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JIS A 1962 : 2005

**Indoor air — Determination of formal-
dehyde and other carbonyl com-
pounds — Active sampling method**

ICS 13.040.20

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Foreword

This translation has been made based on the original Japanese Industrial Standard established by the Minister of Land, Infrastructure and Transport through deliberations at the Japanese Industrial Standards Committee.

This Standard has been made based on **ISO 16000-3:2001** *Indoor air—Part 3: Determination of formaldehyde and other carbonyl compounds—Active sampling method* for the purpose of making it easier to compare this Standard with International Standard; to prepare Japanese Industrial Standard conforming with International Standard; and to propose a draft of an International Standard which is based on Japanese Industrial Standard.

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In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

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Indoor air—Determination of formaldehyde and other carbonyl compounds—Active sampling method

Introduction This Japanese Industrial Standard has been prepared based on the first edition of **ISO 16000-3** *Indoor air—Part 3 : Determination of formaldehyde and other carbonyl compounds—Active sampling method* published in 2001 with some modifications of the technical contents.

The portions given sidelines or dotted underlines are the matters in which the contents of the original International Standard have been modified. A list of modifications with the explanations is given in Annex 1 (informative).

This Standard is intended to be used for characterizing indoor air following the sampling strategy of formaldehyde in indoor air in **JIS A 1961**. 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.

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 Standard determines formaldehyde and other carbonyl compounds by reaction with 2,4-dinitrophenylhydrazine coated onto 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 Standard.

In this Standard, reagents (DNPH-formaldehyde derivatives) and cartridges to be used are presupposed as own works, however, those available commercially may be used in the case where the quality and performance are confirmed.

Formaldehyde and certain other carbonyl compounds have a high toxic potential [2].

Information : The content in **JIS A 1961** is equivalent to that of **ISO/DIS 16000-2**.

1 Scope This Standard describes a procedure for the determination of formaldehyde (HCHO) ⁽¹⁾ and other carbonyl compounds ⁽¹⁾ (aldehydes and ketones) in air. The method is specific for formaldehyde but, with modification, at least thirteen other carbonyl compounds can be detected and quantified. It is suitable for determination of formaldehyde and other carbonyl compounds in the concentration range of approximately 1 µg/m³ to 1 mg/m³. The sampling method gives a time-weighted average (TWA) sample. It can be used for long-term [1 h to 24 h, sampled in low flowrate (for example, 0.1 L/min)] or short-term [1 h or under, sampled in high flowrate (for example, 1 L/min)] sampling of air for formaldehyde. This Standard describes a sampling and

analysis procedure for formaldehyde and other carbonyl compounds that involves collection from air onto cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) and subsequent analysis by high performance liquid chromatography (HPLC) with detection by ultraviolet absorption [1], [3].

The procedures described are written specifically for the sampling and analysis of formaldehyde in air using an adsorbent cartridge and HPLC. The method also permits the determination of other aldehydes and ketones collected from air.

This Standard is applicable to the following carbonyl compounds :

Formaldehyde, Crotonaldehyde, *o*-Tolualdehyde, Acetaldehyde, Valeraldehyde, *m*-Tolualdehyde, Benzaldehyde, Isovaleraldehyde, *p*-Tolualdehyde, Propionaldehyde, 2,5-Dimethylbenzaldehyde, Hexanal, Butyraldehyde, Acetone.

Note ⁽¹⁾ Instead of the nomenclature according to International Union of Pure and Applied Chemistry (IUPAC) regulations, the more common names are used in this Standard.

Names used in this Standard	Names by the nomenclature according to IUPAC
formaldehyde	: methanal
acetaldehyde	: ethanal
acetone	: 2-propanone
butyraldehyde	: butanal
crotonaldehyde	: 2-butenal
isovaleraldehyde	: 3-methylbutanal
propionaldehyde	: propanal
<i>m</i> -tolualdehyde	: 3-methylbenzaldehyde
<i>o</i> -tolualdehyde	: 2-methylbenzaldehyde
<i>p</i> -tolualdehyde	: 4-methylbenzaldehyde
valeraldehyde	: pentanal

Remarks : The International Standard corresponding to this Standard is as follows.

In addition, symbols which denote the degree of correspondence in the contents between the relevant International Standard and JIS are IDT (identical), MOD (modified), and NEQ (not equivalent) according to ISO/IEC Guide 21.

ISO 16000-3 : 2001 *Indoor air—Part 3 : Determination of formaldehyde and other carbonyl compounds—Active sampling method* (MOD)

2 Normative references The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. If the indication of the

year of coming into effect is given to these referred standards, only the edition of the indicated year constitutes the provision of this Standard but the revision and amendment made thereafter do not apply. The normative references without the indication of the year of coming into effect apply only to the most recent editions (including amendments).

JIS A 1960 *Indoor air—General aspects of sampling strategy*

Remarks : ISO/DIS 16000-1 : 2001 *Indoor air—Part 1 : General aspects of sampling strategy* is equivalent to the said standard.

JIS A 1961 *Indoor air—Sampling strategy for formaldehyde*

Remarks : ISO/DIS 16000-2 : 2001 *Indoor air—Part 2 : Sampling strategy for formaldehyde* is equivalent to the said standard.

JIS A 1963 *Indoor air—Determination of formaldehyde—Diffusive sampling method*

Remarks : ISO/DIS 16000-4 : 2001 *Indoor air—Part 4 : Determination of formaldehyde—Diffusive sampling method* is equivalent to the said standard.

JIS K 8180 *Hydrochloric acid*

JIS K 8223 *Perchloric acid*

JIS K 8480 *2,4-Dinitrophenylhydrazine*

JIS K 8872 *Formaldehyde solution*

JIS Q 17025 : 2000 *General requirements for the competence of testing and calibration laboratories*

Remarks : ISO/IEC 17025 : 1999 *General requirements for the competence of testing and calibration laboratories* is equivalent to the said standard.

JIS Z 9900 : 1994 *Quality management and quality assurance standards Part 1 : Guidelines for selection and use*

Remarks : ISO 9000-1 : 1994 *Quality management and quality assurance standards—Part 1 : Guidelines for selection and use* is equivalent to the said standard.

ISO 9000-2 : 1997 *Quality management and quality assurance standards—Part 2 : Generic guidelines for the application of ISO 9001, ISO 9002 and ISO 9003*

EN 45001 : 1989 *General criteria requirements for the operation of testing laboratories*

3 Principle This Standard 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 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 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 Standard 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 Standard. 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.

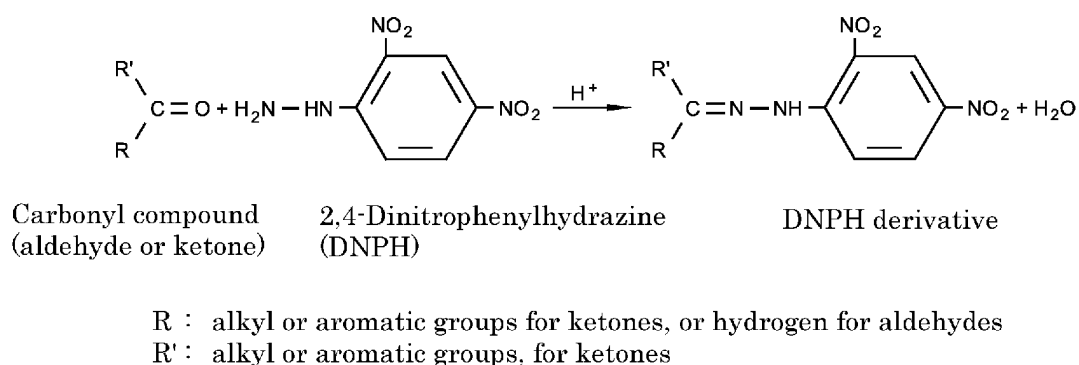


Figure 1 Reaction of carbonyl compounds

4 Limitations and interferences

4.1 General The sampling flowrate, as described in this Standard, has been validated for sampling rates up to 1.5 L/min. This flowrate 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 personal sampling pumps.

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. Organic compounds that have the same retention times and significant absorbance at 360 nm as the DNPH derivative of formaldehyde will interfere. Such interferences can often be overcome by altering the separation conditions (for example, 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 acetonitrile for ultraviolet absorption measurement and high performance liquid chromatography. 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 secondary artefacts and should be avoided [4].

This method cannot be used for accurate quantification of acrolein in air. Inaccurate results for acrolein may result from the formation of multiple derivative peaks and the instability of the peak ratios [9].

NO₂ reacts with DNPH. High concentrations of NO₂ (for example, for gas cooking stoves) may cause problems as the retention time of the nitro—DNPH derivative may be similar to that of the formaldehyde—DNPH derivative, depending on the HPLC column and the parameters [14], [15], [16].

4.2 Ozone interference If there is suspicion that abnormally high levels of ozone may be 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 [5]. 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/m³ and 80 µg/m³, respectively) [6]. 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 may 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 0.64 cm outside diameter by 0.46 cm inside diameter copper tubing, 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 described is about 200 µg ozone/m³ 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 [7]. 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 [8].

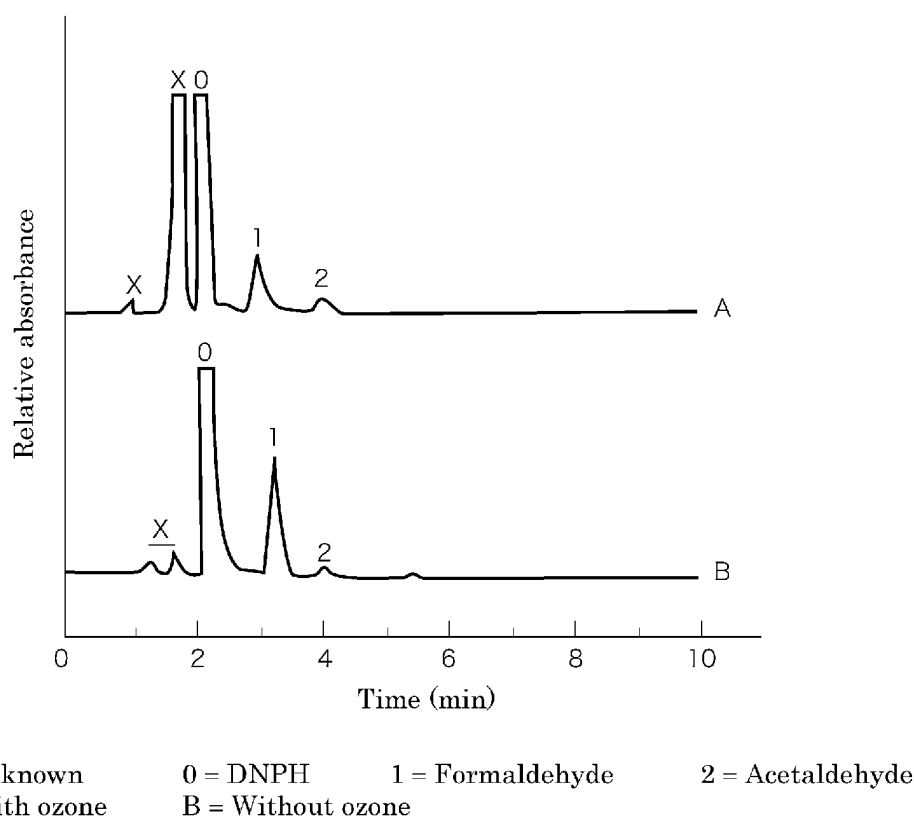


Figure 2 Example of chromatogram of an air stream with and without ozone in sampling cartridge

5 Safety measures This clause does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2,4-Dinitrophenylhydrazine is explosive in the dry state and shall be handled with extreme care. It is also toxic (LD 50, rat = 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.

6 Apparatus Ordinary laboratory apparatus.

6.1 Sampling

6.1.1 Sampling cartridge Packed with silica gel and coated with DNPH in accor-

dance with clause 8 and also available commercially. For example, the cartridge shall contain a minimum quantity of 350 mg of silica gel coated 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 may exhibit lower pressure-drops, which will permit the use of battery-operated personal sampling pumps.

6.1.2 Air sampling pump Capable of accurately and precisely sampling at a flowrate of 0.1 L/min to 1.5 L/min.

6.1.3 Flow controller Mass flowmeters and mass flow controllers or other suitable device for metering/setting air flowrate of 0.50 L/min to 1.20 L/min through sample cartridge.

6.1.4 Flow calibrator Such as a rotameter, soap-bubble meter or wet test meter.

6.2 Sample preparation

6.2.1 Cartridge containers Borosilicate glass culture tubes (20 mm by 125 mm) with polypropylene screw caps or other suitable containers to transport coated cartridges.

6.2.2 Polyethylene gloves To handle silica gel cartridges.

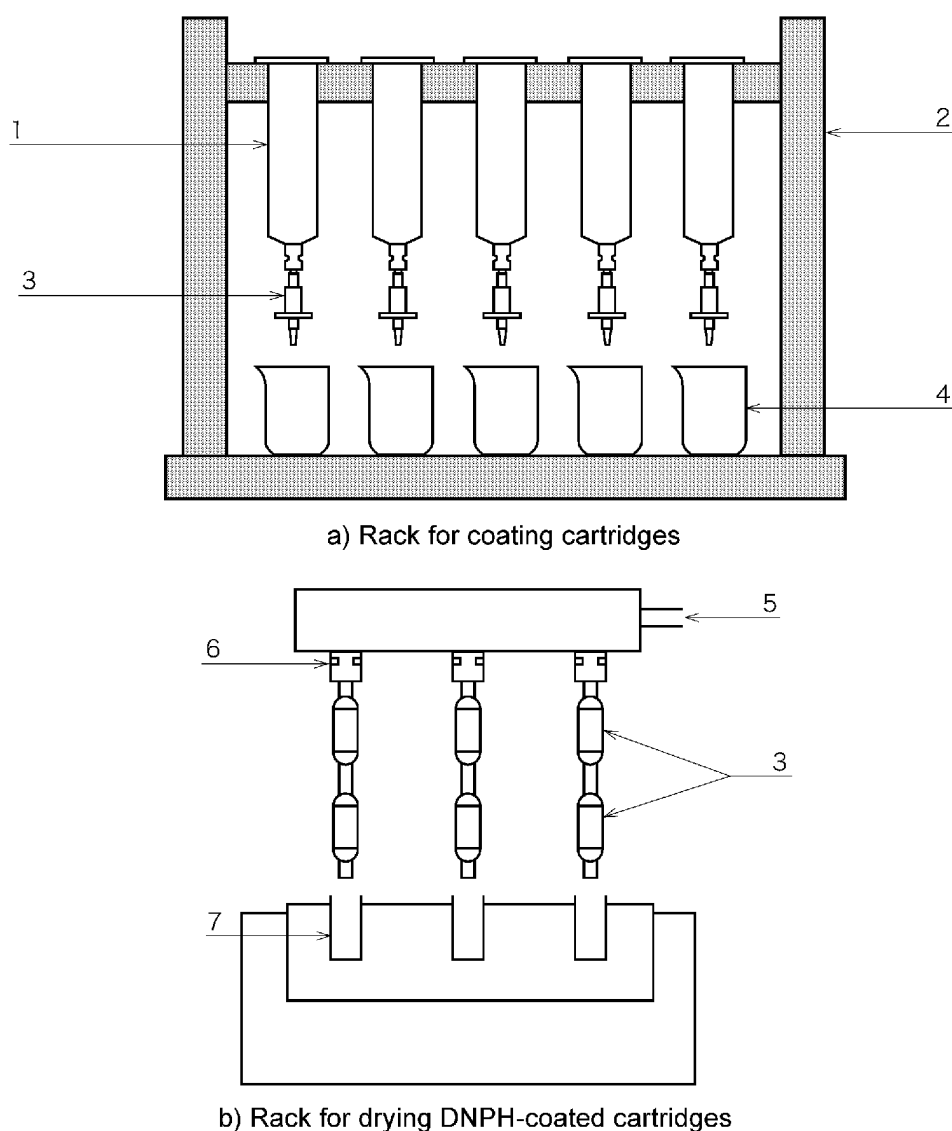
6.2.3 Transportation containers Friction-top metal cans (e.g. of volume 4 L) or other suitable containers, with polyethylene air-bubble packing or other suitable padding to hold and cushion the sealed cartridge containers.

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

6.2.4 Support for coating cartridges Such as a syringe rack, made from an aluminium plate (0.16 cm × 36 cm × 53 cm) with adjustable legs on four corners (see figure 3). A matrix (5 × 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).

6.2.5 Cartridge-drying manifold Such as a support with gas connectors and with multiple standard male syringe connectors (see figure 3).

NOTE : The apparatus described in 6.2.4 and 6.2.5 are needed only if the user chooses to make his own DNPH-coated cartridges.



Designation

1	10 ml glass syringes	2	Test tube rack	3	Cartridges	4	Waste beakers
5	N ₂ gas stream	6	Syringe fitting	7	Waste vials		

Figure 3 Syringe rack for coating and drying sample cartridges

6.3 Sample analysis

6.3.1 HPLC system This system consists of a mobile phase reservoir ; a high-pressure pump ; an injection valve (automatic sampler with a 25 µl or other convenient loop volume) ; a C18 reverse phase (RP) column (length : 25 cm, inside diameter : 4.6 mm, particle size : 5 µm) ; a UV detector or diode array detector operating at 360 nm ; and 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.

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

2 There is no description of installation of a column thermostat bath in ISO Standard, however, it is desirable to install a column thermostat bath.

6.3.2 Syringes and pipettes

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

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

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

6.3.2.4 Pipettes Positive-displacement, repetitive-dispensing, with capacities in the 0 ml to 10 ml range.

7 Reagents

7.1 2,4-Dinitrophenylhydrazine Specified in JIS K 8480 recrystallized at least twice with acetonitrile for ultraviolet absorption measurement or high performance liquid chromatography before use.

7.2 Acetonitrile For ultraviolet absorption measurement or high performance liquid chromatography (each batch of solvent should be tested before use).

7.3 Water For high performance liquid chromatography (distilled water).

7.4 Perchloric acid 60 % (wt/wt), 1.51 kg/L in density specified in JIS K 8223.

7.5 Hydrochloric acid 36.5 % to 38 % (wt/wt), 1.19 kg/L in density, guaranteed reagent specified in JIS K 8180.

7.6 Formaldehyde 37 % solution (wt/wt) specified in JIS K 8872.

7.7 Aldehydes and ketones High purity, used for the preparation of DNPH derivative standards (optional).

7.8 Ethanol or methanol Equivalent to that for high performance liquid chromatography.

7.9 Nitrogen High purity grade [at least 99.999 % (wt/wt)].

7.10 Activated carbon Granular (the best source).

7.11 Helium High purity grade [at least 99.999 % (wt/wt)].