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Workplace atmospheres — Controlling and characterizing errors in weighing collected aerosols

Atmosphères des lieux de travail — Contrôle et caractérisation des erreurs de pesée des aérosols collectés

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 15767 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Introduction

Assessment of airborne aerosol hazards in the occupational setting entails sampling onto a collection medium, followed by analysis of the collected material. The result is generally an estimated concentration of a hazardous material in the air. The accuracy of such estimates depends on several factors, one of which relates to the specific type of analysis employed.

This International Standard deals with a specific type of analysis which finds the most general application in the sampling of aerosols, namely the weighing of sampled material. Gravimetric analysis, though apparently simple, is subject to errors from instability in the mass of the sampling medium and other elements which must be weighed. An example is provided by aerosol samplers designed to collect particles so as to agree with the inhalable aerosol sampling convention. For some sampler types, filter and cassette are weighed together to make estimates. Therefore, if the cassette, for example, absorbs or loses water between the weighings required for a concentration estimation, then errors may arise. This International Standard describes such potential errors and provides solutions for their minimization.

Workplace atmospheres — Controlling and characterizing errors in weighing collected aerosols

1 Scope

This International Standard provides recommendations for controlling the analytical uncertainty associated with aerosol collection medium instability, where collection medium or substrate includes any article used to collect particles (e.g. filter or foam material) as well as those supporting elements which must be analysed by weighing.

This International Standard is applicable to results compiled both from the literature and, if necessary and feasible, through laboratory experiment. Expected errors associated with given aerosol capture methods are quantified where possible. Recommendations as to materials to be used are given. Means of controlling or correcting errors arising from instability are provided. Recommendations for the weighing procedure are given. A procedure for estimating weighing errors is described. Finally, recommendations are given for the reporting of measured masses.

2 Normative references

The following referenced documents are indispensable for the application 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*

EN 482, *Workplace atmospheres — General requirements for performance of procedures for the measurement of chemical agents*

EN 13205:2001, *Workplace atmospheres — Assessment of performance of instruments for measurement of airborne particle concentrations*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
substrate
aerosol sampling filter, foam, etc., together with whatever mounting is weighed as a single item

NOTE As an example of the converse, the 25-mm or 37-mm plastic filter cassette often used for “total dust” sampling in either its closed-face or open-face version is *not* part of the substrate in the definition above, since it is not weighed.

3.2
equilibration time
time constant characterizing an approximately exponentially damped approach of the mass of an aerosol collection medium to a constant value

NOTE 1 The constant can be defined as the mean difference of the mass from equilibrium per mean mass loss or gain rate as measured over a finite time interval.

NOTE 2 There may be important instances in which several time constants are required to describe the approach to equilibrium.

NOTE 3 Equilibration time is expressed in seconds.

3.3
field blank
blank substrate that undergoes the same handling as the sample substrate, generally including conditioning and, often, loading into the samplers or transport containers, as well as transportation between lab and sampling site, but without being exposed to sampling

3.4
lab blank
blank substrate that undergoes the same handling as the sample substrate in the laboratory, including conditioning and loading into the samplers or transport containers if this is done in the laboratory

3.5
blank substrate
collection medium or substrate taken from the same batch as the sampling medium, but unexposed to sampling

3.6
limit of detection
LOD
three times the estimated standard deviation of the mass of the sample, accounting for the double weighing (exposed vs. unexposed) and for the uncertainty associated with any correction blanks used

NOTE The value LOD can be used as a threshhold value to assert the presence of a substance with confidence in the method. Annex B describes how to estimate, on the basis of the method evaluation, the false positive rate in such assertions.

3.7
limit of quantitation
LOQ
ten times the estimated standard deviation of the mass of the sample

NOTE The value LOQ can be used as a threshhold value to assure measurement of a substance accurately. For details, see Annex B.

4 Weight instability — Causes and minimization

4.1 General

Weight instability of sampling substrates can be attributed to several causes [1] to [11]. The following subclauses address the more important of these.

4.2 Moisture sorption

4.2.1 Moisture sorption is the most common cause of weight instability. Water can be directly collected by the filter or foam or other substrate material that is weighed. Water sorption by any part of the sampling system which is weighed must be suspected as well. For example, the sampling cassette itself, if weighed, can be the cause of significant error [1].

4.2.2 The effects of water sorption can be reduced by using non-sorptive materials. However, there may exist specific sampling needs for which a hydrophobic material is not feasible. Table 1 presents a list of common aerosol sampling substrates with different water adsorption features.

Table 1 — Water sorption characteristics of some aerosol sampling media

Substrate or cassette type	Water sorption			
	Very low	**Low**	**High**	**Very high**
Cellulose fibre filter			*	
Glass fibre filter		*		
Quartz fibre filter		*		
Cellulose ester membrane filter			*	
Polytetrafluoroethylene filter	*			
PVC membrane filter		*	*	
Polycarbonate filter	*			
Silver membrane filter	*			
Polyurethane foam				*
Greased Mylar impaction substrate		*	*	
Greased aluminium foil impaction substrate		*		
Carbon-filled resin				*
Aluminium cassette		*	*	
Stainless steel cassette	*			

NOTE 1 References [2] to [4] provide further details. Also, reference [5] reports that filters of evidently the same material, but originating from different manufacturers, can have widely differing variabilities.

NOTE 2 There is generally a trade-off between hydrophobicity and conductivity in many materials [9]. Therefore, one must be aware of the possibility of creating sampling problems when reducing hygroscopicity.

NOTE 3 Pre-treatments of substrates, such as greasing, can also affect water sorption.

4.3 Electrostatic effects

Electrostatic effects are a common source of weighing problems. These effects can usually be minimized by discharging the substrate through the use of a plasma ion source or a radioactive source. Using conductive materials may reduce such problems. See also reference [7].

4.4 Effects of volatile compounds (other than water)

4.4.1 Volatile compounds can be present in unused collection media [3], or can be adsorbed onto media during sampling.

4.4.2 Desorption of volatiles from unused media can be controlled, for example, by heating or oxygen plasma treatment prior to conditioning and weighing. Alternatively, losses may be compensated by the use of blanks (see Clause 5).

4.4.3 When volatile materials collected during sampling form part of the intended sample, standardized written procedures are required to ensure that any losses are minimized or at least controlled, for example by conditioning under tightly specified conditions.

4.4.4 When volatile materials collected during sampling are not part of the intended sample, it may be difficult to eliminate them if weighing is the only form of analysis. Non-sorptive media should preferably be used.

4.5 Handling damage

4.5.1 If friable substrates are used, procedures are needed to avoid mechanical damage.

4.5.2 The air-sampling equipment should be designed so that the substrate is not damaged during assembly and disassembly.

4.5.3 Flat tipped forceps are recommended for handling filters. Non-oxidizing metal tins may be used to weigh delicate substrates without direct handling.

4.5.4 Parts to be weighed shall not be touched with the hands, unless gloved.

4.5.5 Gloves, if used, shall leave no residue on what is weighed.

4.5.6 Handling shall take place in a clean environment, to avoid contamination.

4.6 Buoyancy changes

Corrections for air buoyancy [8], equal to the density of air multiplied by the air volume displaced, are not necessary for small objects, such as a 37-mm diameter membrane filter. However, there may exist circumstances (e.g. if an entire sampling cassette were weighed without the use of correcting blanks) in which the object to be weighed is so large that buoyancy must be corrected. For example, if the volume weighed exceeds 0,1 cm^3, then correction would be required in order to weigh down to 0,1 mg if pressure changes of the order of 10 % between weighings are expected (e.g. at different altitudes). If such a correction is necessary, the atmospheric pressure and temperature at the time of weighing should be recorded.

5 Correcting for weight instability by use of blanks

5.1 General

Many approaches to controlling weight instability exist [12] to [20]. The use of blanks is the most important practical tool for reducing errors due to weight instability. Correction for weight instability depends on the specific application and should follow a written procedure. The general principles are as follows. Blank sampling media are exposed, as closely as possible, to the same conditions as the active sampling media, without actually drawing air through. Correction is effected by subtracting the average blank mass change from the mass change of the active samples. Of course, if the atmosphere to be sampled contains water (or other volatile) droplets, then the use of blanks alone cannot correct. Blanks shall be matched to samples, i.e. if the sample consists of a filter within a cassette which is weighed, the blank shall be the same type of filter within the same type of cassette.

NOTE The effect of filter variations due to their manufacture is generally eliminated through the use of blanks.

5.2 Minimum number of blanks

Generally, at least one blank is recommended for each 10 samples. Measurement schemes in current use require between one and four blanks per batch. See Annex A for advantages of multiple blanks.

5.3 Weighing times and sequence

Blanks shall be interspersed with samples, before and after use, so as to detect systematic variations in mass (e.g. due to sorption or evaporation of a contaminant during weighing).

5.4 Conditioning times

Conditioning times for reaching equilibrium with the weighing environment may vary from a few hours to several weeks, depending on the specific sampling media. Typically, for workplace sampling applications, overnight conditioning is satisfactory. For sampling media with longer conditioning times, error correction through the use of blank substrates is particularly important.

5.5 Storage stability

Unused substrates shall be stored prior to weighing and conditioning in a clean laboratory, whose environmental conditions do not differ too greatly from the environment of the balance. Pre-weighed substrates shall be stored together with weighed blanks and used in any case within the assigned shelf-life. The assigned shelf-life and storage requirements shall be documented as part of a written weighing procedure.

NOTE Shelf-life depends on substrate material, storage conditions, cassette material and required LOQ or LOD.

Archived samples shall be stored together with weighed blanks in a clean laboratory whose environmental conditions do not differ too greatly from the environment of the balance. Note that transfers of mass between filters and cassettes could occur where these media are stored together.

6 Transport of samples to laboratory

6.1 General

The transportation of samples shall form part of a written procedure. The transport procedure shall be validated to ensure that significant losses do not occur. Follow the test method given in Annex D.

The main problems occurring during handling and transport of sampling media are described below.

- With substrates designed to be separated from sampling cassettes, dust can migrate from substrate to the transport container, and hence be lost.
- On the other hand, contamination of the sampling cassette and cover lid (if supplied) can be a significant source of error if the cassette (including cover lid) is part of the substrate.
- If a cover lid is not supplied, dust can be lost from the cassette to the transport container.
- Dust can migrate from sampling cassette to substrate.

NOTE Transportation losses are discussed in references [12] and [13].

6.2 Recommended packaging

6.2.1 Each substrate that is not mounted in a sampling cassette shall be transported in a Petri dish, tin or a similar closed container.

6.2.2 Sampling cassettes (i.e. with mounted filters) should preferrably have cover lids during transport. If the sample consists of all dust deposited inside the sampling cassette (with filter), then dust which migrates during transport from cassette to cover lid shall also be weighed.

6.2.3 The sealed substrates shall be transported in a suitable container or package. The floor, ceiling and walls of the container should be lined with a spongy material (preferably electrically conducting) which may absorb some mechanical shock and thus protect the samples during transport.

6.2.4 The samples shall be protected from excessive heating or cooling during transport.

NOTE 1 Special procedures are generally used for the transport of unstable particles or biological materials.

NOTE 2 If there is a possibility for dust to be lost from the substrate, the losses can be recovered by transporting the substrate within a container that can itself be weighed.

7 Weighing equipment and procedure

7.1 The balance

The balance should be matched to the task. The choice of balance depends on the desired limits of quantitation for the application (see Clause 8) and on the maximum tare masses of the samples to be weighed.

Workplace-air sampling typically requires a balance capable of weighing to an accuracy of either five or six figures. The balance shall be regularly calibrated using reference masses traceable to International Standards.

NOTE The performance of different balances was compared and reported in reference [5]. In one experiment, repeat weighings of 25-mm filters were made with filters stored between weighings in ventilated tins with conditions not strictly controlled. A balance weighing to 1 µg (six figures) was compared to a balance weighing to 10 µg (five figures). It was concluded that using a 1-µg balance *vs.* a 10-µg balance approximately halves the standard deviation of repeat weighing. Intra-day standard deviation was smaller than the inter-day deviation and is expected to be of greater importance when blanks are used to correct inter-day variation in the balance room. (See also reference [11].)

7.2 Recommended environmental controls

7.2.1 Equilibration and weighing shall be carried out under the same conditions, i.e. in the same room or chamber. Environmental control can be achieved in different ways:

- by means of a balance room containing balance, samples and the weighing personnel;
- by means of an environmentally-controlled chamber containing balance and samples, sited within a clean laboratory.

NOTE It may be possible to achieve an adequate level of environmental control without the need for active air conditioning. However the quality of gravimetric analysis depends strongly on the quality of the environmental control.

7.2.2 For sensitive (i.e. hygroscopic) samples, temperature and humidity control in the weighing chamber or balance room are important. In these cases, temperature should be maintained constant within ± 2 °C of the set point, and humidity should be constant to within ± 5 % relative humidity (RH) at the target temperature. The target temperature and humidity should be in the range of operating conditions recommended by the manufacturer of the balance [e.g. (20 ± 2) °C and (50 ± 5) % RH]. Very dry atmospheres (e.g. < 20 % RH) are to be avoided, as electrostatic buildup on the samples is more likely in such conditions. The environmental controls shall be capable of compensating for heat and humidity sources, such as people working in the room or electrically-powered instruments in the room [3].

NOTE Air conditioning in a weighing chamber is not necessary, e.g. filtered laboratory air can be fed into a positive-pressure chamber.

7.2.3 The particulate content of the balance room or chamber air should be minimized by filtration [e.g. by High Efficiency Particulate Air (HEPA) filtration].

7.2.4 Fresh air should be supplied consistent with the health and comfort requirements of personnel working in the balance room or laboratory. Turbulent air movement generated by ventilation or humidity control in the balance room or chamber should be minimal, so as not to affect the balance reading.

7.3 Other equipment requirements

The balance should be located in an area which is free from excessive vibration [e.g. due to lifts (elevators) or rotating machinery]. A massive weighing table (e.g. one made of 200 kg of marble) is one means to dampen ambient vibration. The area should be away from doors, windows, air ducts, and sources of radiant energy such as direct sunlight or ovens. The electrical supply to the balance should be stable, and the balance should not be located near sources of strong electromagnetic radiation.

7.4 Procedure

7.4.1 The weighing procedure shall be documented.

7.4.2 Equilibration of the sample to the temperature and humidity of the balance room or chamber shall take place for a period appropriate to the sample. The samples shall be kept in clean containers but open to the atmosphere so that equilibration can occur.

NOTE Desiccation prior to equilibration is sometimes used to remove excess water from the samples taken in a humid environment. This only applies to samples with excess water. (See also references [21] to [23].)

7.4.3 Elimination (if possible) of static electricity from the sample is extremely important, and should be done immediately prior to placement of the sample on the balance pan. Alternatively, a static eliminator can be placed inside the balance chamber.

7.4.4 The balance reading shall not be recorded until after it has stabilized.

7.4.5 Re-zero the balance as determined necessary.

NOTE A defective substrate can sometimes be identified by an abnormal initial mass.

8 Recommendations for the reporting of measured mass relative to LOD and LOQ

8.1 If the measured mass is above the limit of quantitation (LOQ, Annexes A to C), then it is reported.

8.2 If the result falls between the limit of detection (LOD, Annexes A to C) and LOQ, then it is reported that the measured mass is between the values of LOD and LOQ, and the measured mass is reported as well.

8.3 If the measured mass falls below the value of the LOD, it is reported that the estimate is below the value of the LOD.

NOTE 1 If the value of the LOD is exceeded, then the false-positive error rate in asserting detection is $<$ 1 % if the method is evaluated with as many degrees of freedom (25) as specified in Annexes A to C.

NOTE 2 In some applications a *series* of measured masses, each below the the value of the LOD, may be of help, e.g. in asserting the presence of mass over the entire series, even if the individual measurements are too small to assert detection with confidence. Applications such as these employ actual measured values (even if negative).

8.4 LOD and LOQ values shall be determined and shall be given in the report. Annexes A to C contain suitable procedures for these determinations.

Annex A
(normative)

Estimation of measurement errors

A.1 Symbols (and abbreviated terms)

The following symbols and abbreviated terms are used in this annex.

CV_{max}	maximum relative standard deviation acceptable in quantifying collected mass
LOD	value of the limit of detection: $3 \times s_w$, expressed in micrograms
$LOD_{1-\gamma}$	value of the LOD confidence limit, expressed in micrograms
LOQ	value of the limit of quantitation: $10 \times s_w$, expressed in micrograms
$LOQ_{1-\gamma}$	value of the LOQ confidence limit, expressed in micrograms
N_{b}	number of blanks per substrate set
b	batch index (1, …, B)
B	number of substrate batches in method evaluation
f	substrate index (1, …, F)
F	number of substrates (e.g. Filters) in each batch tested in method evaluation
s	estimate of σ, expressed in micrograms
s_w	estimate of σ_w, expressed in micrograms
U	overall uncertainty
α	detection error rate
β	mean substrate mass change during evaluation experiment
Δm_{fb}	substrate mass change, expressed in micrograms
ε_{fb}	substrate mass change residual random variable with variance σ^2, expressed in micrograms
ε_{b}	substrate mass change random variable representing inter-batch variability, expressed in micrograms
γ	method evaluation error rate
ν	number of degrees of freedom in method evaluation

σ	uncorrectable (e.g., via blank correction) standard deviation in (single) mass-change measurement, expressed in micrograms
$\sigma_{1-\gamma}$	confidence limit on σ, expressed in micrograms
σ_w	standard deviation in collected mass determination, expressed in micrograms
Φ	cumulative normal function
χ^2	chi-squared random variable
$\chi_{\gamma,\nu}{}^2$	chi-squared quantile

A.2 The uncertainty σ_w in mass estimates

A.2.1 General

The standard deviation σ_w in any collected mass estimate depends on the number of blanks (preferably field blanks) used to correct for correlated sampling medium variation. The collected mass uncertainty estimate s_w is determined as outlined here in Annex A through an extensive evaluation of blank samples. The estimate s_w is important for computing the limit of detection LOD ($3 \times s_w$) and the limit of quantitation LOQ ($10 \times s_w$) of the method.

Annex B interprets the meaning of LOD in terms of the rate of false-positive mass detection assertions at a specific confidence in the method evaluation. Similarly, Annex B interprets the meaning of LOQ, in terms of the accuracy achieved at a given confidence in the system evaluation. Annex C provides a worked example of how the method evaluation is analysed.

NOTE s_w corresponds to the combined uncertainty of reference [24].

A.2.2 No blanks

Because of its inaccuracy, this measurement scheme is generally not to be used. Aside from the fact that the uncertainty σ_w may be excessive, its estimation is difficult. A large number of repeated measurements of samples would necessarily be carried out on separate days. Between measurements, the samples would be exposed to environments of expected application so as to include realistic effects of environment on substrate [25]. From such a set of measurements, σ_w can be estimated. Because of the difficulty in covering all or most environments of intended use, the confidence in the estimate can be low. In addition to uncertainty in individual weighings, bias between pre- and post-weighing of subtrates can be significant and difficult to characterize.

A.2.3 One or more blanks

In the case that N_b blanks per sample are used, the uncertainty is given by

$$\sigma_w{}^2 = \sigma^2 \, [1 + (1 / N_b)] \tag{A.1}$$

The quantity σ^2 is the uncorrectable variance associated with each mass difference measurement requiring two balance readings (before and after exposure). The first term of equation (A.1) reflects the fact that only a single *sample* mass difference is measured. The factor $1 / N_b$ quantifies how the *blank* mass-change is more accurately known using multiple blanks, which therefore can reduce measurement uncertainty to a degree, at the cost of weighing extra blanks. Furthermore, at $N_b \geqslant 2$, a protocol could be established for voiding a sample if the blank values differ excessively. Also, at $N_b \geqslant 3$, one of the blanks could be eliminated if an outlier.

NOTE 1 A “balance reading” may actually consist of the mean of several readings for minimizing errors in the operation of the balance.

NOTE 2 Laboratory blanks are sometimes used instead of field blanks if it can be verified that the uncertainty in weighing is representative of field conditions.

A.3 Estimation of the uncorrectable mass-change uncertainty σ

The uncertainty σ required in equation (A.1) is estimated through a set of method evaluation experiments. One approach to the estimation of σ is presented here. Equivalent schemes can be devised. Condition and weigh a batch of at least six blank substrates. Place the substrates in clean transport containers or sampling heads and remove them from the balance room or weighing chamber for a suitable period. If the expected handling and sampling environment is suspected of affecting the sampling medium, then all the samples should be placed in such an environment (without exposure to dust) for a normal sampling period. Repeat with at least four additional batches of blank substrates. Typically five different days would be required at a minimum.

Suppose then that a number F (e.g. 6) of substrates are weighed twice in each of the B (e.g. 5) batches, giving a set of measured mass differences $\{\Delta m_{\mathrm{fb}}\}$, f = 1, …, F; b = 1, …, B. Then Δm_{fb} is modelled via:

$$\Delta m_{\mathrm{fb}} = \beta + \varepsilon_{\mathrm{b}} + \varepsilon_{\mathrm{fb}} \tag{A.2}$$

The various quantities in equation (A.2) are interpreted as follows. The constant β is a mean mass gain over all the blanks. ε_{b} is a random variable with zero mean and assumed normal distribution, expressing the inter-batch variability. Finally, $\varepsilon_{\mathrm{fb}}$, the term of real interest, is the only remaining quantity upon forming the difference of one substrate's mass measurement, relative to a difference in blank substrate masses within the same batch. $\varepsilon_{\mathrm{fb}}$ is approximated as normally distributed about zero, with standard deviation σ. Note that σ involves uncorrelated medium instability as well as balance uncertainty and therefore will generally exceed the value appropriate to a standard mass difference.

NOTE 1 Interaction between filter, foam or cassette dimensional variations and environmental change is assumed negligible.

NOTE 2 The uncertainty of weighing can vary from season to season.

Each batch b provides its own estimate s_{b} of σ via:

$$s_{\mathrm{b}}^2 = (F-1)^{-1} \sum \left(\Delta m_{\mathrm{fb}} - \Delta m_{.\mathrm{b}}\right)^2 \tag{A.3}$$

where the summation is over f denoting the sample blank in batch b, and where $\Delta m_{.\mathrm{b}}$ is the mean over the substrates in the batch b. Pooling the batch estimates then gives the value s^2 as a summation over the batches:

$$s^2 = B^{-1} \sum s_{\mathrm{b}}^2 \text{ with } \nu = (F-1) \cdot B \text{ degrees of freedom} \tag{A.4}$$

Annex C provides an example of estimating σ.

NOTE A nearly identical evaluation experiment was reported in reference [25].

A.4 The estimate s_w

The uncertainty σ_w is therefore [Equation (A.1)] estimated as s_w from:

$$s_w{}^2 = s^2 \cdot [1 + (1/N_{\mathrm{b}})] \tag{A.5}$$

A.5 The limit of detection

Following references [26] to [29], the limit of detection LOD is reported as the value

$$LOD = 3 \times s_w \qquad \text{(A.6)}$$

The presence of a substance can be asserted if its measured value exceeds the value of LOD. The accuracy of such assertions is given in Annex B.

A.6 The limit of quantitation

Similarly, if the uncertainty σ_w is constant at small loadings, the limit of quantitation LOQ is generally defined (in the absense of systematic error) by the value

$$LOQ \equiv 10 \times s_w \qquad \text{(A.7)}$$

NOTE The only known situation with aerosol weighing for which the uncertainty is not approximately constant at small loadings involves instability of the collected material itself. Characterization of this uncertainty requires statistical modelling of this instability and is not covered in this International Standard. See, however, the recommendation in 4.4.3.

Annex B
(informative)

Interpretation of LOD and LOQ

B.1 False-positive rate upon using the LOD for detection assertion

Suppose the uncertainty σ_w is independent of the sampled mass at small loadings. Denote the false-positive rate in asserting the presence of a substance by α (e.g. 5 %). If σ_w were known exactly (which it is not), then an ideal limit of detection LOD_{ideal} would be defined as

$$LOD_{\mathrm{ideal}} \equiv \Phi^{-1}[1 - \alpha] \cdot \sigma_w \tag{B.1}$$

where Φ is the cumulative normal function. Only a fraction α of estimates exceeds LOD_{ideal} if the true mass sampled is zero.

Generally, however, σ_w is not known exactly, but is estimated by s_w with ν degrees of freedom (e.g. 25). By definition of the chi-squared variable, the quantity $\nu \cdot s_w{}^2 / \sigma_w{}^2$ is chi-squared distributed with ν degrees of freedom. Therefore, at evaluation confidence level $(1 - \gamma)$ (e.g. 95 %), the single-sided confidence limit on σ_w is

$$\sigma_{1-\gamma} = \sqrt{\nu / \chi_{\gamma,\nu}{}^2} \cdot s_w \tag{B.2}$$

where the constant $\chi_{\gamma,\nu}{}^2$ may be found in standard statistics tabulations and is defined implicitly as the value for which

$$\mathrm{prob}[\chi^2 > \chi_{\gamma,\nu}{}^2] = 1 - \gamma \tag{B.3}$$

Therefore the $(1 - \gamma)$ confidence limit on LOD_{ideal} itself is

$$LOD_{1-\gamma} \equiv \sqrt{\nu / \chi_{\gamma,\nu}{}^2} \cdot \Phi^{-1}\left[1 - \alpha\right] \cdot s_w \tag{B.4}$$

If the quantity $LOD_{1-\gamma}$ is used (rather than LOD_{ideal}) to decide detection, then with confidence $(1 - \gamma)$ in the method evaluation, the false-positive rate is less than α. Equating the value LOD of Equation (A.6) with $LOD_{1-\gamma}$ [Equation (B.4)] then determines the false-positive rate α via:

$$\sqrt{\nu / \chi_{\gamma,\nu}{}^2} \cdot \Phi^{-1}\left[1 - \alpha\right] = 3 \tag{B.5}$$

Let $\gamma = 5$ % (meaning 95 % confidence in the system evaluation), then at $\nu = 25$ degrees of freedom, as in the suggested system evaluation experiment, Equation (B.5) implies that the false-positive rate is less than 1 %. Similarly, if the concentration is large enough to sample LOD on average, then the false-negative (Type 2 error) rate is equal to 50 % due to the symmetry of the distribution of the residual errors.

B.2 Interpretation of LOQ

As in Equation (B.1), define an ideal value LOQ_{ideal}

$$LOQ_{\mathrm{ideal}} \equiv \sigma_w / CV_{\mathrm{max}} \tag{B.6}$$

where CV_{max} is the maximum relative standard deviation acceptable in the quantitation. Then the $(1-\gamma)$ confidence limit is

$$LOQ_{1-\gamma} \equiv \sqrt{\nu / \chi_{\gamma,\nu}{}^2} \cdot s_w / CV_{\mathrm{max}} \qquad \text{(B.7)}$$

Equating LOQ [Equation (A.7)] and $LOQ_{1-\gamma}$ [Equation (B.7)] means that the true sampled mass must be large enough to exceed the value of the LOQ in order to attain

$$CV_{\mathrm{max}} = \sqrt{\nu / \chi_{\gamma,\nu}{}^2} \; / \; 10 \qquad \text{(B.8)}$$

at the $(1-\gamma)$ confidence level in the method evaluation. With 95 % confidence in the evaluation at ν equal to 25 degrees of freedom, the maximum acceptable error is less than 13 % if the value of the LOQ is exceeded.

NOTE 1 The NIOSH accuracy criterion [29] to [32] requires $CV < 13$ % at the 95 %-confidence level for methods without uncorrectable bias or systematic error.

NOTE 2 Similarly, $CV < 13$ % implies that the overall uncertainty (see EN 482) $U < 30$ % in the absence of bias and of significant errors other than gravimetric at masses exceeding the value of the LOQ.

NOTE 3 Therefore, occupational or environmental exposure limits lower than the value corresponding to a method's LOQ may indicate that improvement in the method is required.

NOTE 4 Although gravimetric error can, in fact, dominate at small sampled masses, other sources of sampling and analytical error may exist. Such errors can arise from several sources:

- sampling pump-flowrate bias,
- flow fluctuation (in the case of sampling with internal aerodynamic separation),
- variation in sampler physical dimensions,
- electrostatic effects on sampling, or
- bias relative to the appropriate sampling convention.

NOTE 5 The interpretation of LOD and LOQ given here closely relates to the concept of the *tolerance interval*. Detection assertion always refers to the confidence in the method evaluation. An alternative measurement scheme requiring a large number of blanks for each mass measurement could give the detection assertion error rate directly at each mass measurement, but would normally require an impractical number of blanks to ensure a low error rate. In this case, the system would be essentially evaluated at each mass measurement.

Annex C
(informative)

Method evaluation example

The following table gives an example of typical results for the experiment to determine system measurement accuracy. Columns correspond to the substrate number of a given batch, and rows to separate batches. For the purposes of illustration, masses (in micrograms) were simulated using mean mass gain (over all the batches) equal to 5 µg, batch variability equal to 5 µg, and uncorrelated weighing error equal to 5 µg. This means that the mass-difference standard deviation, the quantity to be estimated from the data, is $\sigma = \sqrt{2} \times 5\ \mu\text{g} = 7{,}1\ \mu\text{g}$.

Table C.1 — Substrate mass difference measurements

Batch	**Substrate** µg						**Estimated variance**
	1	2	3	4	5	6	(s_b^2)
1	21	21	15	18	14	18	8,6
2	−4	−11	2	2	−6	2	30
3	9	22	−12	0	12	12	140
4	−2	6	20	6	8	6	51
5	−11	11	4	5	0	1	54
Mean variance estimate (s^2)							56

Taking the square root of the mean variance estimate gives the estimated mass-difference standard deviation:

$$s = \sqrt{56} = 7{,}5\ \mu\text{g} \text{ with 25 degrees of freedom,}$$

which compares well with the true value 7,1 µg.

Furthermore, Equation (B.2) results in the 95% confidence limit:

$$s_{95\,\%} = \sqrt{25/14{,}61} \times 7{,}5\ \mu\text{g} = 9{,}8\ \mu\text{g}$$

Now suppose that in actual application, three blanks are to be used. Then Equation (A.5) indicates that the estimated mass determination uncertainty s_w is given by

$$s_w = 8{,}6\ \mu\text{g}$$

Therefore, the limits of detection and quantitation, the values of LOD and LOQ [Equations (A.6) and (A.7)], would be

$$LOD = 26\ \mu\text{g}$$

$$LOQ = 86\ \mu\text{g}$$

Annex D
(normative)

Test of transportation integrity

D.1 General

The purpose of this test is to help minimize mass measurement errors due to either material loss or substrate contamination during the transportation of samples between field and laboratory. The test proposed here is an alternative to the method of EN 13205:2001, Annex D, since most substrate weighing laboratories have no capacity for generating monodisperse aluminium oxide powders. The main differences are that EN 13205 requires:

a) a mixture of monodisperse aluminium oxide, rather than “real” dust,

b) a laboratory orbital shaker table, rather than “real” shipping of collection media,and

c) a maximum deposit equal to (sampler flowrate) × (8 h) × max (TLV [5 mg/m^3 or 10 mg/m^3]), rather than definition by the laboratory.

D.2 Procedure

D.2.1 Weigh at least 30 substrates plus blanks as required by the written procedures of the laboratory.

D.2.2 Deposit dust onto at least 3 groups of 10 substrates each, with dust masses equal to:

a) the limit of quantitation of the weighing system,

b) the maximum dust deposit for which the laboratory intends the method to be used, and

c) a midrange value between the previous extreme values of dust deposits.

D.2.3 Instead of monodisperse particles, use a dust type with a continuous size distribution, including particles in both the smaller and larger size ranges expected following a pre-sampler conforming to the relevant sampling convention. Use a non-volatile, non-reactive, non-sticky and non-hygroscopic dust. It is not necessary to deposit the dust in a laboratory. The dust may be deposited onto the substrates at the workplaces. However, extra care shall then be taken to avoid that the sample particles which are most easily lost have already been lost when the samples arrive at the laboratory.

D.2.4 Weigh the substrates according to the written procedures of the laboratory.

D.2.5 Pack the substrates according to the written procedures of the laboratory.

D.2.6 Dispatch the transport containers by mail, consigned delivery system or by the end-user's own vehicle (whatever is most common/appropriate) to a trusted addressee/consignee at a remote location. Ask the addressee/consignee to return the package containing the test substrates, with the same transport system without opening it.

D.2.7 Weigh the active substrates plus blanks according to the written procedures of the laboratory.

D.2.8 Determine the relative transport losses for each of the three levels of dust deposit.

D.3 Requirements

D.3.1 The relative dust loss due to transport shall be less than 5 %.

D.3.2 The substrate mass range for which this requirement is met shall be documented.

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