DETERMINATION OF VOLATILE ALDEHYDES IN AMBIENT AIR Air sampling and analysis	Page 1 of 11 AM-01

Replaces:	Dated:	Author:	Date:	AM-No.:
New	New	Nils Arne Jentoft	18.06.2014	AM-01

0 CHANGES

This procedure is new.

1 SCOPE

This document describes a procedure for the determination of volatile aldehydes (esp. formaldehyde and acetaldehyde) in workplace air acc. to Occupational Exposure Limits (OEL) and Short-Term Exposure Limits (STEL). The procedure can also be used for monitoring indoor air, emission to the atmosphere or in the exhaust air of an emission test chamber.

The method is based on chemosorption of volatile aldehydes with 2.4-dinitro-phenylhydrazine impregnated silica tubes or cartridges with subsequent solvent desorption, clean-up and liquid chromatographic analysis. The method permits measurement of several aldehydes including formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, isovaleraldehyde, hexanal, benzaldehyde, 2,5-dimethylbenzaldehyde, tolualdehydes, crotonaldehyde in the concentration range of approximately 1 µg/m³ to 1 mg/m³ depending on air sampling flow rate and duration (see ISO 16000-3).

2 PRINCIPLE

A sufficient volume of air is sucked through a silica gel tube or cartridge impregnated with DNPH reagent with an appropriate air flow rate. Any aldehyde and other carbonyl compounds present will react to form non-volatile dinitrophenylhydrazones (in the following: DNPH). Desorption is done with acetonitrile. The resulting solution is analysed using high performance liquid chromatography (HPLC) with ultraviolet (UV) detection. The DNPH peaks from formaldehyde, acetaldehyde and other aldehydes are identified on the basis of both their respective retention times and their UV responses and comparison with a derivative product (where available) or standard. Quantification is done by comparison with a relevant aldehyde or a DNPH standard.

3 APPARATUS AND CHEMICALS

3.1. Apparatus

3.1.1 Sampling cartridge

Commercially available tubes or cartridges filled with DNPH coated silica.

Note: Waters Sep-Pak DNPH Silica Cartridge, Part No WAT037500, is suitable for this application.

3.1.2 Sampling pump

A proper air sampling pump capable of a flow rate of 50 – 200 ml per minute. For indoor air or emission chamber sampling flow rates of 1 – 2 litre per minute might be appropriate.

Note: SKC Workhorse, Part No 222-3, is well suited for stationary as well as personal occupational hygiene sampling (see Appendix 1).

3.1.3 Tubing

Tubing of appropriate diameter to ensure a leak-proof fit to both pump and sample tube. Silicon or Tygon tubing is appropriate.

Note: If there is a need for tubing upstream of the sorbent tube, PTFE, glass or stainless steel shall be applied to avoid loss of substance due to reaction with tubing walls.

3.1.4 Flow meter calibrator

Bubble flow meter or other appropriate suitable device for gas flow calibration.

3.1.5 High performance liquid chromatograph (HPLC)

A typical apparatus for HPLC, with ultraviolet (UV) detector. An example of a typical elution profile is given in Appendix 2.

3.2. Chemicals

3.2.1 Acetonitrile

HPLC grade.

3.2.2 Water

HPLC grade.

3.2.3 Standards

Commercially available DNPH-aldehyde derivatives (or their solution(s) in acetonitrile).

If the DNPH-aldehyde derivatives are prepared in the laboratory, the respective reagents described in ISO 16000-3 shall be used.

4 PROCEDURE

4.1. Air sampling

Open the sealed tubes or remove the caps from the sampling cartridge and assemble the sampling line. An example of a typical sampling setup is shown in Appendix 1.

At the end of the sampling period disconnect the sampling cartridge from the sampling line and seal both ends using inert caps. For further details, see ISO 16000-2 and the manual of the specific adsorbent used.

All relevant sampling information MUST be registered. Attached form can be used (see Appendix 3).

Note 1: The recommended sampling flow rate is in the range of 50 – 200 mL/min.

Note 2: The OEL is normally based on 8 hours exposure, whilst STEL is based on 15 minutes exposure. Therefore occupational hygiene sampling times must be adjusted accordingly.

Note 3: To control sampling efficiency, two sampling cartridges can be coupled in series with the downstream sampling cartridge serving as a control section, unless a sampling cartridge with a sampling section and a control section is used.

4.2 Storage of loaded sampling cartridges

Store each sampling cartridge sealed and isolated from sources of volatile aldehydes. Store the sampling cartridges at a temperature below 10°C and protected from light. The time between sampling and analysis shall be as short as possible and shall not exceed 14 days.

4.3 Blanks

It is recommended to run blanks at least once per batch of sampling cartridge or adsorbent to define the background level for aldehydes.

Take one sampling cartridge equivalent to the ones used for sampling. Subject the blank samples to the same handling procedure in the laboratory as the actual samples except for the actual period of sampling, i.e. repeat the sampling procedure up to the point of actual sample collection. Do not perform sampling but repeat normal post-sampling procedure for the sampling tubes. Mark, store, and analyse blank samples in sequence with the actual samples.

4.4 Analysis

4.4.1 Cleaning of glassware

Before use, clean all glassware to remove any residual grease or chemicals by soaking overnight in laboratory detergent solution and then rinsing thoroughly with water. Alternatively, use a laboratory washing machine.

4.4.2 Sample cartridges desorption

Desorb samples and blanks by slowly passing a small amount of acetonitrile through the cartridges as described in ISO 16000-3.

4.4.3 Standard solutions

Prepare standard solutions in the analytical range of interest from commercially available DNPH-aldehyde derivatives (or their solution(s) in acetonitrile), or from self-produced DNPH-aldehyde derivatives as described in ISO/DIS 16000-3. Store all standard solutions in tightly capped containers in a refrigerator and protected from light. Allow them to equilibrate to room temperature before use. They should be replaced after four weeks.

4.4.4 Calibration of liquid chromatograph

Calibrate the system by injecting a known fixed volume (e.g. 25 µl) of at least five standard solutions covering the analytical range of interest into the liquid chromatograph using UV detection as described below. A standardised injection technique is required to obtain reproducible peak heights/areas. Prepare a calibration graph of UV response versus analyte concentration in the standard solutions as described in ISO 16000-3.

Once linear response (correlation coefficient of at least 0.999 for response versus concentration) has been documented, an intermediate concentration standard near the anticipated levels of component, but at least ten times the detection limit, should be chosen for daily calibration.

The day to day response of the analytical system for the various components shall be registered on a control card or in a corresponding electronic data system and should be within 20 %. If greater variability is observed the system shall be checked, re-calibrated, and fresh standards shall be prepared.

4.4.5 Analysis of desorbed sample solutions

Inject a known fixed volume of the desorbed sample solution into the liquid chromatograph. Determine the UV response at the retention times being specific for the respective DNPH-aldehyde derivatives and read the concentration of the analyte in the sample from the calibration graph. Analyse the sample blank in the same way.

Note: A variety of chromatographic conditions may be used for the analysis of volatile aldehydes in solution (see Appendix 2). The choice will depend largely on the nature of interfering compounds, which may affect the chromatographic analysis. Typical conditions are:

Column dimensions	100 mm length x 4.6 mm ID
Column packing	Reverse Phase C18
Mobile phase	Acetonitrile / Water, linear gradient (see Appendix 2)
Flow rate	1 mL/min
UV detector	360 nm (and/or diode array detector if available)

5 IDENTIFICATION AND CALCULATIONS

5.1 Identification of aldehydes

A positive identification can be assumed if the retention time of a peak corresponds to the retention time of the DNPH-aldehyde derivative standard compound.

Note: For a more secure identification of the aldehydes, analyse the samples with the UV detector operating at one wavelength and scan full UV spectra for all detected compounds. Alternatively, operation at two wavelengths may be used. A positive identification can be assumed if both the UV spectrum in the chromatogram and a standard spectrum of a DNPH-aldehyde derivative match to a high degree and if the retention time corresponds to the retention time of the DNPH-aldehyde derivative standard compound.

5.2 Concentration of analytes in the sampled air

Calculate the volume, V_S, in litres, of each air sample. Calculate the aldehyde concentration c in the sample (in µg/mL), by comparison with standard solutions as described in ISO 16000-3. Correct for blanks as follows:

$$C_m = (c_{sample} - c_{blank}) \times V_d / V_s$$

where:

C_m is the concentration of analyte in the air sample, in mg/m³

c_{sample} is the total concentration of analyte in the sample (all sections/tubes/cartridges in series), µg/mL

c_{blank} is the concentration of analyte in the blank, µg/mL

V_s is the volume of air sampled, in litres;
V_d is the desorption volume, in mL

Conversion of mg/m³ to ppm:

1 ppm = 1 mg/m³ x 24,45 / MW

Where:
24,45 = the molar gas volume at 25 °C and 760 mm Hg
MW = the molar weight of the relevant aldehyde

6 LIMIT OF DETECTION (LOD) AND LIMIT OF QUANTIFICATION (LOQ)

The LOD and LOQ for the air concentrations will depend on the sampled air volumes. For formaldehyde and Waters Sep-Pak 2,4-DNPH, the following example is valid:

Long term (6 hrs / 60 L air): LOD = 0,0005 ppm, LOQ = 0,002 ppm

Short term (15 minutes / 2,5 L air): LOD = 0,01 ppm, LOQ = 0,05 ppm

7 INTERFERENCES

Since a range of aldehydes and ketones will react with the 2,4-DNPH reagent, the procedure should be checked for possible interference. If there are overlapping peaks the chromatographic conditions should be optimised accordingly. One example of frequently interfering compounds are acetone and acrolein.

Note: Exposure of the DNPH-coated cartridges to direct sunlight may cause degradation and should be avoided.

8 PRECISION AND BIAS

Determine the repeatability and the accuracy of this method as part of method validation, preferably by sampling from known atmospheres of ppb level. If a laboratory has no access to such atmospheres, repeatability shall be determined by repeated sampling from a constant atmosphere. Accuracy can be determined by analysing commercially available control or reference samples.

Note: The uncertainty of the analytical method has been determined as 6 to 12 % for formaldehyde and 12 to 15 % for acetaldehyde with the higher uncertainty at lower levels.

9 TEST REPORT

The test report shall include:

a) A reference to this procedure
b) The purpose of the measurement
c) The time and date of the sampling
d) A description of the sampling procedure, esp. the sampling duration
e) A description of the analytical procedure
f) The sampled air volume in litres
g) The concentrations of identified compounds

10 REFERENCES

1. ISO 16000-1:2004; Indoor air - Part 1: General aspects of sampling strategy.

2. ISO 16000-2:2004; Indoor air - Part 2: Sampling strategy for formaldehyde.

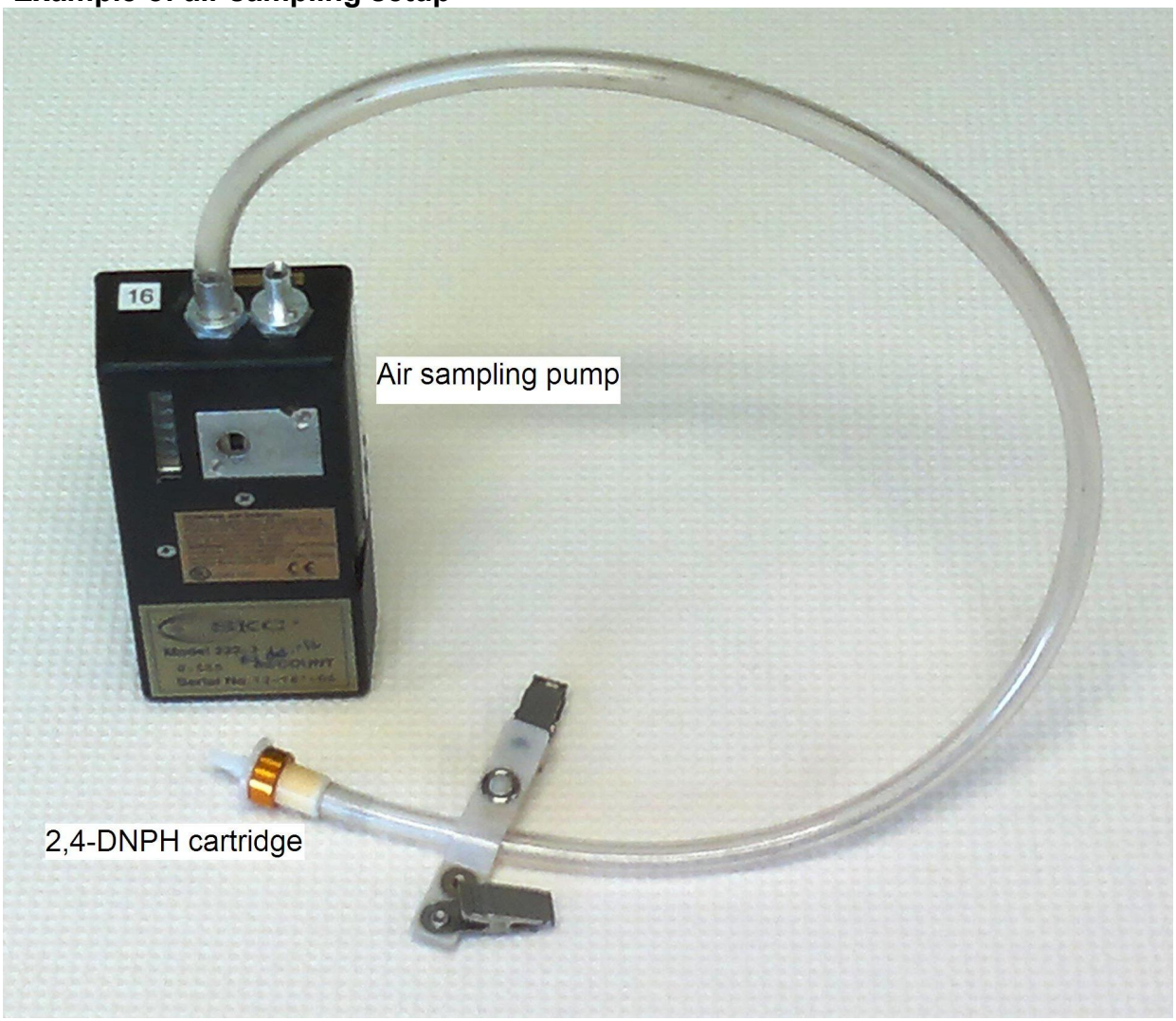
3. ISO 16000-3:2001; Indoor air - Part 3: Determination of formaldehyde and other carbonyl compounds - Active sampling method.

4. ENV 13999-3; Adhesives - short term method for measuring the emission properties of low-solvent or solvent-free adhesives after application. Part 3 - Determination of volatile aldehydes

5. US EPA Method TO-11A; Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography.

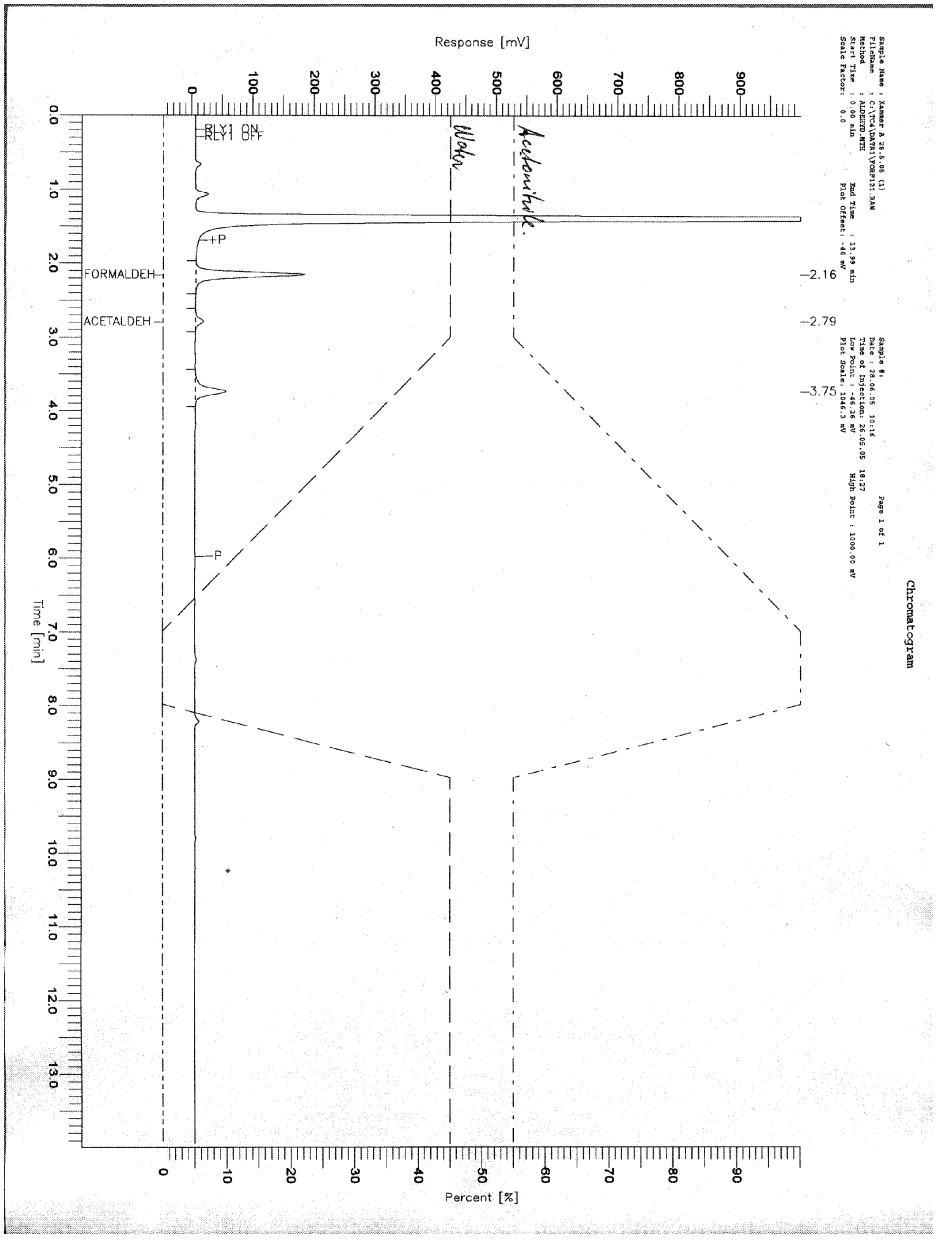
Appendix 1

Example of air sampling setup



Appendix 2

Example of gradient elution profile



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Appendix 3

Occupational Hygiene Monitoring Sampling Form

Date ✸ .....

Place/Company ✸ .....

Weather conditions Outdoor temp (°C) ..... Pressure (mb) .....

Sunny/cloudy/rain .....

Indoor climate Temperature (°C) ..... Relative humidity (% RH) .....

Work operation ✸ .....

Compounds ✸ .....

❑ **Stationary sampling** ✸ Location .....

.....

❑ **Personal sampling** ✸ Name .....

Department .....

Sampling data

Pump no. ✸ ..... Flow (ml/min) .....

Adsorbent ..... Sample/Adsorbent no. ✸ .....

Sampling, start ✸ ..... Counter, start ✸ .....

Sampling, stop ✸ ..... Counter, stop ✸ .....

Air volume (l) ..... Net sampling time (min) .....

Information marked ✸ MUST BE filled in

Performed by (sign/date) .....