Standard Practice for
Controlling and Characterizing Errors in Weighing Collected Aerosols[1]

1. Scope

1.1 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 possibly hazardous material in the air. The uncertainty in such estimates depends on several factors, one of which relates to the specific type of analysis employed. The most commonly applied method for analysis of aerosols is the weighing of the sampled material. Gravimetric analysis, though apparently simple, is subject to errors from instability in the mass of the sampling medium and other elements that must be weighed. An example is provided by aerosol samplers designed to collect particles so as to agree with the inhalable aerosol sampling convention (see ISO 7708, Guide D6062, and EN 481). 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 practice covers such potential errors and provides solutions for their minimization.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D4096 Test Method for Determination of Total Suspended Particulate Matter in the Atmosphere (High–Volume Sampler Method)

D4532 Test Method for Respirable Dust in Workplace Atmospheres Using Cyclone Samplers

D6062 Guide for Personal Samplers of Health-Related Aerosol Fractions

2.2 *International Standards:*[3]

EN 481 Workplace Atmospheres—Size Fraction Definitions for Measurement of Airborne Particles in the Workplace

EN 13205 Workplace Atmospheres—Assessment of Performance of Instruments for Measurement of Airborne Particle Concentrations

2.3 *ISO Standards:*[4]

ISO 7708 Air Quality—Particle Size Fraction Definitions for Health-related Sampling

ISO 20581 Workplace Atmospheres—General Requirements for Performance of Procedures for the Measurement of Chemical Agents

ISO 20988 Air Quality—Guidelines for Estimating Measurement Uncertainty

ISO GUM Guide to the Expression of Uncertainty in Measurement (1998)

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this practice, refer to Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *blank substrate*—a collection medium or substrate coming from the same batch as the sampling medium, but unexposed.

3.2.2 *equilibration time*—For the purposes of this practice, a time constant (seconds) characterizing an approximate exponentially damped approach of the mass of an aerosol collection medium to a constant value. 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.

3.2.2.1 *Discussion*—There may be important instances in which *several* time constants are required to describe the approach to equilibrium.

3.2.3 *estimated overall uncertainty (U)*—2 × estimated standard deviation of estimated mass, in the case of negligible uncorrectable bias (see ISO 20581).

3.2.4 *field blank*—a blank substrate that undergoes the same handling as the sample substrate, generally including conditioning and loading into the samplers or transport containers, as well as transportation to the sampling site, but without being exposed.

3.2.4.1 *Discussion*—If blanks are not actually loaded into samplers, losses due to handling could be underestimated.

3.2.5 *lab blank*—a blank substrate that undergoes the same handling as the sample substrate in the laboratory, including conditioning and loading into the samplers or transport containers when this is done in the laboratory.

3.2.6 *limit of detection (LOD)*—a value for which exceedence by measured mass indicates the presence of a substance at given false-positive rate: 3 × estimated standard deviation of the measured blank substrate mass (see Annex A2).

3.2.7 *limit of quantitation (LOQ)*—a value for which exceedence by measured mass indicates the quantitation of a substance at given accuracy: 10 × estimated standard deviation of the measured blank substrate mass (see Annex A2).

3.2.8 *substrate*—sampling filter, foam, and so forth together with whatever mounting is weighed as a single item.

3.2.8.1 *Discussion*—The 25 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.

3.3 *Symbols:*

α	= detection error rate
B	= number of substrate batches in method evaluation
b	= batch index (1, ..., B)
β	= mean substrate mass change during evaluation experiment
CV_{max}	= maximum relative error acceptable in quantifying collected mass
$\Delta m_{fb}(\mu g)$	= substrate mass change
ε_b (μg)	= substrate weight-change random variable representing inter-batch variability
ε_{fb} (μg)	= substrate weight change residual random variable with variance σ^2
f	= substrate index (1, ..., F)
F	= number of substrates (for example, filters) in each batch tested in method evaluation
γ	= method evaluation error rate
LOD (μg)	= limit of detection: 3 × s_w
$LOD_{1-\gamma}$ (μg)	= LOD confidence limit
LOQ (μg)	= limit of quantitation: 10 × s_w
$LOQ_{1-\gamma}$ (μg)	= LOQ confidence limit

N_b	= number of blanks per substrate set
v	= number of degrees of freedom in method evaluation
Φ	= cumulative normal function
χ^2	= chi-square random variable
$\chi_{\gamma,v}^2$	= chi-square quantile (that is, a fixed number that exceeds the random variable χ^2 at probability γ)
RH	= relative humidity
u (μg)	= uncertainty component in two balance readings, an estimate of σ
u_w (μg)	= weighing uncertainty, estimate of σ_w
σ (μg)	= uncorrectable (for example, by way of blank correction) standard deviation in (single) mass-change measurement
$\sigma_{1-\gamma}$ (μg)	= confidence limit on σ
σ_w (μg)	= standard deviation in collected mass determination
U	= overall uncertainty

4. Significance and Use

4.1 The weighing of collected aerosol is one of the most common and purportedly simple analytical procedures in both occupational and environmental atmospheric monitoring (for example, Test Method D4532 or D4096). Problems with measurement accuracy occur when the amount of material collected is small, owing both to balance inaccuracy and variation in the weight of that part of the sampling medium that is weighed along with the sample. The procedures presented here for controlling and documenting such analytical errors will help provide the accuracy required for making well-founded decisions in identifying, characterizing, and controlling hazardous conditions.

4.2 Recommendations are given as to materials to be used. Means of controlling or correcting errors arising from instability are provided. Recommendations as to the weighing procedure are given. Finally, a method evaluation procedure for estimating weighing errors is described.

4.3 Recommendations are also provided for the reporting of weights relative to LOD (see 3.2.6) and LOQ (see 3.2.7). The quantities, LOD and LOQ, are computed as a result of the method evaluation.

5. Weight Instability, Causes, and Minimization

5.1 Weight instability of sampling substrates may be attributed to several causes. The following subclauses address the more important of these.

5.1.1 *Moisture Sorption:*

5.1.1.1 Moisture sorption is the most common cause of weight instability. Water may be directly collected by the filter or foam or other substrate material that is weighed. Water sorption by any part of the sampling system that is weighed must be suspected as well. For example, the sampling cassette itself, if weighed, may be the cause of significant error (1)[5] (see also 8.2.2).

---

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

5.1.1.2 The effects of water sorption can be reduced by using nonsorptive 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.

NOTE 1—Gonzalez-Fernandez, Kauffer et al, and Lippmann (2-4) provide further details. Also, Vaughan et al (5) report that filters of evidently the same material, but originating from different manufacturers, may have widely differing variabilities.

NOTE 2—There is generally a trade-off between hydrophobicity and conductivity in many materials (6). Therefore, one must be aware of the possibility of creating sampling problems while reducing hygroscopicity.

NOTE 3—Pretreatments of substrates, such as greasing, may also affect water sorption.

5.1.2 *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. Lawless and Rodes (7) present details on electrostatic effects and their minimization (see also Engelbrecht et al (8)).

5.1.3 *Effects of Volatile Compounds (other than water)*—Volatile compounds may be present in unused collection media (3) or may be adsorbed onto media during sampling.

5.1.3.1 Desorption of volatiles from unused media may 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 Section 6).

5.1.3.2 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.

NOTE 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. Preferably nonsorptive media should be used.

5.1.4 *Handling Damage*—Lawless and Rodes (7) give recommendations on minimizing balance-operator effects. If friable substrates are used, procedures are needed to avoid mechanical damage during gravimetric analysis.

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

5.1.4.2 Flat tipped forceps are recommended for handling filters. Nonoxidizing metal tins may be used to weigh delicate substrates without direct handling.

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

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

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

5.1.5 *Buoyancy Changes*—Corrections (9) for air buoyancy, 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 (for example, 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 to weigh down to 0.1 mg if pressure changes of the order of 10 % between weighings are expected. If such a correction is necessary, the atmospheric pressure and temperature at the time of weighing should be recorded.

6. Correcting for Weight Instability

6.1 *Recommended Method for Correction by Use of Blanks*—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 weight gain from the weight gain 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. Kauffer et al (3) note that blanks may also offer correction for filter material losses. Blanks shall be matched to samples, that is, if the sample consists of a filter within a cassette that is weighed, the blank shall be the same type of filter within the same type of cassette.

6.1.1 An alternative procedure employs matched weight filters consisting of two nearly equal-weight filters, one placed in front of the other, with the sampler following employed as blank. The collected mass is estimated simply by subtracting the filter masses following sampling. Analysis of uncertainty is similar to the presentation here, but also involves estimation of the uncertainty of the filter matching.

6.2 *Minimum Number of Blanks*—Generally, at least one blank is recommended for each ten samples. Measurement schemes in current use require between one and four blanks per batch. See A1.1 for advantages of multiple blanks.

6.3 *Weighing Times and Sequence*—Blanks shall be interspersed with samples, before and after use, so as to detect systematic variations in mass (for example, due to sorption or evaporation of a contaminant during weighing).

TABLE 1 Water Sorption Characteristics of Some Aerosol Sampling Media

Substrate or Cassette Type	Very Low	Low	High	Very High
Cellulose fiber filter			*	
Glass fiber filter		*		
Quartz fiber filter		*		
Cellulose ester membrane filter			*	
Polytetrafluoroethylene filter		*		
PVC membrane filter	*			
Polycarbonate filter		*		
Silver membrane filter		*		
Polyurethane foam				*
Greased polyester film impaction substrate		*		
Greased aluminum foil impaction substrate		*		
Carbon-filled resin				*
Aluminum cassette	*			
Stainless steel cassette	*			

6.4 *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. Charell and Hawley (**10**) indicate that extremely short equilibration times exist for some filters.

6.5 *Storage Stability*—Unused substrates shall, where possible, be stored prior to weighing and conditioning in a clean laboratory whose environmental conditions do not differ too greatly from the balance environment. Preweighed 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 5—Shelf life depends on substrate material, storage conditions, cassette material, and required LOQ or LOD.

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

7. Transport of Samples to Laboratory

7.1 *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 test method of Annex A4.

7.1.1 The main problems occurring during handling and transport of sampling media are:

7.1.1.1 With substrates designed to be separated from sampling cassettes, dust may migrate from substrate to the transport container, and hence be lost.

7.1.1.2 On the other hand, contamination of the sampling cassette and cover lid (when supplied) can be a significant source of error if the cassette (including cover lid) is part of the substrate.

7.1.1.3 If a cover lid is not supplied, dust may be lost from the cassette to the transport container.

Note 6—Transportation losses are discussed in Awan and Burgess and van Tongeren et al (**11, 12**).

7.2 *Recommended Packaging:*

7.2.1 Each substrate that is not mounted in a sampling cassette shall be transported in a petri dish, a tin, or a similar closed container that prevents contact with the surface of the collection medium.

7.2.2 Sampling cassettes (that is, with mounted filters) should preferably have cover lids during transport. If the sample consists of all dust deposited inside the sampling cassette (with filter), then dust that migrates during transport from cassette to cover lid shall also be weighed. The only foolproof way to handle this is to weigh the cover lid with the sampling cassette.

7.2.3 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.

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

Note 7—Special procedures are needed for the transport of unstable particles or biological materials.

Note 8—When there is a possibility for dust to be lost from the substrate, the losses may be recovered by transporting the substrate within a container that can itself be weighed.

8. Weighing Equipment and Procedure

8.1 *Balance*—The balance should be matched to the task. The choice of balance will depend on the desired limits of quantitation (see 3.2.7) for the application and on the maximum tare weights of the samples to be weighed. Workplace air sampling typically requires either a five- or six-figure balance. The balance shall be regularly calibrated using reference weights traceable to International Standards.

Note 9—The performance of different balances was compared and reported in Vaughan et al (**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. A1-µg (six-figure) balance was compared to a 10-µg (five-figure) balance. It was concluded that using a 1-µg versus 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 Feeney et al (**13**)).

8.2 *Recommended Environmental Controls:*

8.2.1 Equilibration and weighing shall be carried out under the same conditions, that is, in the same room or chamber. Environmental control can be achieved in different ways: (*1*) by means of a balance room containing balance, samples, and the weighing personnel; or (*2*) by means of an environmentally-controlled chamber containing balance and samples, sited within a clean laboratory.

Note 10—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.

8.2.2 For sensitive (that is, 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 % 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 (for example, 20 ± 2°C and 50 ± 5 % RH). Very dry atmospheres (for example, <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**).

8.2.3 The particulate content of the balance room or chamber air should be minimized by filtration (for example, by HEPA filtration).

8.2.4 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.

8.3 *Other Equipment Requirements*—The balance should be located in an area that is free from excessive vibration (for example, from elevators and rotating machinery). A massive weighing table (for example, 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 strong sources of electromagnetic radiation.

8.4 *Procedure:*

8.4.1 The weighing procedure shall be documented.

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

NOTE 11—If sampling took place in a humid environment, then, prior to equilibration, dessication may be needed to remove excess water from the samples.

8.4.3 Elimination 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.

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

8.4.5 Rezero the balance between every reading.

8.4.6 Defective substrates may be identified and rejected if their initial weights differ from normal.

9. Reporting of Measured Weight

9.1 Details on reporting weights depends on the specific application. The following is an example of a minimal reporting policy.

9.1.1 If the measured mass exceeds the LOQ (see Annex A1 – Annex A3), then it would be reported.

9.1.2 If the result falls between the LOD (see Annex A1 – Annex A3) and the LOQ, then it would be reported that the measured mass is between LOD and LOQ.

9.1.3 If the estimate falls below the LOD, it would be reported that the mass is below the LOD.

NOTE 12—If 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 Annex A1 – Annex A3.

NOTE 13—In some applications, a series of measured masses, each below the LOD, may be of value, for example, in asserting the presence of mass over the entire series, even if the individual measurements are too small to assert detection with confidence.

9.1.4 LOD and LOQ shall be determined as described in Annex A1 – Annex A3 and shall be given in the report.

10. Keywords

10.1 blank; control filter; filter; foam; gravimetric; limit of detection; limit of quantitation; LOD; LOQ; sampling media; weighing; weight

ANNEXES

(Mandatory Information)

A1. ESTIMATION OF MEASUREMENT UNCERTAINTY

A1.1 The Variance σ_w^2 in Weight Estimates

A1.1.1 The variance σ_w^2 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 u_w is determined as outlined here in Annex A1 through an extensive evaluation of blank samples. The estimate s_w is important for computing the LOD ($3 \times u_w$) and the LOQ ($10 \times u_w$) of the method.

A1.1.2 Annex A2 interprets the meaning of LOD in terms of the rate of false-positive mass detection assertions at specific confidence in the method evaluation. Similarly, Annex A2 interprets the meaning of LOQ in terms of the accuracy achieved at given confidence in the system evaluation. Annex A3 provides a worked example of how the method evaluation is analyzed.

A1.1.3 *No Blanks*—Because of its inaccuracy, this measurement scheme is generally not to be used. Aside from the fact that the variance σ_w^2 may be excessive, its estimation is difficult. A large number of repeat 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 **(14)**. From such a set of measurements, the uncertainty component u_w may be estimated. Because of the difficulty in covering all or most environments of intended use, the confidence in the estimate may be low. In addition to imprecision, bias between pre- and post-weighing of substrates may be significant and difficult to characterize.

A1.1.4 *One or More Blanks*—In the case that N_b blanks per sample are used, the variance is given by:

$$\sigma_w^2 = \sigma^2 \times (1 + 1/N_b) \qquad (A1.1)$$

The quantity σ^2 is the uncorrectable variance associated with each mass difference measurement requiring two balance readings (before and after exposure). The factor, $1/N_b$, quantifies how the blank weight-change is more accurately known using multiple blanks, which therefore can reduce the overall variance to a degree, at the cost of weighing extra blanks.

Furthermore, at $N_b \geq 2$, a protocol could be established for voiding a sample if the blank values differ excessively. Also, at $N_b \geq 3$, one of the blanks could be eliminated if an outlier.

NOTE A1.1—If lab blanks are used instead of field blanks, it should be verified that the variance in weighing is representative of field conditions.

A1.2 Determination of the Uncorrectable Weight-Change Uncertainty u

A1.2.1 The variance σ^2 required in Eq A1.1 is estimated through a set of method evaluation experiments. One approach to the estimation of σ^2 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.

A1.2.2 Suppose then that a number F (for example, 6) of substrates is weighed twice in each of the B (for example, 5) batches, giving a set of measured weight differences $\{\Delta m_{fb}\}$, $f = 1, \ldots, F$; $b = 1, \ldots, B$. Then Δm_{fb} is modelled by means of:

$$\Delta m_{fb} = \beta + \varepsilon_b + \varepsilon_{fb} \qquad (A1.2)$$

A1.2.3 The various quantities in Eq A1.2 are interpreted as follows. The constant β is a mean weight gain over all the blanks. ε_b is a random variable with zero mean and assumed normal distribution, expressing the inter-batch variability. Finally, ε_{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. ε_{fb} is approximated as normally distributed about zero with standard deviation σ. Note that σ involves uncorrelated medium instability as well as balance imprecision and therefore will generally exceed the value appropriate to a standard weight difference.

NOTE A1.2—Interaction among filter, foam or cassette dimension variations, and environmental change is assumed negligible.
NOTE A1.3—The imprecision of weighing may vary from season to season.

A1.2.4 Each batch b provides its own uncertainty value u_b of σ by means of:

$$u_b^2 = (F-1)^{-1} \sum (\Delta m_{fb} - \Delta m_{\cdot b})^2 \qquad (A1.3)$$

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

$$u^2 = B^{-1} \sum u_b^2 \text{ with } \nu = (F-1) \times B \text{ degrees of freedom} \qquad (A1.4)$$

Annex A3 provides an example of estimating σ.

A1.3 The Uncertainty Component u_w

A1.3.1 The uncertainty u_w is therefore (see Eq A1.1) determined from:

$$u_w^2 = u^2 \times (1 + 1/N_b) \qquad (A1.5)$$

A1.4 Limit of Detection (LOD)

A1.4.1 The LOD is reported as [14, 15, 16, 17]

$$LOD = 3 \times u_w \qquad (A1.6)$$

A1.4.2 The presence of a substance may be asserted if its measured value exceeds the value, LOD. The accuracy of such assertions is given in Annex A2.

A1.5 Limit of Quantitation (LOQ)

A1.5.1 Similarly, if the variance σ_w^2 is constant at small loadings, the LOQ is generally defined (in the absence of systematic error) by:

$$LOQ = 10 \times u_w \qquad (A1.7)$$

A2. INTERPRETATION OF LOD AND LOQ

A2.1 False-positive Rate upon Using LOD for Detection Assertion

A2.1.1 Suppose the variance σ_w^2 is independent of the sampled mass at small loadings. Denote the false-positive rate in asserting the presence of a substance by α (for example, 5 %). If σ_w were known exactly (which it is not), then an ideal limit of detection, LOD_{ideal}, would be defined as:

$$LOD_{ideal} = \Phi^{-1}[1 - \alpha] \times \sigma_w \qquad (A2.1)$$

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

A2.1.2 Generally, however, σ_w is not known exactly, but is estimated by u_w with ν degrees of freedom (for example, 25). By definition of the chi-square variable, the quantity $\nu u_w^2/\sigma_w^2$ is chi-square distributed with ν degrees of freedom. Therefore, at evaluation confidence level $(1 - \gamma)$ (for example, 95 %), the single-sided confidence limit on σ_w is:

$$\sigma_{1-\gamma} = Sqrt[\nu/\chi_{\gamma,\nu}^2] \times u_w \qquad (A2.2)$$

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

$$prob[\chi^2 > \chi_{\gamma,\nu}^2] = 1 - \gamma \qquad (A2.3)$$

A2.1.3 Therefore the $(1 - \gamma)$-confidence limit on LOD_{ideal} itself is:

$$LOD_{1-\gamma} = Sqrt[\nu/\chi_{\gamma,\nu}^2] \times \Phi^{-1}[1 - \alpha] \times u_w \qquad (A2.4)$$

A2.1.4 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 LOD of Eq A1.6 with $LOD_{1-\gamma}$ (see Eq A2.4) then determines the false-positive rate α by means of:

$$\text{Sqrt}[\nu/\chi_{\gamma,\nu}^2] \times \Phi^{-1}[1-\alpha] = 3 \qquad (A2.5)$$

A2.1.5 Let γ equal 5 % (meaning 95 % confidence in the system evaluation). Then at ν equals 25 degrees of freedom, as in the suggested system evaluation experiment, Eq A2.5 implies that the false-positive rate is less than 1 %. Similarly, if the concentration is large enough to sample LOD in the mean, then the false-negative (Type 2 error) rate is equal to 50 % due to the symmetry of the distribution of the residual errors.

A2.2 Interpretation of LOQ

A2.2.1 As in Eq A2.1, define an ideal value LOQ_{ideal}:

$$LOQ_{ideal} = \sigma_w/CV_{max} \qquad (A2.6)$$

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

$$LOQ_{1-\gamma} = \text{Sqrt}[\nu/\chi_{\gamma,\nu}^2] \times u_w/CV_{max} \qquad (A2.7)$$

A2.2.2 Equating LOQ (see Eq A1.7) and $LOQ_{1-\gamma}$ (see Eq A2.7) means that the true sampled mass must be large enough to exceed LOQ in order to attain:

$$CV_{max} = \text{Sqrt}[\nu/\chi_{\gamma,\nu}^2]/10 \qquad (A2.8)$$

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 standard deviation is less than 13 % if LOQ is exceeded.

NOTE A2.1—The National Institute for Occupational Safety and Health (NIOSH) accuracy criterion (18) requires CV < 13 % at the 95 % confidence level for methods without uncorrectable bias or systematic error.

NOTE A2.2—Similarly, CV < 13 % implies that the overall uncertainty (see ISO 20581) U < 30 % in the absence of bias and of significant errors other than gravimetric masses exceeding the LOQ.

NOTE A2.3—Therefore, appropriate occupational or environmental exposure limits would normally be set at values that are greater than the value corresponding to the LOQ.

NOTE A2.4—Although gravimetric error may, in fact, dominate at small sampled masses, other sources of sampling and analytical error should also be considered. Such errors may arise from several sources: (1) sampling pump-flowrate bias, (2) flow fluctuation (for example, in the case of respirable aerosol sampling), (3) variation in sampler physical dimensions, (4) electrostatic effects on sampling, or (5) bias relative to the appropriate sampling convention.

NOTE A2.5—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. Essentially, in this case, the system could be evaluated at each mass measurement.

A3. METHOD EVALUATION EXAMPLE

A3.1 Table A3.1 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 correspond to separate batches. For the purposes of illustration, masses (μg) were simulated, using mean weight 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 weight-difference standard deviation, the quantity to be estimated from the data, is σ = Sqrt[2] × 5 μg = 7.07 μg.

TABLE A3.1 Substrate Mass Difference Measurements (μg)

Substrate No. →1	2	3	4	5	6	Estimated Variance (s_b^2)
Batch ↓						↓
1	21	21	15	18	14	18	8.6
2	−4	−11	2	2	−6	2	29.5
3	9	22	−12	0	12	12	137.8
4	−2	6	20	6	8	6	50.7
5	−11	11	4	5	0	1	53.5
Mean variance estimate (s^2)							56.0

A3.2 Taking the square root of the mean variance estimate gives the estimated weight-difference uncertainty:

$$u = \text{Sqrt}[56.0] = 7.5 \text{ μg with 25 degrees of freedom} \qquad (A3.1)$$

which compares well with the true value, 7.07 μg.

A3.3 Furthermore, Eq A2.2 results in the 95 % confidence limit:

$$\sigma_{95\%} = \text{Sqrt}[25/14.61] \times 7.5 \text{ μg} = 9.8 \text{ μg} \qquad (A3.2)$$

A3.4 Now suppose that in actual application, three (3) blanks are to be used. Then Eq A1.5 indicates that the estimated mass determination uncertainty u_w is given by:

$$u_w = 8.6 \text{ μg} \qquad (A3.3)$$

A3.5 Therefore, the LOD and the LOQ (see Eq A1.6 and A1.7), would be:

$$LOD = 26 \text{ μg} \qquad (A3.4)$$

$$LOQ = 86 \text{ μg} \qquad (A3.5)$$

A4. TEST OF TRANSPORTATION INTEGRITY

A4.1 General

A4.1.1 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 lab. The tests proposed here are alternative to the method of EN 13205, Annex D, since most substrate weighing laboratories have no capacity for generating monodisperse aluminum oxide powders. The main differences are that EN 13205 requires: (*1*) a mixture of monodisperse aluminum oxide versus 'real' dust, (*2*) a laboratory orbital shaker table versus 'real' shipping of collection media, and (*3*) a maximum deposit equal to (sampler flow rate) × (8 h) × max (TLV [5 or 10 mg/m^3]) versus definition by the laboratory.

A4.2 Procedure

A4.2.1 Weigh at least 30 substrates plus blanks as required by the written procedures of the laboratory.

A4.2.2 Deposit dust onto at least three groups of ten substrates each with dust weights equal to (*1*) the limit of quantitation of the weighing system, (*2*) the maximum dust deposit for which the laboratory intends the method to be used, and (*3*) a midrange value in between the previous extreme dust deposits.

A4.2.3 Instead of monodisperse particles, use a dust type with a continuous size distribution, including particles both in the smaller and larger size ranges expected, following a presampler conforming to the relevant sampling convention. Use a nonvolatile, nonreactive, nonsticky, and nonhygroscopic dust.

Note A4.1—It is not necessary to deposit the dust in a laboratory. The dust may be deposited onto the substrates at workplaces. However, extra care must then be taken to avoid that the particles of the sample, which are most easily lost, are not lost already when the samples have arrived back at the laboratory.

A4.2.4 Weigh the substrates in accordance with the written procedures of the laboratory.

A4.2.5 Pack the substrates in accordance with the written procedures of the laboratory.

A4.2.6 Dispatch the transport containers by mail, consigned delivery system, or by the end-user's own vehicle (whichever 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.

A4.2.7 Weigh the active substrates plus blanks in accordance with the written procedures of the laboratory.

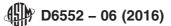A4.2.8 Determine the relative transport losses for each of the three levels of dust deposit.

A4.3 Requirement

A4.3.1 The relative dust loss due to transport shall be less than 5 %.

A4.3.2 The substrate mass range for which this requirement is met shall be documented.

REFERENCES

(1) Smith, J. P., and Bartley, D. L., "Laboratory Investigation of the Mass Stability of Sampling Cassettes from Inhalable Aerosol Samplers," *American Industrial Hygiene Association Journal*, Vol 59, 1999, pp. 582–585.

(2) Gonzalez-Fernández, E., "Toma de muestras de contaminantes con filtros de membrana: sus distintas aplicaciones y metodos de analisis" ("Sampling of Contaminants with Membrane Filters: Their Various Applications and Analysis Methods"), offprint of report presented at the I. Ibero-American Congress on the Environment, 1975.

(3) Kauffer, E., Vigneron, J.C., and Fabriès, Jean-François, "Mesure de la concentration pondérale de polluants particulaires atmosphériques en hygiène professionnelle: Etude de quelques média filtrants" ("Mass Concentration Measurement of Atmospheric Airborne Pollutants in Occupational Hygiene: Study of some Filtration Media"), *Analusis*, Vol 17, 1989, pp. 389–393.

(4) Lippmann, M., *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, eds. B.S. Cohen and S.V. Hering, ACGIH, Cincinnati, 1995.

(5) Vaughan, N. P., Milligan, B. D., and Ogden, T. L., "Filter Weighing Reproducibility and the Gravimetric Limit," *Annals of Occupational Hygiene*, Vol 33, 1989, pp. 331–337.

(6) Chen, C. C., and Baron, P. A., "Aspiration Efficiency and Inlet Wall Deposition in the Fiber Sampling Cassette," *American Industrial Hygiene Association Journal*, Vol 57, 1996, pp. 142–152.

(7) Lawless, P. A., and Rodes, C. E., "Maximizing Data Quality in the Gravimetric Analysis of Personal Exposure Sample Filters," *Journal of Air & Waste Management Association*, Vol 49, 1999, pp. 1039–1049.

(8) Engelbrecht, D. R., Cahill, T. A., and Feeney, P. J., "Electrostatic Effects on Gravimetric Analysis of Membrane Filters," *Journal of the Air Pollution Control Association*, Vol 30, 1980, p. 391.

(9) Schoonover, R. M., and Jones, F. E., *Analytical Chemistry*, Vol 53, 1981, p. 900.

(10) Charell, P. R., and Hawley, R. E., "Characteristics of Water Adsorption on Air Sampling Filters," *American Industrial Hygiene Association Journal*, Vol 42, 1981, pp. 353–360.

(11) Awan, S., and Burgess, G., "The Effect of Storage, Handling and Transport Traumas on Filter-Mounted Dusts," *Annals of Occupational Hygiene*, Vol 40, 1996, pp. 525–530.

(12) van Tongeren, M. J. A., Gardiner, K., and Calvert, I. A., "An Assessment of the Weight-Loss in Transit of Filters Loaded with Carbon Black," Vol 38, 1994, pp. 319–323.

(13) Feeney, P. J., Cahill, T. A., Olivera, J., and Guidar, R., "Gravimetric Determination of Mass on Lightly Loaded Membrane Filters," *Journal of the Air Pollution Control Association*, Vol 31, 1984, p. 376.

(14) Lehmann, E., Fröhlich, N., Heidermanns, G., and Hansen, M., "Gravimetrie als einfaches Meßverfahren für Staubmessungen—

Einsatzmöglichkeiten und Grenzen" ("Gravimetric Filter Analysis as a Simple Method for Dust Measurements: Applicability and Limitations"), *Staub—Reinhaltung der Luft*, Vol 52, 1992, pp. 80–92.

(15) American Chemical Society (ACS), "Principles of Environmental Analysis," Subcommittee on Environmental Improvement, *Analytical Chemistry*, Vol 55, 1983, pp. 2210–2218.

(16) Royal Society of Chemistry, Analytical Methods Committee, *Analyst*, Vol 112, 1987, p. 199.

(17) Kennedy, E. R., Fischbach, T. J., Song, R., Eller, P. M., and Shulman, S. A., "Limits of Detection and Quantitation," Appendix 3, *Guidelines for Air Sampling and Analytical Method Development and Evaluation*, DHHS (NIOSH) Publication Nos. 95-117, Cincinnati, 1995.

(18) Busch, K. A., "SCP Statistical Protocol," *Documentation of the NIOSH Validation Tests*, eds. D. G. Taylor, R. E. Kupel, and J. M. Bryant, DHEW (NIOSH) Pub. Nos. 77-185, Cincinnati, 1977.