system and to cap prepared cartridges.

7.3.2.4 Pipettes positive-displacement, repetitive-dispersing type, with capacities in the 0 ml to 10 ml range ISO 8655-2[1].



a) Rack for coating cartridges