BS ISO 12828-1:2011

BSI Standards Publication

Validation method for fire gas analysis

Part 1: Limits of detection and quantification

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National foreword

This British Standard is the UK implementation of ISO 12828-1:2011.

The UK participation in its preparation was entrusted to Technical Committee FSH/16, Hazards to life from fire.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Validation method for fire gas analysis —

Part 1: Limits of detection and quantification

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Partie 1: Limites de détection et de quantification

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Contents

Page

Foreword ..... **iv**

Introduction ..... **v**

1 Scope **1**

2 Normative references **1**

3 Terms and definitions **2**

4 Symbols **2**

5 General considerations **3**
5.1 Limit of detection: table of risks **3**
5.2 Limit of quantification: effect on repeatability r **3**
5.3 Typically accepted values for limits of detection and quantification **4**

6 Methods for determining limits of detection and quantification **5**
6.1 Principles and summary of methods **5**
6.2 Main method 1 – Determination of L_D and L_Q from matrix data from blank samples **6**
6.3 Main method 2 – Determination of L_D and L_Q from the linearity of calibration data **8**
6.4 Main method 3 — Checking a given or prescribed quantification limit **9**
6.5 Other methods **11**

7 Presentation of results **11**
7.1 Minimum requirements **11**
7.2 Reporting results from analyses **12**

Annex A (informative) **Examples of applications** **14**

Annex B (informative) **Examples of importance of limits of detection and of quantification** **18**

Bibliography **20**

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 12828-1 was prepared by Technical Committee ISO/TC 92, *Fire safety*, Subcommittee SC 3, *Fire threat to people and environment*.

ISO 12828 consists of the following parts, under the general title *Validation method for fire gas analysis*:

— *Part 1: Limits of detection and quantification*

The validation of the quantification method will be covered in a future Part 2.

Introduction

A major cause of injury and death in fire is exposure to the mobile fire effluent, which typically contains many toxic and irritant chemical species such as gases and vapours in addition to solid and liquid particulates (aerosols) such as visible smoke. In addition, fire effluents, especially those released from fires which are large and relatively prolonged, have the potential to contaminate a wider environment, both through the airborne smoke plume and the residues remaining on the ground which can affect the soil and watercourses.

Clearly, a knowledge of the composition and concentration of fire effluents and how they change during a fire is a vital requirement for assessing the potential for injury, death and environmental impact from fires.

Chemical and physical measurements of the harmful components of fire effluents are obtained from a wide variety of standard and ad-hoc fire tests on materials and finished products, often with the capability of varying the combustion conditions (e.g. temperature and air availability). Such tests can range in size from those using small-scale bench-top apparatus to those utilizing full-scale structures, often simulating a specific real-fire scenario.

When used for the assessment of hazards to life from fire, these data have been increasingly applied through the use of equations (e.g. fractional effective dose) developed specifically for quantifying the effects of the effluent on humans and, in particular, for an estimation of the times before specific hazards in a fire (ISO 13571).

Procedures are also currently being developed within ISO/TC 92 SC 3 for dealing with the environmental threats from fire effluent.

Recent advances in fire-safety engineering, including the calculation of time available for escape, have led to an increased demand for accurate detailed quantitative measurements of the chemical components of the fire effluent. It is clearly important, therefore, that the methods used to obtain these data be suitably validated for use in the specific application required. It is also important to define the required limits of detection and quantification (L_D and L_Q) values for a given analysis and application to avoid setting unnecessarily low limits which could prove expensive, time consuming and impose undue technical restraints, with little or no effect on the accuracy and precision of the end-use of the data.

This part of ISO 12828 provides guidance on methods for ensuring that any chemical or physical method of analysis for specific chemical species in fire effluents is suitably validated for correct use of limits of detection and limits of quantification for a given application of the data. It provides information to assist compliance with general requirements for the competence of testing and calibration laboratories (ISO/IEC 17025).

INTERNATIONAL STANDARD **ISO 12828-1:2011(E)**

Validation method for fire gas analysis —

Part 1: Limits of detection and quantification

1 Scope

In this part of ISO 12828, limits of detection (L_D) and limits of quantification (L_Q) are defined and calculated. It provides methods for determining suitable values for these two parameters for a specific analytical procedure and for a specific chemical species. It does not provide detailed guidance on methods of sampling and analysis of specific species which might be present in fire effluents. This guidance is contained in ISO 19701 and ISO 19702. The use of this part of ISO 12828 fulfils the requirement in ISO/IEC 17025 that a laboratory carrying out chemical analysis (e.g. of fire effluents) is able to characterize and evaluate a method by such parameters as L_D, L_Q and uncertainty. Examples of where the information contained in this part of ISO 12828 can be applied are:

a) Method validation: The parameters L_D and L_Q are required for all chemical analytical methods; they are as important as measurements of accuracy and precision.

b) Classifications based on toxicity indexes: Methods selected for analysis of effluents must have a minimum limit of quantification, consistent with the critical concentration used to calculate the contribution of each effluent to toxicity index. Furthermore, a toxicity index is not considered as zero when concentrations of toxic species are detected but not quantified (as they are below the limit of quantification). In this case, a contribution at least equal to the limit of detection for each measured species can be registered. Examples are shown in Annex B.

c) Round-robin comparison between two analytical methods: For a given working range, two methods can be compared only if the limits of these methods (calculated by using this part of ISO 12828) are similar for the lower range of concentrations to be measured. For example, if one laboratory provides values near its own limit of detection, and another laboratory gives results well above its own limit of detection, the reproducibility R assessment of the round robin can be artificially overestimated. In many round-robin tests, bad reproducibility R values can be found if some values are close to the limit of quantification and/or limit of detection. In such cases, no conclusion on the round robin can be given without an assessment of the limit of quantification value and the expression of results as described in this part of ISO 12828.

This part of ISO 12828 is intended for use by operatives familiar with chemical and physical analysis of fire effluents.

Examples of existing standards where the information contained in this part of ISO 12828 can be used are the analytical chemical methods in ISO 19701, ISO 19702, ISO 5660-1, and the chemical measurements in the methods discussed in ISO/TR 16312-2.

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 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 13571:2007, *Life-threatening components of fire — Guidelines for the estimation of time available for escape using fire data*

ISO 13943, *Fire safety — Vocabulary*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 19701, *Methods for sampling and analysis of fire effluents*

ISO 19702, *Toxicity testing of fire effluents — Guidance for analysis of gases and vapours in fire effluents using FTIR gas analysis*

ISO 19706, *Guidelines for assessing the fire threat to people*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13943, ISO 5725-1 and the following apply.

NOTE There is no consensus for an exact definition of the following two limits, especially for the limit of detection. However, two references have been used as guidance for the definitions cited here: ISO 11843-1 and ISO 11843-2.

3.1
limit of detection
L_D
smallest quantity of an analyte in a sample that can be detected and considered with a stated probability as different from the detector output from a blank sample

NOTE It should be noted that the actual quantity of the analyte need not be stated and that the symbol "y_{L_D}" is used to express the limit of detection in terms of a detector signal value, converted (via a calibration technique) into a mass, volume or concentration term.

3.2
limit of quantification
L_Q
smallest quantity of an analyte which is possible to quantify under the specific experimental conditions described in the chosen method, where the variability of the method has been defined (i.e. a variation coefficient has been determined)

NOTE The symbol "y_{L_Q}" is used to express the limit of quantification in terms of a detector signal value, converted (via a calibration technique) into a mass, volume or concentration term.

4 Symbols

u Actual analyte concentration or terms which use this

y Value of the analyte concentration as measured by the analytical system (detector output as "raw data")

$U(x)$ Enlarged absolute uncertainty on measurement of x

σ_i Standard deviation for i

5 General considerations

5.1 Limit of detection: table of risks

There are two contingencies or risks associated with L_D:

— a risk designated "α" where the substance may be detected in the sample even though the substance is not actually present;

— a risk designated "β" where the substance is not detected in the sample even though the substance is actually present.

These risks can be illustrated using a simple table of analysis result versus reality as in Table 1.

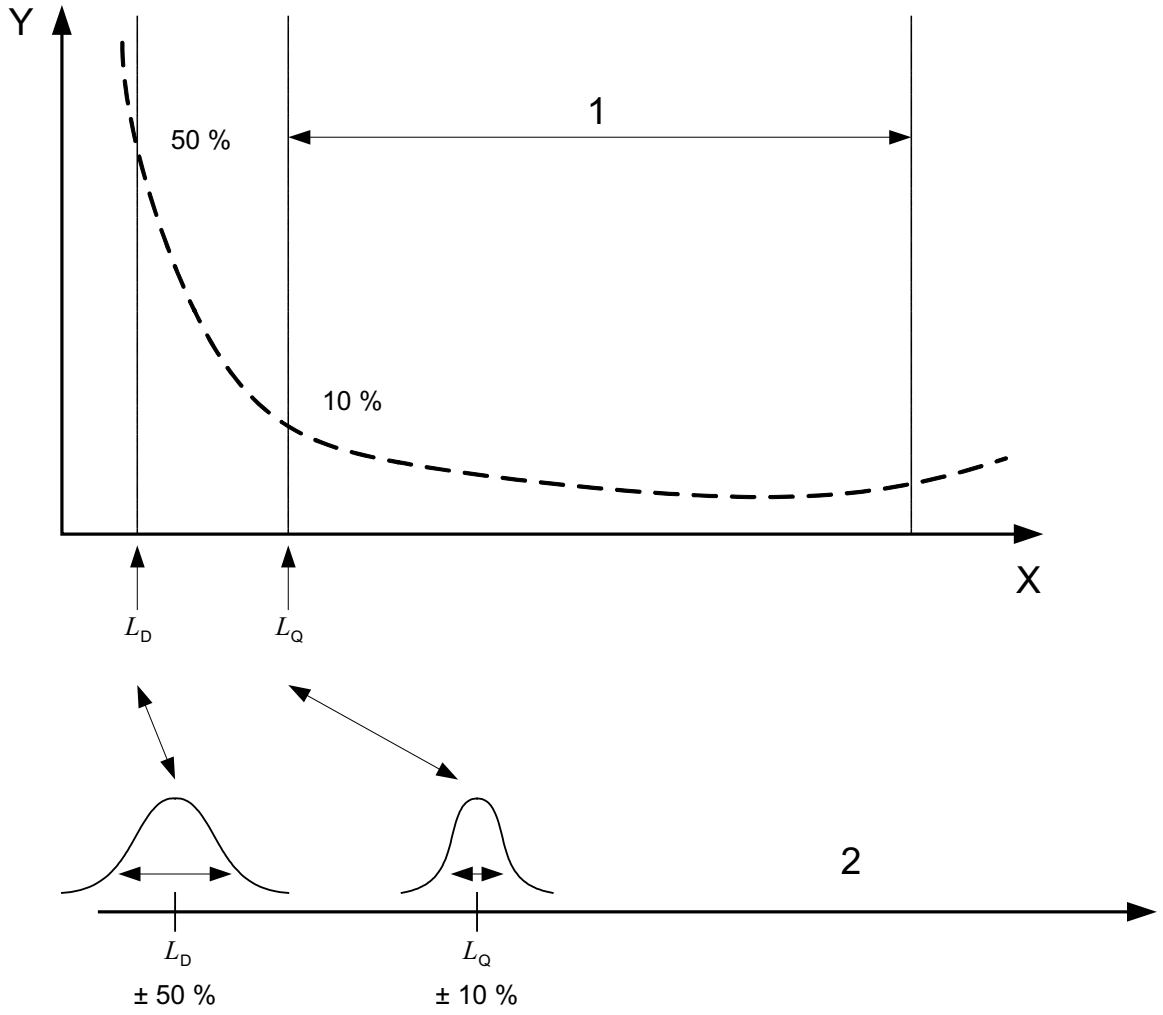
Table 1 — Table of risks: analysis result versus reality

		Analysis result	
		Not present	**Present**
Reality	**Not present**	Good decision Probability 1 – α	Probability α FALSE POSITIVE
	Present	Probability β FALSE NEGATIVE	Good decision Probability 1 - β

It is important that false negatives be eliminated. Failing to observe the presence of a particular toxicant, especially if it is present at a toxicologically important level, can lead to a false sense of safety in an engineering calculation. False positives may indicate a hazard that is not actually present. This conservative outcome is less harmful than the outcome from a false negative. It can be considered as a "fail safe" result.

5.2 Limit of quantification: effect on repeatability r

Near the limit of quantification, the accuracy of measurement is lower than in the region over which an analysis system has been calibrated. The limit of quantification, however, may be substantially lower than the lowest extremity of the calibrated region for an analytical system and is essentially the lowest point where the analytical method may give an acceptable quantified measurement.



Key

X amount of a substance
Y repeatability, r, (%)
1 calibration range
2 value

Figure 1 — Position of L_D and L_Q on calibration range
(based on the work of Horwitz[8], and Brown *et al* [9])

5.3 Typically accepted values for limits of detection and quantification

The limit of quantification is usually considered to be 10 % of the measurement repeatability r, and the limit of detection is usually considered to be three times the standard deviation of a matrix of blank sample results, σ_b. If the standard deviation is constant between zero and the limit of quantification, the limit of quantification is equal to 10 times the standard deviation of a matrix blank result. The limit of detection is therefore usually considered as 50 % of the repeatability r.

The value of 10 % is derived from Equation (1)

$$L_Q = 10 \times \sigma_b \qquad \frac{\sigma_b}{L_Q} = 10\ \% \tag{1}$$

6 Methods for determining limits of detection and quantification

6.1 Principles and summary of methods

Validation of a chemical or physical method of analysis for a specific species in the fire effluent can be considered as a four-step process:

a) Step 1. Define the final objective/end-use of the data.

When undertaking a chemical or physical analysis of a fire effluent, the objective/end-use of the analytical data can be considered. For example, the objective might be to contribute to the fire-safety engineering design of a building (e.g. through a fractional effective dose calculation of Available Safe Egress Time – ASET), to determine the accuracy of a numerical fire model, the relevance of a small-scale physical fire model or the determination of the toxic potency of the effluent from a particular combustible item.

b) Step 2. Determine the lowest concentrations and degree of accuracy and precision required.

Having established the end-use of the data, the lowest concentrations and the appropriate degree of accuracy and precision required in the chemical analysis can be determined. For example, in a fractional effective dose calculation (where the cumulative effects over fixed time intervals of reducing tenability due to a specified range of species is considered), interest might range from concentrations which could incapacitate people of average sensitivity to the species measured, to concentrations which show negligible toxic effect over a long exposure period. It is also important to appreciate that it is not normally necessary to attempt such measurements with any greater precision than that resulting from the precision of the end-use of these data. This can avoid undue technical and economic restraints in obtaining measurements.

c) Step 3. Select an appropriate sampling and analytical method.

The ultimate requirement of any chemical analysis of a species in the fire effluent is to obtain mass, volume or concentration data for the species which is as close as practicable (given the considerations of step 2) to the actual mass, volume or concentration of the species in the effluent being measured. The two main stages to consider are the sampling procedures and the analytical methodology. Sampling may be continuous or take place over discrete time intervals but either procedure may be subject to potential losses through a variety of effects. Analysis of a species may be carried out continuously or intermittently during the fire or from stored samples.

d) Step 4. Evaluate the specific methodology chosen.

For chemical analyses, as with any other measurement, it is important to evaluate a specific methodology for its ability to provide appropriate, sufficient and adequate data for a particular application. This evaluation normally has to consider a range of factors, including repeatability r, reproducibility R, and a measurement of uncertainty, especially for laboratories working under the rules in ISO/IEC 17025. For fire-effluent toxicity, these requirements are discussed in ISO 19706.

Two key parameters in the evaluation of a method (e.g. when it is required to compare different methods for a particular application) are

1) the lower concentrations of particular species which are able to be detected adequately (limits of detection), L_D, and

2) the lower concentrations of particular species which are able to be quantified adequately (limits of quantification), L_Q.

Knowledge of the L_Q value is essential when comparing small concentrations of fire effluent gases measured by different methods. Both the L_D and L_Q parameters in specific analytical methods are relevant to the assessment of the contribution of gases to a fractional effective dose (FED) or fractional effective concentration (FEC) calculation, as set out in ISO 13571. Both parameters are also important in the evaluation

of the repeatability r and reproducibility R in a “round-robin” assessment of, for example, a physical fire model, following the procedures set out in ISO 5725-1.

The values of these two parameters are affected by practices that are specific to a fire laboratory. Each laboratory therefore can characterize and validate its analytical techniques using calculation methods for determining L_D and L_Q, such as those provided in this part of ISO 12828.

There are three main methods that are suitable for determining limits of detection and quantification. (See 6.2, 6.3 and 6.4). The choice of the method(s) to be used depends on the particular circumstances of the required analysis. These three methods are as follows:

— main method 1: Study of matrix data from blank samples;

— main method 2: Study of linearity of calibration data;

— main method 3: Checking a chosen quantification limit.

Each of these main methods is described in the following subclauses.

6.2 Main method 1 – Determination of L_D and L_Q from matrix data from blank samples

6.2.1 Principle

In this method, a large number of independent measurements, y_n, (signal strength of a detector) of the chemical species of interest are made for a sample that does not contain this chemical species (i.e. a blank sample). The number of measurements, n, must be at least 5. Outlier points are eliminated either by visual examination of the plotted data or by statistical tests (e.g. the Grubbs test as presented in ISO 5725-1, or the extended Shapiro-Wilk static test[10].)

It should be noted that; in the Shapiro-Wilk test, W is given by Equation (2)

$$W = \frac{\left(\sum a_i x_{(i)}\right)^2}{\sum \left(x_i - \bar{x}\right)^2} \tag{2}$$

where $x_{(i)}$ is the i-th largest order statistic. Royston[10] gives approximations and tabled values that can be used to compute the coefficients a_i, and obtain the significance level of the W statistic.

Calculation is then made of the mean value, $\bar{y}$, and σ_b, which is the statistical “noise” around zero detector output in the analytical system. This value is then linked mathematically with the limit of detection.

In this method, the limit of detection (signal strength of detector) is equated to a value three times the standard deviation of the detector output or response, and the limit of quantification ten times the value of the standard deviation of the detector output or response, as in Equation (3)

$$y_{L_D} = \bar{y} + 3\sigma_b \qquad y_{L_Q} = \bar{y} + 10\sigma_b \tag{3}$$

An example of this method is shown in A.1. The magnitude for limit of detection and limit of quantification are calculated as a parameter, together with the sensitivity s of the system, as shown in Equation (4)

$$L_D = \frac{y_{L_D} - \bar{y}}{s} \qquad L_Q = \frac{y_{L_Q} - \bar{y}}{s} \tag{4}$$

The sensitivity value corresponds to the sensitivity of the analytical system for values near the limits. In the case of a linear regression, the sensitivity value used can be the slope of the calibration function.

In some standards, a noise value called “root mean square” (rms) is calculated. It corresponds to the square root of the arithmetic mean of the squares of a set of numbers. If the numbers are x_1, x_2, x_3,…, x_n, the root mean square is given by Equation (5).

$$\text{rms} = \sqrt{\frac{x_1^2 + x_2^2 + x_3^2 + \ldots + x_n^2}{n}} \tag{5}$$

It is valuable as an average of the magnitudes of quantities, and it is not affected by the signs of the quantities. For example, in ISO 5660-1, the rms value is required for oxygen measurement. This value can then be used directly to determine, for example, the lowest oxygen depletion which can be measured, and therefore the lowest value of heat release (using oxygen depletion calorimetry) which it is possible to measure with the specific system in use. The rms is close to σ_b.

6.2.2 Advantages of main method 1

The method is very simple to use.

The determined values of L_D and L_Q are linked to the blank and are always above the statistical variation in the particular analytical chemical method.

There is no dependence on the particular regression model used.

6.2.3 Disadvantages of main method 1

The method places a high reliance on the use of blank tests. The blanks must have no trace of the analyte of interest but should retain a similar mix of species apart from the analyte of interest. Such a suitable blank can be difficult to obtain.

Interfering species can modify the blank sample “noise” signal and therefore modify the L_D and L_Q values. To limit this effect, the matrix blank must be as close as possible to the matrix in a real measurement, including possible interfering species.

a) In order to allow for the effect of interfering species, they can be included in various proportions in the blank sample. However, this approach may increase the value of the standard deviation of the blank and change the values of the limits. The interfering species may also give rise to a detector signal over the concentration range required to be measured.

b) For some analytical techniques, these blank tests can extend over a relatively long time. The impact of variable measurement conditions during the blank tests also has to be evaluated, especially for measurements over long periods and periods of instability.

c) For some analytical techniques, blank samples are not available. In these cases, “grey blanks” (gb) are used. These consist of very low concentrations of solutions of the required analyte used to determine standard deviation σ_{gb}. The limit of detection (signal strength) is then given by Equation (6):

$$y_{L_D} = 3\sigma_{gb} \tag{6}$$

6.2.4 Examples of applications of main method 1

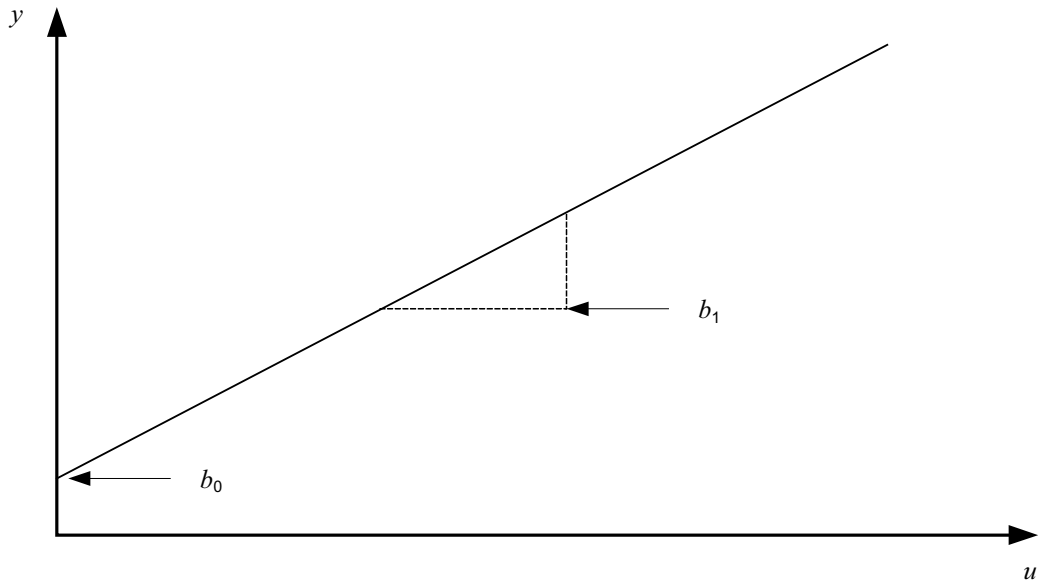
For FTIR measurements, as in ISO 19702. The method can be applied to the baseline noise, to determine additionally the limit of quantification of non-calibrated compounds.

When liquid chromatographic (ILC and HPLC) measurements (Reference [14] and as in ISO 19701) are to be evaluated, the blank samples used to generate a data matrix may consist of solutions containing all expected interfering compounds, but must not contain the species of interest. The standard deviation is only determined over the region of the retention time of the species of interest. An example is given in A.1

6.3 Main method 2 – Determination of L_D and L_Q from the linearity of calibration data

6.3.1 Principle

This method uses a single set of measurements performed on known concentrations of the species of interest. It is important to consider that this set has to include low values, close to the limit of quantification, in order to obtain the sensitivity of the detector for low concentrations. In the case of a linear calibration function, $y = b_0 + b_1 u$, where the intercept b_0 represents the signal for a blank sample, y represents the measured concentrations of the analyte and u represents the actual concentrations of the analyte (see Figure 2). The best values of the intercept, b_0, and the slope, b_1, of the line are obtained from a "least squares" regression analysis fit to the data. The u values are assumed to have a very low uncertainty in comparison with the uncertainty of the y values.



Key

u actual concentrations of the analyte
y measured concentrations of the analyte
b_0 intercept
b_1 slope

Figure 2 — Representation of a linear calibration curve

The standard deviation of the blank samples, σ_{b_0}, is obtained from this regression. As in main method 1, y_{L_D} and y_{L_Q} are given in terms of the signal using the following relations as shown in Equation (7):

$$y_{L_D} = b_0 + 3\sigma_{b_0} \qquad y_{L_Q} = b_0 + 10\sigma_{b_0} \tag{7}$$

The magnitudes of the limits of detection and of quantification (in terms of analyte concentration) are expressed as follows in Equation (8):

$$L_D = \frac{3\sigma_{b_0}}{b_1} \qquad L_Q = \frac{10\sigma_{b_0}}{b_1} \tag{8}$$

In carrying out this method, it is important to be aware of the following:

a) The calculation of the limits of detection and quantification assumes that the model is a good representation of the response of the system near the limit of detection and the intercept is not statistically significant after a blank correction compared to the associated standard deviation.

b) This calculation of the limits of detection and quantification assume that the "residual standard deviation" $\sigma_{(y)}$ is constant over the concentration range. A Cochran statistic test (ISO 5660-1) can be used for checking this assumption.

c) Commonly, u values are distributed as a normal distribution. In this case, the expression is $y_{L_D} = b_0 + t_{N-2}\sigma_{b_0}$, where t_{N-2} is the "Student" coefficient. The value of 3 times the standard deviation used in the general formula is an approximation for a sufficient number of observations N and a confidence of 99,97 %. For non-Gaussian u values, another coefficient may be used, as derived from the distribution law for u values.

d) The relationship between the analyte concentration and the response of the analytical system may not always be linear, e.g. it may be exponential or follow a power law. In these cases, the technique can still be used but the calculations are more complex.

6.3.2 Advantages of main method 2

The method is very simple to use for many analytical situations and uses only simple equations (linear or polynomial depending on the shape of the calibration plot).

Only calibration points are needed: no further tests or data are needed.

6.3.3 Disadvantages of main method 2

The method depends on the regression model being applied to all the data points, not just to the smallest values and close to zero. The method also depends on how the regression model fits across the entire calibration range to achieve representative limits of detection and of quantification. For example, the regression model may represent low data values including the lowest calibration point.

The limit of detection determined can be lower than the system noise. This is an invalid result that is not detected by this method. The lowest calibration value must not be too far away from the limit of detection and limit of quantification.

6.3.4 Examples of applications

The method is suitable where the final value has been converted from the input data physical measurement. It is useful for rapid determinations of these limits without further analyses. However, further experiments may be needed to confirm the values. Examples of applications are

— FTIR calibration curves according to ISO 19702,

— ICP measurements, GC-MS measurements according to ISO 19701,and

— spectrophotometric measurements.

An example is given in A.2.

6.4 Main method 3 — Checking a given or prescribed quantification limit

6.4.1 Principle

The method may be used to determine if a given or prescribed limit of quantification is acceptable. The data are obtained by analysing a given number (n) of solutions with a concentration equivalent to the predefined limit of quantification required for the specific application being addressed. The mean value and the standard deviation of these data are then calculated. The minimum value of replicates (n) is 10.

σ_{L_Q} standard deviation of the n measured values of the n number of solutions.

$\overline{u}_{L_Q}$ mean value of the n measured values.

Initially, $\overline{u}_{L_Q}$ may be comparable to the given limit. The limit of quantification value is then exact (accuracy criterion) if it is as shown in Equation (9):

$$\left| \frac{L_Q - \overline{u}_{L_Q}}{\frac{\sigma_{L_Q}}{\sqrt{n}}} \right| < 10 \tag{9}$$

In addition, if $(5\sigma_{L_Q}) < L_Q$, then 0 is not acceptable as L_Q. It is the precision criterion. This criterion can be expressed as a coefficient of variation C_V, written as in Equation (10):

$$C_V = \frac{\sigma_{L_Q}}{L_Q} < 20\% \tag{10}$$

If the given limit passes both these criteria, the limit of detection is calculated from the limit of quantification divided by 3, as in Equation (11):

$$L_D = \frac{L_Q}{3} \tag{11}$$

WARNING — The outlying points must be first eliminated by either an examination of the plotted data or a statistical test (e.g. Shapiro-Wilk statistic test for a normal distribution, or Grubbs, Dixon, Mandel tests according to ISO 5725-1).

6.4.2 Advantages of main method 3

The method is useful for the comparison of different methods when a desired limit of quantification is defined or prescribed.

If a sufficient limit of quantification is achieved, a limit of detection can be deduced without separate measurement.

The method is useful to validate limits of detection and of quantification calculated by another analytical method.

The method is useful to validate a chosen limit of quantification, e.g. to enable the choice of the most appropriate analytical technique to achieve a given limit.

6.4.3 Disadvantages of main method 3

The limit of quantification determined by this method is equal to or greater than the potential limit of the analytical method, i.e. the analytical method may be capable of achieving a lower L_D or L_Q.

The sample concentrations used must be chosen with a knowledge of the desired or prescribed limit of quantification.

6.4.4 Applications

Validation of values determined by other methods.

Methods selection: comparisons of alternative methods within given limits (e.g. minimum contribution to a conventional toxicity index, or minimum acceptable value for a ratio L_Q/L_{C50}). An example is given in A.3.

6.5 Other methods

6.5.1 Horwitz method

The Horwitz method (References [8] and [12] is based on the nature of limits of detection and quantification (see Clause 3). Many determinations of analytical response are required from many different solutions of analyte in solvent. The technique requires three steps:

1) For each solution studied, a coefficient of variation C_V is determined as in Equation (12)

$$C_{V\,i} = \frac{\sigma_{(y_i)}}{\bar{y}_i} \tag{12}$$

where

$\sigma_{(y_i)}$ is the standard deviation of the measurements for the "ith" solution;

$\bar{y}_i$ is the average concentration found.

For a good estimate of C_V, at least eight analyses have to be carried out for each solution.

2) The values of C_{Vi} are plotted vs $\bar{y}_i$ and a regression curve is fitted to the points.

3) The limit of detection is the value of concentration corresponding (from this curve) to a C_V value of 50 %. The limit of quantification is defined as the concentration corresponding to a C_V of 10 %.

The method is very easy to use, but requires what may often be a prohibitive number of measurements on each solution for many solutions. It can only be used for very simple and fast measurement techniques. An example is given in A.4.

6.5.2 Determination of the limit of detection from a qualitative analysis

This method requires the use of a potentially large number of known concentrations of analyte.

A solution of a concentration y_i of the analyte in a representative matrix (a solution with similar constituents and similar concentrations of those constituents to the solution containing the solute to be analysed) is prepared, and a qualitative analysis carried out at least ten times. The outcome of the analyses is effectively Boolean logic (e.g. positive "yes" or negative "no"). An example would be to carry out a chemical precipitation reaction for identifying a specific analyte. The limit of detection corresponds to the minimum value of y_i where there are more positive than negative responses. If there are many more positive than negative responses, a new solution that is less concentrated is prepared and the test is repeated.

The method can be used to determine the limit of detection using non-quantitative techniques, such as a halogen determination with the Lassaigne technique (Reference [15]).

7 Presentation of results

7.1 Minimum requirements

Each of the methods described can give rise to different values of L_D and L_Q. The limits of detection and of quantification depend on many factors, including the analytical technique, the laboratory environment, and the operators in a given laboratory. The values found cannot be extrapolated to other laboratories, techniques or conditions.

There exists a so-called "instrumental" value of the limit of detection. This value is the theoretical minimum value of the limit for a given instrument.

Determination of limits of detection and of quantification are also subject to many other parameters, such as the calculation method used, number of measurements, experimental conditions, and the matrix upon which the analysis is performed. All these parameters must be reported. They constitute the first part of the method validation process. It is therefore considered that the minimum requirements for conducting and reporting a successful limits determination are:

a) reference and adherence to this guidance;

b) reference to documents containing details of the analytical technique used;

c) statement of the method used;

d) statement of the parameters of the method used

- numerical parameters used (e.g. “Student” factor in main method 1),
- number of samples studied, and
- calibration data;

e) presentation of the complete set of data used [e.g. standard deviation for b_0 (main method 2)];

f) statement of the limits found.

For example, in an interlaboratory trial, it is essential to have complete information on these limits for each laboratory, each analytical technique and each set of data analysed. All participants should have this information.

It is essential that the two values (L_D and L_Q) be reported separately, with the precision of the method used to determine them stated in each case.

7.2 Reporting results from analyses

For reporting an analytical result close to the limits, four approaches may be used.

a) The value is considered as zero or not relevant.

b) The value found is presented with the uncertainty stated.

c) The limit of detection value is explicitly used.

d) The limit of quantification value is explicitly used.

No information on what approach to use is given in the relevant standards (e.g. Eurachem Guide [13]), Current practice is often to simply report the concentration found and whether it has a positive, null or negative value.

Therefore, a suitable way to report analytical results is summarized in Table 2:

Table 2 — Reporting analytical results

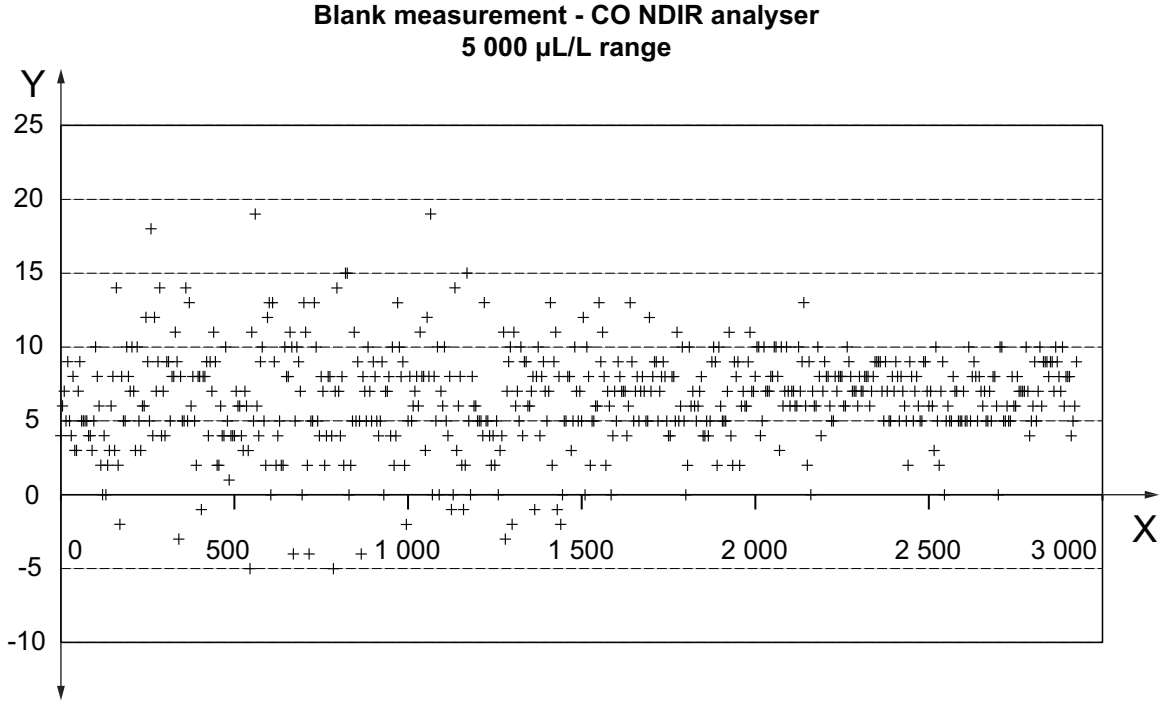
Value found < L_D	L_D < **value found** < L_Q	**Value found** > L_Q
x: not detected The limit of detection is L_D	x: not quantified The limit of quantification is L_Q The limit of detection is L_D	$x \pm U(x)$
x: Value found, expressed in quantity L_D: Value of limit of detection L_Q: Value of limit of quantification $U(x)$: Uncertainty of x measurement (expanded)		

Annex A
(informative)

Examples of applications

A.1 Main method 1 – Using results of matrix blank samples (i.e. samples containing a similar range and concentration of analytes to the sample containing the unknown species, but not containing the unknown species)

EXAMPLE Measurement of a carbon monoxide (CO) blank using a non-dispersive infrared (NDIR) analyser. The blank was sampled over 45 min. The values obtained are plotted versus time as shown in Figure A.1.



Key

X times (s)

Y CO measured (µL/L)

Figure A.1 — NDIR CO analyser background noise (blank)

The statistics of this analysis are presented below:

Resolution: 1 µL/L

Average: 6,5 µL/L

Standard deviation: 3,3 µL/L

Using the method described in 6.2, the final L_D and L_Q values found for CO in this example are:

L_D = 17 µl/l L_Q = 40 µl/l

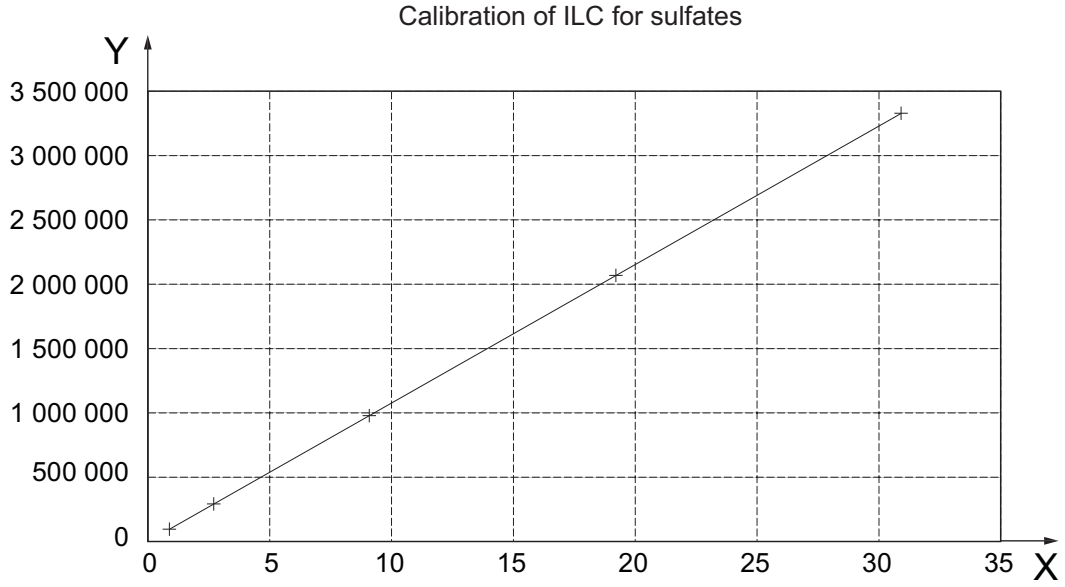
A.2 Main method 2 – Using the calibration function

EXAMPLE The analysis of sulfur dioxide (SO_2), which is absorbed by a hydrogen peroxide solution, followed by analysis using ion chromatography of the resulting sulfates. The method is described in ISO 19701. The example also demonstrates the limitations of this method.

The values obtained during calibration are presented in Table A.1 and plotted in the chart in Figure A.2.

Table A.1 — Calibration data obtained

Amount (mg/l)	**Area**
0,887	95 487
2,706	291 389
9,087	978 418
19,207	2 068 008
30,913	3 328 352



Key

X concentration (mg/L)

Y response area

Figure A.2 — Calibration curve for sulfate ions in HPIC

Linear regression:

Slope	b_1	$1{,}076 \times 10^5$
Standard deviation of slope	σ_{b_1}	1,050
Intercept	b_0	19,895
Standard deviation of intercept	σ_{b_0}	17,673

The value of b_0 is not significant regarding $2 \times \sigma(b_0)$. The final L_D and L_Q values found for this example are:

$L_D = 4{,}9 \times 10^{-4}$ mg/l $\qquad$ $L_Q = 16{,}4 \times 10^{-3}$ mg/l

The calibration function gives a poor representation of the system close to the limits. Therefore, values are highly underestimated and new sets of data are needed to quantify the sensitivity near the limit. In this case, the acceptable limit of detection is overestimated by the first standard concentration (0,887 mg/L).

A.3 Main method 3 – Checking a given or prescribed quantification limit

EXAMPLE This example uses a fractional effective concentration (FEC) technique for irritant species. The prescribed maximum limit of quantification when using an FEC equation has been defined as 10 % of the FEC contribution for one gas. Considering acrolein contribution and the information in ISO 13571:2007, the F factor (for FEC = 1 considering acrolein contribution alone) is equal to 25 parts per million (ppm). A suitable limit of detection to achieve the objective is therefore: 2,5 µL/L.

Three different methods are used to analyse a 2,5 µL/L certified gas cylinder of acrolein. Table A.2 presents actual values obtained for eight replicates:

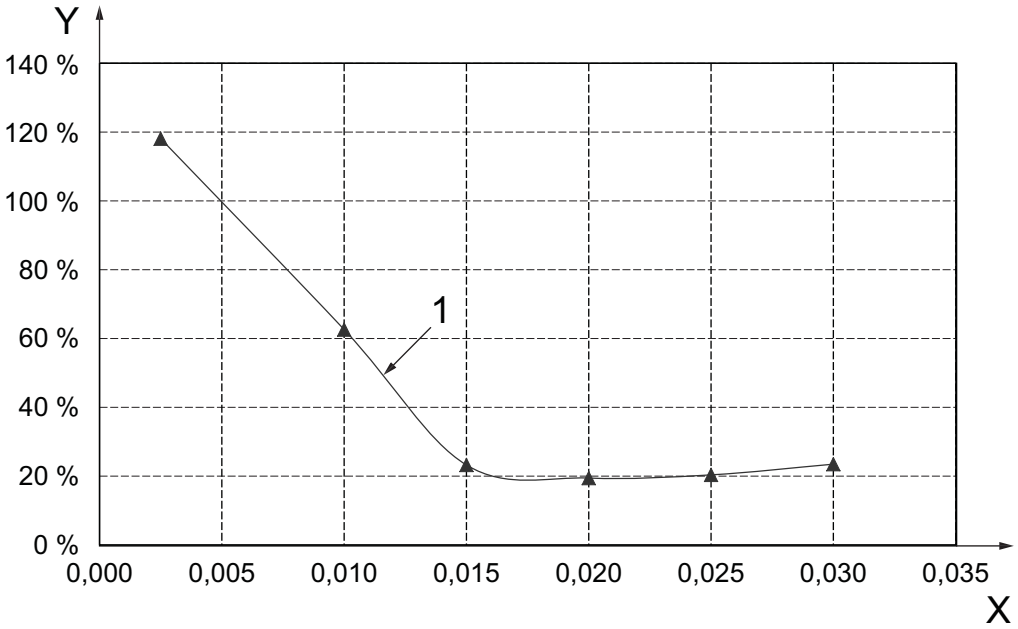
Table A.2

Replicate	Device 1	Device 2	Device 3
1	2,4	2,3	20,2
2	2,5	4,1	20,0
3	2,5	2,6	20,4
4	2,5	1,2	20,5
5	2,7	2,2	19,8
6	2,5	2,7	20,4
7	2,6	3,2	19,5
8	2,5	1,1	20,0
Average	2,525	2,425	20,1
Standard deviation	0,09	0,99	0,34
Trueness criteria	0,80	0,21	145,45
Precision criteria	4 %	41 %	2 %

The criteria according to 6.3 shall be: *Trueness criteria < 10* and *Precision criteria < 20 %.* In the present case, Device 1 passed both tests. Devices 2 and 3 are not suitable to reach the target limit of quantification.

A.4 Horwitz method

EXAMPLE Analysis of bromide ion as measured by HPIC (Reference [14] adapted from ISO 19701). The coefficients of variation (standard deviation divided by the average) are determined on eight replicate measurements per concentration, for six different concentrations near the limit of detection. Figure A.3 shows the plot of experimental coefficient of variation C_V versus concentration.



Key

X concentration (mg/l)

Y C_V %

1 bromide

Figure A.3 — Horwitz curve for bromide by HPIC

The coefficient of variation C_V decreases from about 120 % to 20 %. The method is therefore appropriate for this ion under these analytical conditions. It allows the estimation of an L_D of 0,012 mg/L corresponding to C_V = 50 %.

Nevertheless, for concentrations of bromide ions from 0,002 5 to 0,015 0 mg/L, the peak areas found in HPIC are too low to be correctly dissociated from the background noise. For a concentration of 0,020 mg/L, detection is carried out with a coefficient of variation close to 20 %. The L_D of the bromide ions then lies between 0,015 and 0,020 mg/L.

Annex B
(informative)

Examples of importance of limits of detection and of quantification

B.1 Influence on a pass/fail measurement

Many tests are used to enable a simple “accept”/”reject” decision to be made; the test result is therefore of the “pass/fail” type. An example is the calculation of toxicity indices, by summing the contribution of different species and then comparing these to a defined limit value (e.g. BS 6853, NF F 16-101, CEN/TS 45545-2).

In this case, some species may be found well within a valid measurement range, with other species, in low quantities near the limits. It is therefore important for these limit values to be known and to be defined in the measuring standard, to provide a measure of the minimum performance capability of the methods used to enable a valid “pass/fail” decision to be made.

Additionally, the limits of the measuring standard or of, for example, a regulation based on the index, may take into consideration these parameters. Figure B.1 represents the effect of limits of detection, of quantification and uncertainty on a pass/fail test of a toxicity index determination:

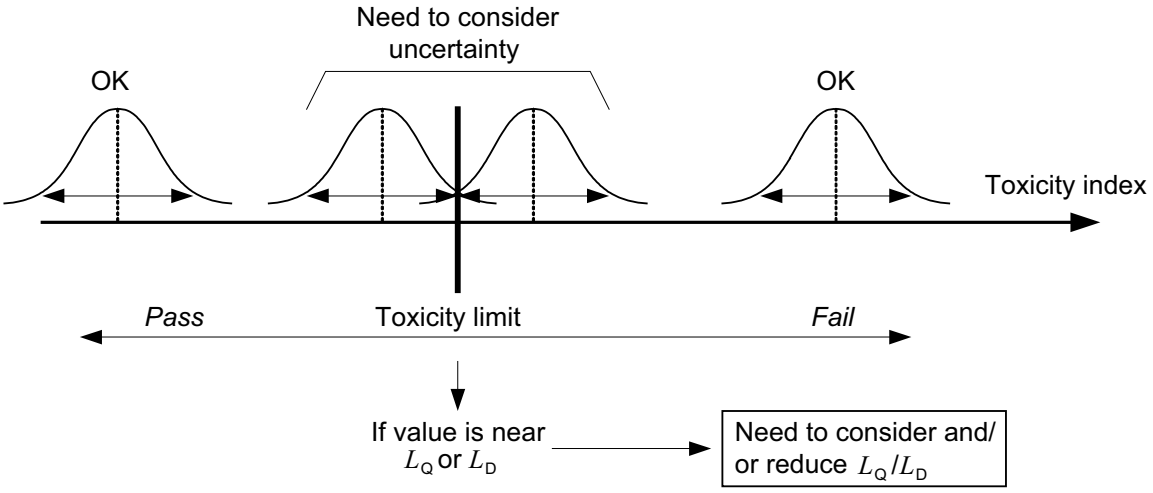


Figure B.1 — Effect of L_D or L_Q on a “pass/fail” determination of toxicity index

B.2 Minimum detectable toxicity threshold

Equations such as those used to evaluate FED or FEC in ISO 13571 require a consideration of the minimum values possible in a given scenario. Conclusions on the cumulative toxicity over time of a given fire effluent have to take into account this aspect. An example is given for FED and for FEC measured with FTIR according to ISO 19702.

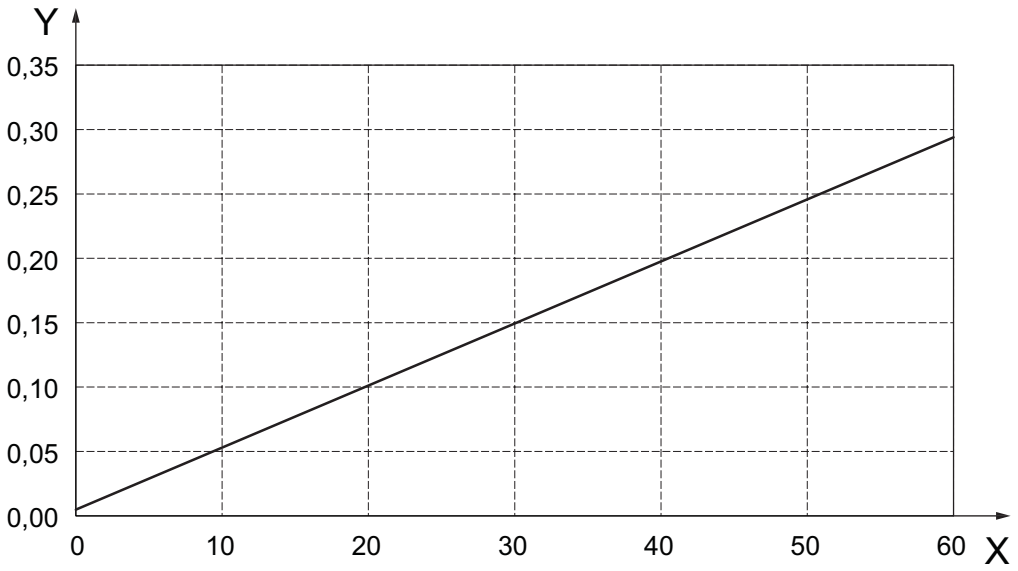
B.2.1 Example for an FED evaluation

The experimental limits of detection determined are for CO, L_D = 2 µL/L and for HCN, L_D = 2 µL/L.

FED is given in ISO 13571:2007 by the equation:

$$\text{FED} = \sum_{t1}^{t2} \frac{\phi_{\text{CO}}}{35\,000} \Delta t + \sum_{t1}^{t2} \frac{\exp\left(\phi_{\text{HCN}}/43\right)}{220} \Delta t$$

Because of the integrated character of the FED equation, the lowest detectable FED is a function of time. A simple plot is shown in Figure B.2, to determine the lowest detectable FED as a function of time.



Key

X time

Y lowest detectable FED

Figure B.2 — Lowest detectable FED

B.2.2 Example for an FEC evaluation

FEC is given by the equation:

$$\text{FEC} = \frac{\phi_{\text{HCl}}}{F_{\text{HCl}}} + \frac{\phi_{\text{HBr}}}{F_{\text{HBr}}} + \frac{\phi_{\text{HF}}}{F_{\text{HF}}} + \frac{\phi_{\text{SO}_2}}{F_{\text{SO}_2}} + \frac{\phi_{\text{NO}_2}}{F_{\text{NO}_2}} + \frac{\phi_{\text{Acrolein}}}{F_{\text{Acrolein}}} + \frac{\phi_{\text{Formaldehyde}}}{F_{\text{Formaldehyde}}}$$

Limits of detection for the gases, F factors and contribution to minimum detectable FEC are presented in Table B.1:

Table B.1

Gas	L_{D}	F**-factor**[a]	**Contribution to FEC**
HCl	8	1000	0,008
HBr	4	1000	0,004
HF	15	500	0,030
SO_2	2	150	0,013
NO_2	10	250	0,040
Acrolein	2	30	0,067
Formaldehyde	6	250	0,024
		Lowest detectable FEC	0,186

[a] The values are given in ISO 13571.

Therefore the lowest detectable value of FEC is 0,186.

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