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# Workplace air — Chemical agent present as a mixture of airborne particles and vapour — Requirements for evaluation of measuring procedures using samplers

*Air des lieux de travail — Agent chimique présent sous forme de mélange de particules en suspension dans l'air et de vapeur — Exigences d'évaluation des procédures de mesure utilisant des dispositifs de prélèvement*

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# Contents

# Foreword

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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).

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This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 137, *Assessment of workplace exposure to chemical and biological agents,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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 document provides a framework for assessing the performance of procedures for measuring a chemical agent present as a mixture of airborne particles and vapour against the general requirements for the performance of procedures for measuring chemical agents in workplace atmospheres as specified in ISO 20581.

This document enables manufacturers, users of samplers, developers and users of procedures for measuring a chemical agent present as a mixture of airborne particles and vapour to adopt a consistent approach to method validation.

This document is based on EN 13936.

# Workplace air — Chemical agent present as a mixture of airborne particles and vapour — Requirements for evaluation of measuring procedures using samplers

## 1 Scope

This document specifies requirements for the evaluation of measuring procedures using samplers for the determination of a chemical agent present in the workplace atmosphere as a mixture of airborne particles and vapour.

The procedures given in this document provide results only for the sum of airborne particles and vapour. The concentration is calculated in terms of mass per unit volume.

NOTE The physical behaviour of a mixture of airborne particles and vapour is described in Annex A. Examples of substances which can be present in multiple phases are toluene diisocyanate, diethanolamine, ethyleneglycol and tributylphosphate.

This document can also be applied to complex mixtures, such as metal working fluids or bitumen fumes.

This document is applicable to samplers and measuring procedures using these samplers in which sampling and analysis are carried out in separate stages.

## 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 7708, *Air quality — Particle size fraction definitions for health-related sampling*

ISO 13137, *Workplace atmospheres — Pumps for personal sampling of chemical and biological agents — Requirements and test methods*

ISO 18158, *Workplace air — Terminology*

ISO 20581, *Workplace air — General requirements for the performance of procedures for the measurement of chemical agents*

ISO 21832, *Workplace air — Metals and metalloids in airborne particles — Requirements for evaluation of measuring procedures*

ISO 22065:2020, *Workplace air — Gases and vapours — Requirements for evaluation of measuring procedures using pumped samplers*

EN 13205-1, *Workplace exposure — Assessment of sampler performance for measurement of airborne particle concentrations — Part 1: General requirements*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18158 and the following apply.

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

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

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

**3.1**
**mixed-phase sampler**
sampler or sampling train that is used to collect airborne particles and vapours onto one or more collection substrates

[SOURCE: ISO 18158:2016, 2.2.2.1.7, modified — the given cross-references have been removed.]

**3.2**
**joint extraction mode**
procedure that simultaneously extracts and analyses all collection substrates contained in the *mixed-phase sampler* (3.1), resulting in a unique quantification of the analyte for each air sample

**3.3**
**separate extraction mode**
procedure that separately extracts and analyses the collection substrates contained in the *mixed-phase sampler* (3.1), resulting in multiple quantifications for each air sample that are summed to give the final result

## 4 Symbols and abbreviated terms

NOTE For symbols used for calculation of combined standard uncertainty see C.2.

| | |
|---|---|
| U.S. EPA | is the United States environmental protection agency |
| $k$ | is the coverage factor |
| $K_\mathrm{v}$ | is the coefficient of variation |
| LV | is the limit value |
| $m_\mathrm{min}$ | is the minimum mass which shall be quantified |
| $m_\mathrm{p}$ | is the mass determined on the collection substrate for airborne particles, in milligrams; |
| $m_\mathrm{v}$ | is the mass determined on the collection substrate for vapour, in the same unit as for $m_\mathrm{p}$. |
| $N$ | is the number of extractions realized to analyse all collection substrates, control sections excluded |
| $Q$ | is the recommended air flow rate of the mixed-phase sampler |
| $R_\mathrm{an}$ | is the analytical recovery |
| RH | is the relative humidity |
| SVOC | is a semi-volatile organic compound |
| $t_\mathrm{min}$ | is the minimum sampling time |
| $u_c$ | is the combined standard uncertainty |
| $U$ | is the expanded uncertainty |
| $\gamma_\mathrm{d,p}$ | is the distribution coefficient for airborne particles, in percentage; |
| $\gamma_\mathrm{d,v}$ | is the distribution coefficient for vapour, in percentage; |
| $\rho_\mathrm{LV}$ | is the limit value considered |
| $x$ | is the fraction of LV |

# 5 Sampler types

Samplers are classified based on differences in the collection substrate because of differences in the analytical procedures.

Where the vapour phase is collected on a sorbent bed, the mixed-phase sampler is classified as type A sampler.

Where the vapour phase is collected on an impregnated filter, the mixed-phase sampler is classified as type B sampler.

NOTE Other systems, for example denuder and filter or impinger and filter, can be used alternatively for specific chemical agents. See Annex B.

# 6 Requirements

## 6.1 General

The measuring procedure used shall comply with the requirements of ISO 20581 and those clauses of ISO 13137, ISO 21832, ISO 22065 and EN 13205-1 which apply.

When the use of a sampler for measurement of a particular mixture of airborne particles and vapour is claimed, the sampler shall meet the requirements specified in 6.2. Measuring procedures shall meet the requirements specified in 6.3.

Known or suspected interferences as well as the results of any tests performed to evaluate interferences, including suitable and sufficient information to minimize their effects shall be presented in the method description as required by 6.3.4.

## 6.2 Sampler requirements

### 6.2.1 General

The sampler shall comply with the general requirements given in EN 13205-1 and with the performance requirements for pumped samplers prescribed in ISO 22065:2020, 6.2.2 to 6.2.6.

### 6.2.2 Flow resistance and stability of the air flow

The back pressure of the mixed-phase sampler shall not exceed the maximum values specified for the pump performance test in ISO 13137, unless the combination of mixed-phase sampler and pump has been tested and shown to be able to sample for the required sampling period.

The air flow through the sampling train associated with the pump shall be measured over the entire sampling period and not deviate more than 5 % as specified in ISO 13137.

Pumps used with size-selective mixed-phase samplers shall also meet the requirements of the pump pulsation test as specified in ISO 13137.

### 6.2.3 Connecting parts

The volume of any connecting parts between collection substrates within the mixed-phase sampler shall be kept to a minimum and any connection shall be made of an inert material that

- does not retain the chemical agent of interest,
- does not react with the chemical agent of interest,
- does not emit chemical agents that can interfere with the one of interest, and

— is resistant to solvents, if applicable.

### 6.2.4 Pumps

Pumps used in the measuring procedure shall conform with ISO 13137.

## 6.3 Measuring procedure requirements

### 6.3.1 Sampling procedure requirements

#### 6.3.1.1 General

Measuring procedures shall specify the use of a mixed-phase sampler designed to collect the inhalable fraction of airborne particles, as defined in ISO 7708, and vapour.

The requirements specified in ISO 22065:2020, 6.3.1, shall apply according to the types of collection substrates that are used in the mixed-phase sampler.

NOTE Due to the particularity of mixed-phase samplers, some requirements are adapted from ISO 22065 as given in 6.3.1.2 and 6.3.1.3.

#### 6.3.1.2 Air flow rate

For type A samplers, the air flow rate constrained by the particle-size selector of the sampler should not exceed the maximal air flow rate of the sorbent tube. If not, the air flow should be split to achieve this requirement.

For type B samplers, the maximum air flow rate to ensure complete sampling according to ISO 22065:2020, 6.3.1.3.1, shall comply with the air flow rate required by the particle-size selector used.

#### 6.3.1.3 Storage condition after sampling

When tested in accordance with the procedure prescribed in 8.2.2, the mean analytical recovery after storage shall not differ by more than 10 % from the value before storage.

### 6.3.2 Analytical procedure requirements

#### 6.3.2.1 General

The requirements given in ISO 22065:2020, 6.3.2, shall apply according to the types of collection substrates that are used in the mixed-phase sampler.

NOTE Due to the particularity of mixed-phase samplers, some requirements are adapted from ISO 22065 as stated in 6.3.2.2 to 6.3.2.5.

#### 6.3.2.2 Extraction of the collection substrates

The extraction procedure shall ensure that all phases are extracted and presented for analysis of total mass of the analyte(s) of interest.

When collection substrates are extracted and analysed separately, the masses determined on each collection substrate shall not be interpreted as an accurate separation of a particle fraction or vapour fraction as these fractions were not stabilized during the sampling period and thus, transfer can occur between collection substrates.

NOTE A preponderance of analyte on the portion of the sampler intended for either particulate or vapour collection can give valuable guidance regarding the environment and the control measures, including respiratory protection measures, which can be needed for implementation. Samplers which consist of a filter and adsorbent are not able to give an accurate assessment of partition, but samplers have been and are being designed to provide more accurate information.

### 6.3.2.3 Analytical limit of quantification

The analytical limit of quantification shall be lower than or equal to $m_{\text{min}}$. The minimum mass of analyte $m_{\text{min}}$ that would be collected for the minimum air sample volume specified in the measuring procedure at the following concentrations is calculated by Formula (1):

$$m_{\text{min}} = \frac{(x \cdot \rho_{\text{LV}})}{N} \cdot Q \cdot t_{\text{min}} \tag{1}$$

where

$m_{\text{min}}$ is the minimum mass which shall be quantified;

$x$ is the fraction of LV considered as follows:

- $x = 0{,}1$ for substances with long-term limit value, and
- $x = 0{,}5$ for substances with short-term limit value;

$\rho_{\text{LV}}$ is the limit value considered;

$N$ is the number of extractions realized to analyse all collection substrates, control sections excluded;

$Q$ is the recommended air flow rate of the mixed-phase sampler;

$t_{\text{min}}$ is the minimum sampling time.

### 6.3.2.4 Analytical recovery

For extraction when tested in accordance with ISO 22065:2020, 8.3.2.2.3, the analytical recovery $R_{\text{an}}$ shall be ≥75 % with $K_{\text{v}}$ ≤ 10 % at each loading.

The values given for analytical recovery are targets; lower values may be used provided equivalent precision is achieved.

### 6.3.2.5 Blank value

In order to obtain acceptable values for the limit of quantification of the method, the blank values of the collection substrates should be as low as technically possible.

When tested in accordance with ISO 22065:2020, 8.3.2.3, the total of the blank values shall be less than one-tenth of the mass calculated by Formula (1).

NOTE Higher blank values can be allowed provided the requirement of 6.3.2.3 is met.

Where it is known that a blank value is significant and varies between batches of samplers, it shall be checked for each batch.

### 6.3.3 Expanded uncertainty

When tested in accordance with ISO 22065:2020, 8.3, the expanded uncertainty of the measuring procedure as a whole, including the measurement of airborne particles and vapour, shall comply with the requirements of ISO 20581. For the uncertainty budget of the airborne particles, the numbers given for inhalable samplers in ISO 21832:2018, C.3.4, can be used.

When fractions are analysed separately, the expanded uncertainty can be calculated according to Clause C.3.

### 6.3.4 Method description

ISO 22065:2020, 6.3.4, shall apply.

# 7 General test conditions

## 7.1 Reagents

Use only reagents of recognized analytical grade.

## 7.2 Apparatus

Test equipment as stated in ISO 22065:2020, 7.2.2 to 7.2.7, shall be used except for 7.2.3.

NOTE 1 A dynamic system for generating, pre-mixing and delivering a known concentration of a test atmosphere that contains known concentrations of vapour and particles of a semi-volatile compound is technically difficult to obtain compared to a test atmosphere containing only vapour as prescribed in ISO 22065. The apparatus described in ISO 22065:2020, 7.2.3, can be used to generate the test atmospheres of pure air in the climatic conditions required by the tests.

NOTE 2 Test atmospheres generated at high concentrations tend to bias towards the aerosol phase compared to lower concentrations that can be observed in the workplace; therefore, it is important that the concentrations in the test atmosphere are relevant to the sampling situations at workplaces.

# 8 Test methods

## 8.1 Spiking method

### 8.1.1 General

The spiking method allows the deposit of the analyte on the collection substrates under controlled conditions. Only if no standard atmosphere chamber for mixtures of vapour and aerosols is available the spiking method described in 8.1.2 shall be used.

Tests prescribed in 8.2 need the analyte to be spiked on the collection substrates. Due to the semi-volatile characteristic of the analyte, this spiking shall be made as required by 8.1.2 to 8.1.4.

### 8.1.2 Deposit of the analyte on the first collection substrate

#### 8.1.2.1 Type A samplers

The first collection substrate of a type A sampler is a filter. A deposit of the analyte in the form of a spot with micropipette or syringe shall be avoided due to the dramatic reduction of the evaporation surface in comparison with the one presented by the micrometric airborne particles collected on the surface of the filter during the sampling period. If so, the transfer of the analyte from the filter to the sorbent bed will not be realistic.

The analyte shall be deposited on the filter by a syringe with a volume of solution that permits to wet 80 % to 90 % of the front surface of the filter. To do so, the analyte can be diluted in a non-interfering solvent to deliver the appropriate mass of analyte on the collection substrate.

To prevent any loss of the analyte of interest, a volatile solvent should be used that evaporates at room temperature within a short period. If this is not possible, the solvent used shall not interfere with the sorbent bed or the analytical method.

#### 8.1.2.2 Type B samplers

As far as possible, the analyte shall be homogeneously deposited on the impregnated filter to ensure that the analyte can react with the reagent of impregnation.

The analyte can be diluted in a non-interfering solvent to deliver the appropriate mass of analyte on the collection substrate.

### 8.1.3 Deposit of the analyte on the other collection substrates of a type A sampler

During tests regarding the analytical method (see ISO 22065:2020, 8.3.2.1), the analytical recovery (see ISO 22065:2020, 8.3.2.2), the verification of sampler capacity (see ISO 22065:2020, 8.3.1.1) and the subsequent collection substrates of a type A sampler, which are sorbent beds, require to be spiked.

The spiking of those collection substrates may preferentially be realized by adding a known mass of analyte corresponding to the required loading of the corresponding test into a small vessel (e.g. empty sampling tube, pipette reservoir), using a micropipette or syringe. The analyte can be pure or diluted in a solvent (usually the desorption solvent). The vessel shall be heated enough to permit the rapid volatilisation of the mass of analyte deposited inside, while air is sampled from the vessel by pumping onto the collection substrate (recommended flow rate and sampling time shall be used). Check that all the analyte has evaporated after sampling by rinsing the vessel and any connections with desorption solvent and analysing the rinsate.

In the case where this technique is not suitable due to the physical properties of the analyte, the analyte can be spiked directly in the sorbent bed by a micropipette or syringe and diluting in a non-interfering solvent, if necessary.

### 8.1.4 Transfer of the analyte

In function of the extraction method and the type of the sampler, air shall be sampled through the sampler during or after the spike to allow the analyte to be transferred through all the collection substrate as it does during a sampling session.

Whatever the sampler type, the tests regarding the limit of quantification (see ISO 22065:2020, 8.3.2.1), the recovery (see ISO 22065:2020, 8.3.2.2), and the evaluation of the conditions of storage (see ISO 22065:2020, 8.3.1.6.1), require to pump pure air through the samplers at (20 ± 2) °C and a relative humidity of (50 ± 5) % during the recommended sampling time at the recommended flow rate.

The sampler capacity verification test (see ISO 22065:2020, 8.3.1.2) requires pumping pure air through the samplers at the recommended maximum flow rate at (20 ± 2) °C and a relative humidity of (80 ± 5) %.

Table 1 summarizes the spiking and transfer conditions in function of the required tests and the extraction mode used.

**Table 1 — Spiking and transfer conditions in function of the required tests and the extraction mode**

| Tests | Joint extraction mode | | Separate extraction mode | |
|---|---|---|---|---|
| | First collection substrate | Subsequent collection substrates | First collection substrate | Subsequent collection substrates |
| ISO 22065:2020, 8.3.1.2<br>Sampler capacity | Spike and pump air at (20 ± 2) °C and (80 ± 5) %RH | | Spike and pump air at (20 ± 2) °C and (80 ± 5) %RH | |
| ISO 22065:2020, 8.3.1.6.1<br>Storage conditions | Spike | Spike and pump air at (20 ± 2) °C and (80 ± 5) %RH | Spike | Spike and pump air at (20 ± 2) °C and (80 ± 5) %RH |
| ISO 22065:2020, 8.3.2.1<br>Limit of quantification | Spike and pump air at (20 ± 2) °C and (50 ± 5) %RH | | Spike | Spike and pump air at (20 ± 2) °C and (50 ± 5) %RH |
| ISO 22065:2020, 8.3.2.2<br>Analytical recovery | Spike | Spike and pump air at (20 ± 2) °C and (50 ± 5) %RH | Spike | Spike and pump air at (20 ± 2) °C and (50 ± 5) %RH |

The temperature chosen should be a temperature considered normal for workplaces and this can vary from the recommended temperature given in ISO 22065.

## 8.2 Evaluation of measuring procedures

### 8.2.1 General

Perform the tests given in ISO 22065:2020, Clause 8, using the procedure and conditioned air prescribed in 8.1 rather than sampling a known concentration of vapour as required in ISO 22065, except for the storage test (see 8.2.2).

### 8.2.2 Storage after sampling

Perform storage tests on samples according to ISO 22065:2020, 8.3.1.6.1, then stabilize the collection substrate as prescribed in the sampling method and verify that the analytical recovery determined from the combined results from the collection substrate for airborne particles and the collection substrate for vapour meets the requirements of 6.3.1.3.

Multiple methods can be used and combined as needed to stabilize the analyte on the collection substrates (see also B.6):

- close without leakage the sampler train, allowing vapour to be passively collected on sorbent bed or impregnated collection substrate,
- close without leakage each collection substrates individually,
- cool the collection substrates below 4 °C,
- transfer the analyte collected on the first filter of a type A sampler to the sorbent bed by pumping additional pure air through the sampler train, until complete transfer, and
- extract the analyte right after the sampling session.
- place in a black box in case of photo-sensitive analyte.

## 8.3 Uncertainty of the measurement

### 8.3.1 Calculation of the combined standard uncertainty

Calculate the combined standard uncertainty $u_c$ taking into account the relevant uncertainty components associated with airborne particles and vapour, according to Annex C.

### 8.3.2 Calculation of the expanded uncertainty

Calculate the expanded uncertainty of the measuring procedure, $U$, using a coverage factor $k$ = 2, according to Formula (2):

$$U = 2 \times u_c \tag{2}$$

# 9 Test report

The test report shall contain at least the following information:

a) a reference to this document, i.e. ISO 23861:2022;

b) detailed description and identification of the sampling system components tested, including all collection substrates and for commercial devices name of manufacturer(s) and product identification(s);

c) complete identification of test atmospheres used plus details of independent measuring methods, where used;

d) details of the pump(s) used for testing;

e) details of analytical methods used for testing;

f) determined values for recovery efficiency, blank value, sampler capacity and storage losses;

g) statistical analyses of the test results and calculations of expanded uncertainty;

h) statement of whether the acceptance criteria are met;

i) any unusual features noted during the determinations;

j) any operations not included in this document that can have influence on the results;

k) the technical justification for omitting or altering any of the tests, if done;

l) the date of test report and testing period.

# Annex A
(informative)

# Physical behaviour of a mixture of airborne particles and vapour

## A.1 Generation of a mixture of airborne particles and vapour

The behaviour of a mixture of airborne particles and vapour at workplace air has been studied (see Reference [1] to [3]). Theoretical models which can calculate the behaviour of such a mixture can be found in the literature, but they are limited to the conditions underlying the mixture which are unknown in most cases of workplace atmospheres.

Semi-volatile compounds are present as a mixture of airborne particles and vapour in workplace air. It is essential that the physical characteristics of the chemical agent of interest are investigated to characterize the state of the chemical agent at the workplace. Even if semi-volatile compounds have low vapour pressure at room temperature, volatility increases with increasing process temperature, so that the process can result in forming aerosol-vapour mixtures. The sampling of a mixture of airborne particles and vapour is strongly influenced by the sampling conditions (e.g. sampling time, flow rate) and environmental conditions (temperature and pressure).

At room temperature, most semi-volatile compounds are liquids but there are also solids with a significant vapour pressure (e.g. arsenic trioxide). At room temperature, semi-volatile compounds normally have quite a low vapour pressure; nevertheless, the way in which a compound is used in the workplace can result in forming droplet-vapour-mixtures. There are two principal mechanisms by which a mixture of airborne particles and vapour is formed:

— A: partial evaporation of chemical agents used as a liquid or solid;

EXAMPLE 1 Processes in which liquids are nebulised during the machining of metals, ceramics etc., processes in which mists are generated by gas-bubbles breaking on the surface of liquids (e.g. electroplating) and liquid spraying processes (e.g. paint spraying).

— B: condensation of a chemical agent in thermal processes in which a semi-volatile compound evaporates and, subsequently cools down to ambient temperature.

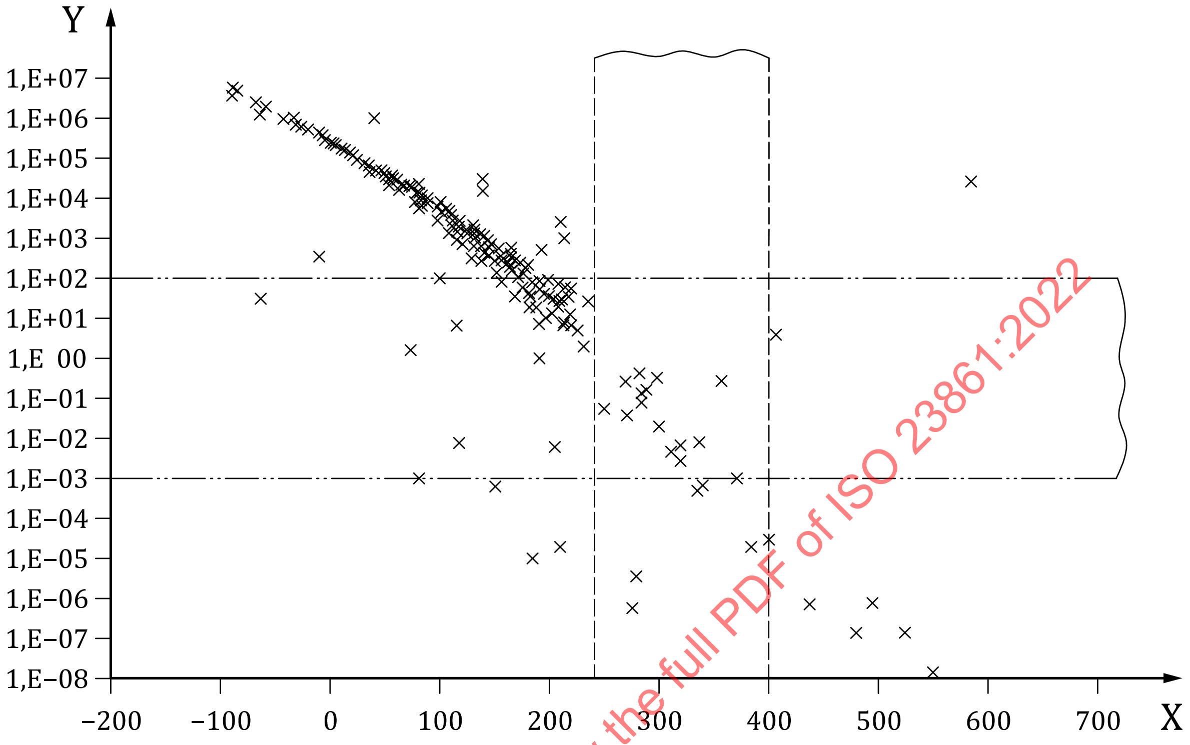
EXAMPLE 2 Hot bitumen application, laser cutting and metalworking processes.

## A.2 Theoretical identification of the semi-volatile behaviour of a chemical agent

There is no generally accepted definition of semi-volatile compounds. The U.S. EPA defined a semi-volatile organic compound (SVOC) as a compound having a boiling point ranging from 240 °C to 400 °C. The advantage of this definition is that boiling point is available for almost all compounds present in the workplace atmospheres. EN 13936 defined a SVOC with the vapour pressure of the compounds, ranging from 0,001 Pa to 100 Pa. The advantage of this definition is that saturated vapour pressure is the real parameter that governs the evaporation of a chemical agent rather than the boiling point. Disadvantage is that the vapour pressure is not available for many substances. EN 13936 also indicates that this corresponds to a range for the boiling point from about 180 °C to about 350 °C.

Figure A.1 presents the saturated vapour pressure of 254 compounds registered in the Metropol database (see Reference [8]), according to their boiling point. Volatile compounds show a good correlation between those parameters. As the volatility decreases, this correlation becomes less clear, likely resulting from the difficulty of making measurements of low vapour pressure.

Experience in recent years has shown that the limits for vapour pressure originally set in EN 13936 were well chosen for semi-volatile materials, but that the limits for the boiling point range are too broad. From the literature, it can be derived that significant amounts of droplet-vapour-mixtures only occur from a boiling temperature of about 200 °C and that substances with boiling points above 320 °C at room temperature only have a low vapour content.



**Key**

| | |
|---|---|
| X | boiling point at atmospheric pressure, in °C |
| Y | saturated vapour pressure at 20 °C to 25 °C, in Pa |
| _ _ _ _ _ | temperature range for semi-volatile compounds according to the U.S. EPA |
| ___.·.___ | saturated vapour pressure range for semi-volatile compounds according to EN 13936 |
| × | compound (data point) |

**Figure A.1 — Saturated vapour pressure in function of the boiling point of 254 compounds registered in the Metropol database** (see Reference [8])

## A.3 Experimental determination of the semi-volatile behaviour of a chemical agent

### A.3.1 General

When saturated vapour pressure is not available in the literature, the theoretical considerations above cannot be applied. Thus, an experimental protocol is proposed to determine if a chemical agent should be sampled and collected as a mixture of particles and vapour or not.

### A.3.2 Sample distribution between the collection substrate for airborne particles and the collection substrate for vapour

**A.3.2.1** Calculate the mass of analyte to be loaded onto the collection substrates in the sample distribution tests for each combination of concentration and time prescribed in Table A.1.

**Table A.1 — Concentration and time used for calculation of mass of analyte**

| Reference period | Concentration | Time |
|---|---|---|
| long-term | 0,1-times limit value | 8 h or recommended sampling time |
| | 2-times limit value | |
| short-term | 1-times limit value | for example, 15 min |

**A.3.2.2** Perform sample distribution tests under each of the following two combinations of test conditions:

- — relative humidity: (50 ± 5) %;
- — temperature: (10 ± 2) °C and (40 ± 2) °C;
- — flow rate: recommended flow rate.

NOTE One way to obtain air with the required conditions of temperature and relative humidity is to use a climatic test chamber as specified in EN 60068-3-11.

**A.3.2.3** Set up at least six mixed-phase samplers per test and add a known mass of analyte to each collection substrate or, where the mixed-phase sampler includes more than one collection substrate, to each of the first collection substrates.

**A.3.2.4** Just before adding the analyte, start drawing air through the mixed-phase samplers under the prescribed test conditions.

**A.3.2.5** Add the analyte using a micropipette or syringe, if necessary, with the analyte diluted in a non-interfering solvent.

**A.3.2.6** Repeat A.3.2.3 and A.3.2.4 for each of the sample loadings calculated in A.3.2.1 and under each of the two combinations of test conditions prescribed in A.3.2.2.

**A.3.2.7** Analyse each collection substrate immediately after sampling and, for each sampler, calculate the distribution coefficients for vapour and airborne particles according to Formulae (A.1) and (A.2):

$$\gamma_{d,p} = \frac{m_p}{m_v + m_p} \cdot 100 \qquad (A.1)$$

$$\gamma_{d,v} = 100 - \gamma_{d,p} \qquad (A.2)$$

where

$\gamma_{d,p}$ is the distribution coefficient for airborne particles, in percentage;

$\gamma_{d,v}$ is the distribution coefficient for vapour, in percentage;

$m_p$ is the mass determined on the collection substrate for airborne particles, in milligrams;

$m_v$ is the mass determined on the collection substrate for vapour, in the same unit as for $m_p$.

Calculate the mean and the coefficient of variation of the replicate samples.

Consider the distribution coefficients between the collection substrates used:

- if, in all cases $\gamma_{\mathrm{d,p}} < 10\ \%$, the collection substrate for airborne particles does not need to be analysed;
- if, in any case $10\ \% \leq \gamma_{\mathrm{d,p}} \leq 90\ \%$, the collection substrates for airborne particles and vapour shall be analysed;
- if, in all cases $\gamma_{\mathrm{d,p}} > 90\ \%$, only the collection substrate for airborne particles needs to be analysed.

# Annex B
(informative)

# Possible approaches to sample mixtures of airborne particles and vapour

## B.1 General

General considerations for the sampling of mixtures of airborne particles and vapour have been reviewed by Perez and Soderholm (see Reference [4]). Sampling mixtures of airborne particles and vapour require an efficient combination of an airborne particle sampler placed in series with a vapour sampler. As basis of this document (see 6.3.1.1), a mixed-phase sampler with an inlet for the inhalable aerosol according to EN 481 shall be used. The aspiration characteristics of the system inlet for inhalable sampling limits the design flow rate of the sampler (for a given geometry) and its inlet geometry (for a given flowrate). In general, it will not be possible to quantify the distribution of (airborne) particle and vapour components separately at the moment of sampling, unless specific conditions are met, for example, the particle component is non-volatile.

For the sampling of mixtures of airborne particles and vapour, filter plus pumped sorbent tube (see B.2), reagent-impregnated systems (see B.3) are the techniques most frequently used. Impingers are used occasionally and a recent approach using denuder is under development.

## B.2 Filter plus pumped sorbent tube

### B.2.1 General

A filter is a particle collection substrate which is used in combination with a device that samples the inhalable fraction according to ISO 7708 or EN 481. A sorbent tube mounted in series is used to sample vapour.

This sampling train will require a specified design flow rate that cannot be altered unless it has been demonstrated to meet the performance requirements for inhalable samplers at other flow rates.

In general, a sorbent tube requires a lower flow rate in order to meet the performance requirements for pumped sorbent tubes (such as breakthrough volume). To combine the sorbent tube and the inhalable sampler, for example, the flow downstream of the filter can be split in order to achieve the desired value. The flow split can only be maintained without active flow control if the pressure drop across the sorbent tube remains constant during the sampling period.

Volatile and semi-volatile compounds (particles) collected on the filter can evaporate when air is drawn through the sampler. Some chemical agents in vapour form can also be adsorbed by the filter or particles collected on the filter. Thus, the original separation of the chemical agents between the particle and vapour phases cannot always be preserved; only the sum of particles and vapour can be quantified.

### B.2.2 Sampling flow rate

Inhalable samplers meeting the requirements of ISO 7708/EN 481 often operate at flow rates of 2 l min$^{-1}$ or more. This flow rate is higher than for typical pumped sorbent tubes; channelling and therefore loss of sample can occur if these are used outside their recommended flow rate range.

To use filter plus pumped sorbent tube at flow rates of 2 l min$^{-1}$ or more, either a longer pumped sorbent tube should be used to counteract the loss of sampling efficiency, or a wider pumped sorbent tube should be used at a more optimal flow velocity, or the flow should be split.

In recent years, sampling systems have been developed especially for the sampling of a mixture of airborne particles and vapour. These sampling systems have a miniaturized sampling head for inhalable aerosols and work with flow rates that are common for adsorption tubes (see References [9], [10] and [11]). These can also be combined with thermal desorption tubes with the designed flow rates for this type of tubes.

NOTE A longer pumped sorbent tube increases the back-pressure, whereas a wider pumped sorbent tube requires more sorbent.

## B.3 Reagent-impregnated sampling system

Reagent-impregnated sampling systems usually collect airborne particles and vapour on the same collection substrate.

This methodology includes coated filters, coated foams, coated sorbent beds and other similar approaches and is only suitable for reactive substances. The type and amount of reagent used in a reagent-impregnated sampling system should be suitable for the intended purpose.

The coated substrate is used in an inhalable sampler which has a specified design flow rate that cannot be altered. In order to collect vapour efficiently, in some instances it can be necessary to combine more than one coated collection substrate to avoid sample loss.

## B.4 Impinger

The impinger sampler consists in the collection of the particles and vapour in a liquid by impaction and diffusion. The liquid, constituted by water or organic solvent, may contain a reagent that is able to react with the analyte to form a non-volatile analyte solubilized in the liquid. A filter should be placed downstream the impinger to collect particles generated by the explosion of the bubbles. Then, the liquid and the filter should be analysed, and the quantities summed to determine the total quantity of the analyte.

The collection efficiency of the impinger depends on the airflow, the quantity of the liquid inside the impinger, the time of sampling, the speed of the reaction between the reagent and the compound to collect, and the size of the particles. The use of impingers is limited to particles with an aerodynamic diameter larger than 0,3 µm.

Handling an impinger as a personal sampler requires some caution as the liquid could spill during movement of the worker and generate risks of explosion in case of organic solvent use and exposure of the workers. Furthermore, the impinger as an aerosol sampler should respect the requirements of ISO 7708 and ISO 20581 to assess the exposure of workers, regarding the fraction of particles sampled and the expanded uncertainty of the method. However, the real fraction sampled by the impingers is not mentioned.

## B.5 Denuder

A denuder consists of one or multiple, parallel or concentric tubes coated with a sorbent allowing to collect the vapour of an aerosol and transmit the particles to another collection device, with minimal particle losses. This technique was firstly developed to eliminate water and organic vapour from the particle phase of an aerosol to correctly analyse the particle phase only. Recent research developed denuders that are associated to a filter plus sorbent or an impregnated filter to collect the particle phase of the aerosol after passing the denuder. That association allows the quantification of the vapour phase and the particle phase separately and provide valuable information on the real exposure of the workers.

A denuder is characterized by its vapour collection efficiency and the particle transmission efficiency through it. The vapour collection efficiency depends on the residence time in the denuder, the length of the denuder, the size of the channels and the collection capacity of the sorbent. It is possible to characterize the particle fraction and vapour fraction knowing the transmission efficiency within the sampler. The transmission efficiency of the particles depends on the size of the particles and the Reynolds number of the flow inside the channels.

A denuder used for personal sampling of a mixture of airborne particles and vapour is reported by References [5] and [6].

## B.6 Transport and storage

Compounds that can form a mixture of airborne particles and vapour at ambient temperature are difficult to handle after sampling, i.e. during transport and storage. Methods are required to ensure that there are minimal losses in total mass after sampling (see 8.2.2). If different collection substrates are used to collect airborne particles and vapour, the potential for losses or gains for each substrate shall be addressed. The method description shall provide detailed information on the procedure used for stabilization of the samples.

Several methods are available to minimize post-sampling changes. For example, samples can be cooled or stored in a fixing solution immediately after sampling. Clean air can be drawn through the sampler after workplace sampling in order to carry volatile compounds from the particle collection substrates of the sampling system onto the vapour collection substrates. Substrates containing volatile compounds should be transported and stored together with a sorbent medium to capture evaporative losses from the system.

# Annex C

(informative)

# Estimation of uncertainty of measurement

## C.1 Uncertainty components

### C.1.1 General

The following is a typical, but non-exclusive, list of uncertainty components:

a) sampled air volume;

b) sampling efficiency;

c) sample storage;

d) effects of temperature and humidity;

e) analytical recovery;

f) analytical variability;

g) calibration;

h) instrument response drift;

i) blank subtraction.

The estimation of these uncertainty components is based on ISO 21832 and ISO 22065.

### C.1.2 Sampled air volume and sampling efficiency

The uncertainty associated with sampled air volume (flow rate measurement, pump flow stability and sampling time) and sampling efficiency for vapour can be determined according to ISO 22065.

The uncertainty associated with sampling efficiency for airborne particles can be determined according to EN 13205-1 and ISO 21832, respectively.

### C.1.3 Sample storage

The uncertainty associated with storage of airborne particles and vapour samples can be determined according to ISO 21832 and ISO 22065.

### C.1.4 Effects of temperature and humidity

The fraction of a chemical agent in the vapour phase depends on the temperature and the humidity. It is not possible to estimate the effects of temperature and humidity on the collected masses of airborne particles and vapour separately.

Calculate the relative uncertainty components associated with temperature and humidity as follows:

a) Calculate the mean of the results for each exposure combination and the maximum difference between means.

b) Divide the maximum difference by the mean results of vapour samples at the reference conditions.

c) Calculate the relative standard uncertainties associated with temperature and humidity effects assuming rectangular distributions.

### C.1.5 Analysis

The uncertainty components associated with the analysis (analytical recovery, analytical variability, calibration, instrument response drift and blank subtraction) can be estimated according to ISO 21832 and ISO 22065.

## C.2 Calculation of combined standard uncertainty

### C.2.1 Samples analysed separately

See ISO/IEC Guide 98-3:2008, 5.1.5 and 5.1.6 and Reference [7] for the calculation of combined standard uncertainty.

The mass concentration for the inhalable fraction of the mixture $\beta_{\text{mix}}$ of airborne particles and vapour as a final result is given by the Formulae (C.1) or (C.2) depending on whether the sampled air volume is the same for both (see C.2.2).

$$\beta_{\text{mix}} = \frac{m_{\text{p}} + m_{\text{v}}}{V_{\text{t}}} = \frac{m_{\text{mix}}}{V_{\text{t}}} \tag{C.1}$$

$$\beta_{\text{mix}} = \frac{m_{\text{p}}}{V_{\text{p}}} + \frac{m_{\text{v}}}{V_{\text{v}}} = \beta_{\text{p}} + \beta_{\text{v}} \tag{C.2}$$

where

$m_{\text{p}}$, $m_{\text{v}}$ and $m_{\text{mix}}$ are the collected masses of airborne particles, vapour and mixture of both, respectively;

$V_{\text{p}}$, $V_{\text{v}}$ and $V_{\text{t}}$ are the air volumes for airborne particles, vapour and both, respectively;

$\beta_{\text{p}}$ and $\beta_{\text{v}}$ are the mass concentrations of airborne particles and vapour, respectively.

### C.2.2 Same sampling volume for airborne particles and vapour

Calculate separately the relative standard uncertainty associated with the collected mass of particles $u_{\text{m,p}}$ and the relative standard uncertainty associated with the collected mass of vapour $u_{\text{m,v}}$ in a similar way to that described in ISO 21832 and ISO 22065 without the uncertainty components associated with sampled air volume (see C.1.2).

Calculate the relative standard uncertainty associated with the collected mass of mixture of airborne particles and vapour $u_{\text{m,mix}}$ using Formula (C.3):

$$u_{\text{m,mix}}^2 = \frac{u_{\text{m,p}}^2 \cdot m_{\text{p}}^2 + u_{\text{m,v}}^2 \cdot m_{\text{v}}^2}{\left(m_{\text{p}} + m_{\text{v}}\right)^2} \tag{C.3}$$

where

$u_{\text{m,p}}$ is the relative standard uncertainty associated with the collected mass of airborne particles;

$u_{\text{m,v}}$ is the relative standard uncertainty associated with the collected mass of vapour;

$m_{\text{p}}$ and $m_{\text{v}}$ are the collected masses of airborne particles and vapour, respectively.