BS EN 12619:2013

BSI Standards Publication

Stationary source emissions — Determination of the mass concentration of total gaseous organic carbon — Continuous flame ionisation detector method

bsi.

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of EN 12619:2013. It supersedes BS EN 12619:1999 and BS EN 13526:2002 which are withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/1, Stationary source emission.

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

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

ISBN 978 0 580 73805 0

ICS 13.040.40

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 January 2013.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 12619

January 2013

ICS 13.040.40

Supersedes EN 12619:1999, EN 13526:2001

English Version

Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon - Continuous flame ionisation detector method

Emissions de sources fixes - Détermination de la concentration massique en carbone organique total - Méthode du détecteur continu à ionisation de flamme

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration des gesamten gasförmigen organisch gebundenen Kohlenstoffs - Kontinuierliches Verfahren mit dem Flammenionisationsdetektor

This European Standard was approved by CEN on 24 November 2012.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

Contents

Page

Foreword

This document (EN 12619:2013) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2013, and conflicting national standards shall be withdrawn at the latest by July 2013.

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

This document supersedes EN 12619:1999 and EN 13526:2001.

The list of the most significant technical changes that have been made in this new edition is to be found in Annex E.

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This European Standard specifies a flame ionisation detector (FID) method. It is intended for use as a standard reference method for the measurement of the mass concentration of gaseous and vaporous organic substances (expressed as TVOC) in stationary source emissions (e.g. emissions from waste incinerators and solvent using processes, emission measurements according to 2010/75/EU) in the concentration range up to 1 000 mg/m³.

This European Standard specifies the requirements for an instrument using flame ionisation detection, together with procedures for its operation. The results obtained using this standard are expressed in milligrams per cubic metre (mg/m³) as total carbon (TVOC).

This European Standard is not applicable for permanently installed automated measuring systems (AMS).

Alternative methods to this method may be used provided that the user can demonstrate equivalence, based on the principles of CEN/TS 14793.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 15259, *Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report*

EN 15267-1, *Air quality — Certification of automated measuring systems — Part 1: General principles*

EN 15267-2, *Air quality — Certification of automated measuring systems — Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process*

EN 15267-3:2007, *Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources*

EN ISO 9169*, Air quality — Definition and determination of performance characteristics of an automatic measuring system (ISO 9169)*

EN ISO 14956*, Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956)*

3 Terms and definitions

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

3.1
combustion air
air supply used for the combustion of fuel gas in an instrument using flame ionisation detection

3.2
detection limit
minimum concentration of a substance which produces an observable response, which is two times the standard deviation at zero

3.3
dilution gas
gas used to dilute sampled flue gas to prevent water condensation

3.4
flame ionisation detector (FID)
instrument using flame ionisation detection

3.5
flue gas
product from a combustion, incineration or solvent process containing gaseous and/or particulate compounds

3.6
fuel gas
gas of known composition used to maintain the flame of the FID

3.7
mass concentration of gaseous total organic carbon
quotient of the mass of total organic carbon to the volume of the dry gas under specified reference conditions of temperature and pressure, normally expressed in milligrams per cubic metre (mg/m^3) as total carbon

3.8
residence time
time period for the sampled gas to be transported from the inlet of the probe to the inlet of the measurement cell

3.9
response factor
dimensionless quotient of the response of the FID with any carbon based compound or compounds to its response to propane, in each case referred to the number of carbon atoms of the molecule

3.10
response time
time which elapses between the moment when a change is produced and the moment when the instrument response reaches a value of 90 % of the final change in instrument response as a consequence of a stepwise change in the total organic carbon concentration

3.11
span gas
test gas used to check and adjust a specific point on a calibration curve

3.12
total volatile organic carbon (TVOC)
total volatile organic compounds which are measured by the FID, expressed in milligrams per cubic metre (mg/m^3) as total carbon

3.13
zero gas
test gas used to check and adjust the zero point on a calibration curve

3.14
uncertainty
parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand

[SOURCE: ENV 13005]

4 The principle of the technique

4.1 Flame ionisation detector (FID)

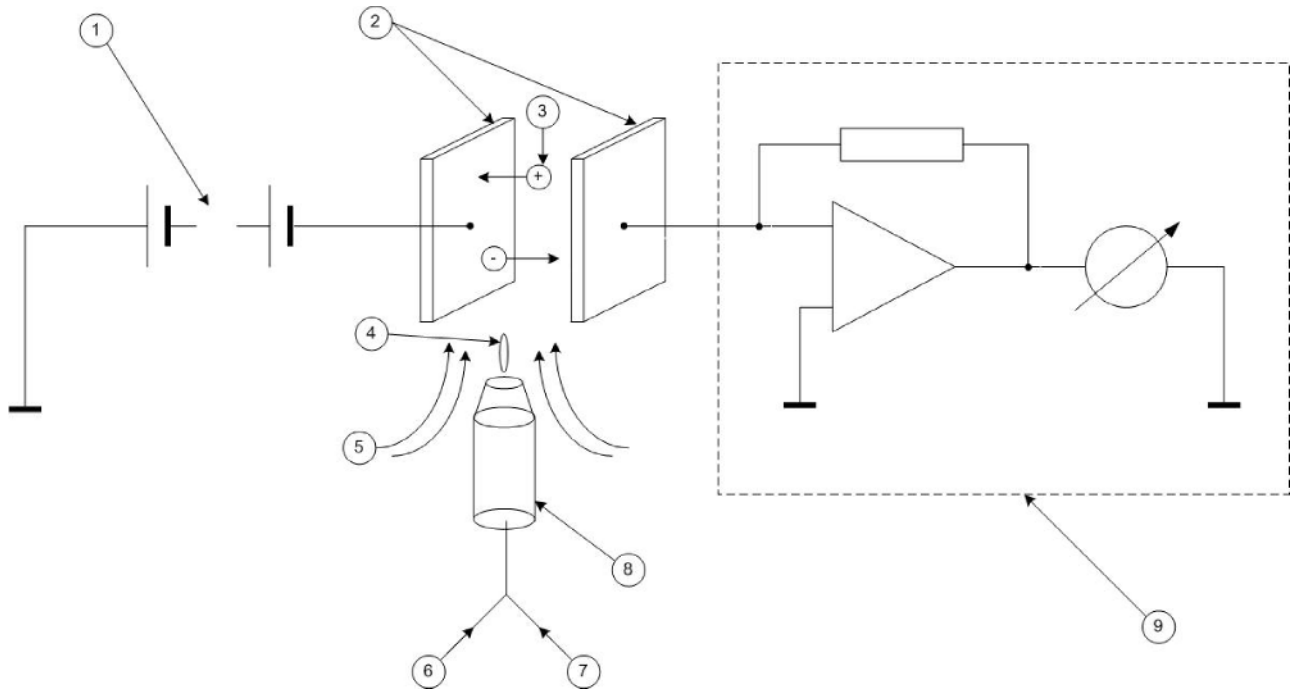
The measurement technique utilised by the flame ionisation detector (FID) is the ionisation of organically bound carbon atoms in a hydrogen flame. The ionisation current measured by the FID depends on the number of C-atoms of organic compounds burning in the fuel gas flame, the form of bonding (straight chain or branched chain) and of bonding partners.

The response factor is a function of the specific design of the detector and the adjusted operating conditions. The advantage of the FID is that it responds to organic carbon compounds and has negligible response to inorganic flue gas compounds (such as CO, CO_2, NO, H_2O).

A number of different instrument configurations exist. Figure 1 is an example of the principle whereby in the detector a sample gas is fed into a hydrogen flame across which a DC electrical potential is placed. The introduction of the sampled gas causes a specific ionisation current to flow, which is measured using suitable equipment. Defined test gases are required to determine the response factors. These can be produced by a number of methods including: static methods (with gas collectors or direct injection) or dynamic methods (e.g. vapour pressure method or certified test gases from compressed gas bottles).

The span of the instrument shall be adjusted with propane (C_3H_8) for which the response factor, defined in this standard, has been set at 1,00. The final value will be expressed as TVOC in milligrams per cubic metre.

Refer to Annex B for more information on the use and effects of an FID instrument.



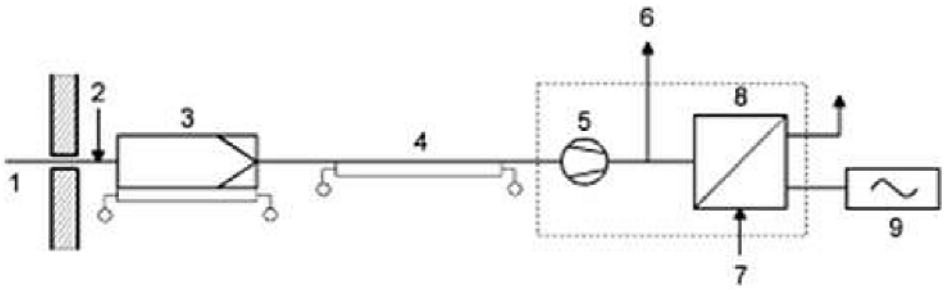
Key
1 polarisation voltage
2 electrodes
3 ions
4 flame
5 combustion air
6 fuel gas
7 sample gas
8 jet
9 amplifier and readout

Figure 1 — Principle of FID

4.2 Sampling and sampling device

Sampling is the process of extracting from the flue gas a partial volume flow which is representative of the composition of the main gas stream.

A partial flow of the flue gas is directly fed into the FID analyser via the sampling probe, the particle filter and the heated sampling line. An example of the set-up of the measuring system is shown in Figure 2. The sampling device including the filter needed to remove fine particles, which could clog the burner, is heated to avoid sample condensation.



Key

1 sampling probe
2 zero and span gas inlet
3 particle filter, heated
4 sampling line, heated
5 external sample pump (optional), heated
6 bypass (optional)
7 test gas inlet for functional tests
8 FID
9 data evaluation system

Figure 2 — Example of the set-up of the measuring system

5 Requirements for apparatus and gases

5.1 Requirements for the measurement system

The sampling system shall meet the following requirements:

— It shall be made of stainless steel, polytetrafluoroethylene or polypropylenefluoride. If an alternative material is used, it shall be proven that it is chemically and physically inert to the constituents of the flue gas under analysis.

— The design and configuration of the sampling device used shall ensure the residence time of the sample gas within the device is minimised in order to reduce the response time of the measuring system. It will be designed to ensure a sample residence time less than 60 s. With long sampling lines or high flow resistance, the use of an external pump with bypass is recommended.

— It shall be heated throughout to at least 180 °C.

NOTE Sampling lines in PTFE have a maximum temperature of 200 °C. All instruments that are certified are tested at 180 °C.

— It shall have a heated filtering device upstream of the sampling line to trap all particles liable to impair the operation of the apparatus.

— It shall have an inlet for applying zero and span gases at or close to the probe inlet of the sampling probe, upstream of the filter. This is to check the sampling system including the filter assembly.

The FID and sampling system shall comply with the performance requirements of EN 15267-3.

The checks in Table 1 shall be carried out with at least the specified frequency.

Table 1 — Minimum frequency of checks for QA/QC during the operation

Check	Minimum frequency	Requirement	Clause
Response time	once for each measurement series	≤ 200 s	A.2
Repeatability standard deviation at zero point	once a year	≤ 2 %	A.4
Repeatability standard deviation at span point	once a year	≤ 2 %	A.5
Lack of fit	once a year and after repair [a] of the instrument	≤ 2 %	A.3
Effect of oxygen	at least once a year and after repair (can be carried out by the manufacturer)	≤ 2 %	A.6
Other interference checks [b]	at least once a year and after repair (can be carried out by the manufacturer)	≤ 2 %	A.7
Response factor determination	as specified by the manufacturer and is relevant for single compound measuring tasks		A.8 and Annex B
Sampling system check	once for each measurement series		6.2.2
Leakage check	once for each measurement series		6.2.2
Zero drift	at the beginning and end of the measuring period and at least once a day	< 5 %	6.2.3
Span drift	at the beginning and end of the measuring period and at least once a day	< 5 %	6.2.3
Regular maintenance of the analyser	as required by the manufacturer		
Cleaning or changing of sampling line and particulate filters [c]	once for each measurement series, if needed		

[a] A repair that might affect the performance of the instrument.

[b] Only those interferences shall be checked which have proven to be relevant during instrument performance testing.

[c] The particulate filter shall be changed periodically depending on the dust load at the sampling site. During this filter change, the filter housing shall be cleaned.

5.2 Operational gases

5.2.1 General

A number of operational gases are required when using this standard.

The use of combustion air or fuel gas whose concentration in TVOC is lower than 0,2 mg/m³ (as carbon) or of purity 99,998 % shall be used. This avoids any risk of influence of this gas on the result of the measurement.

5.2.2 Fuel gases

The fuel gas shall be specified by the equipment manufacturer and according to the certification to EN 15267-1, EN 15267-2 and EN 15267-3. Commonly used gases include:

— hydrogen;

— hydrogen/helium mixture;

— hydrogen/nitrogen mixture.

NOTE The fuel gas pipe will be made from a suitable material for the environment, e.g. stainless steel, copper or PTFE.

5.2.3 Zero gas

The TVOC concentration (mg/m^3 as carbon) of zero gas shall be lower than 0,2 mg/m^3 of carbon or purity 99,998 % shall be used. This avoids any risk of influence of this gas on the result of the measurement. This can be synthetic air or cleaned ambient air.

If a problem occurs at the zero point e.g. negative values, this may be an indication of the effect of oxygen. In this case, it is recommended the zero gas may be replaced with one containing a similar oxygen concentration to the process (nitrogen/oxygen mixture or synthetic air). The worst case for this effect is when a process is running with approximately 10 % excess oxygen. Refer to Annex B for more information on the use and effects of an FID instrument.

5.2.4 Span gas

The span gas shall be propane in synthetic air or in a nitrogen/oxygen mixture. It shall have a known concentration of TVOC and the expanded uncertainty on the analytical certificate of the span gas shall be less than or equal to 2 % for TVOC.

When the analyser is used for regulatory purposes, the span gas shall have a known concentration of approximately the half-hourly ELV or 50 % to 90 % of the selected range of the analyser.

The span gas will be propane with the same oxygen concentration in the complementary gas in the zero and in the span gas to take into account the same level of influence at the zero point and the span point during the adjustment of the analyser.

6 Measurement procedure

6.1 General

The planning and sampling strategy shall follow the requirements of EN 15259.

The following text describes the routine operation procedures required by the standard; a more detailed procedure for determining the instrument performance characteristics is given in Annex A.

6.2 Adjustments and checks

6.2.1 Instrument adjustment

The FID shall be set up according to the manufacturer's instructions in order to ensure that the instrument is correctly adjusted as specified in Table 1. At the beginning of the measuring period, zero and span gases are supplied to the analyser directly, without passing through the sampling system. Adjustments are made until the correct zero and span gas values are given by the data sampling system:

— adjust the zero value;

— adjust the span;

— finally, re-check zero to see if there are no significant changes (zero deviation lower than two times the repeatability at zero). Repeat the adjustment procedure until this is achieved.

6.2.2 Check of the sampling system

Before starting the measurement, the following procedure shall be applied to determine if there is leakage and or impurities in the sampling line: Zero and span gas are supplied to the analyser through the sampling system, as close as possible to the probe inlet (in front of the filter). Any differences between the readings obtained during the adjustment of the analyser (6.2.1) and during the check of the sampling system shall be lower than 2 % of the span value.

NOTE Differences may be due to leakage or impurities in the sampling system leading to memory effects due to adsorption or desorption to or from the surfaces.

Check also the response time of the system.

6.2.3 Zero and span checks after measurement

At the end of the measuring period and at least once a day, zero and span checks shall be performed at the inlet of the sampling system by supplying test gases.

If the span or zero drifts are bigger than 2 % of the span value, it is necessary to correct both for zero and span drifts. Values shall be recorded before any adjustments to the analyser.

NOTE Recorded values can be used for uncertainty calculations.

The drift of zero and span shall be lower than 5 % of the span value; otherwise, the results are not valid.

6.2.4 Determination of the effect of oxygen

Refer to A.6 and EN 15267-3 for the gases and test procedure.

It is known that the effect of oxygen synergy has its peak at levels of about 10 % oxygen. The effect becomes smaller as the oxygen level reduces or increases away from this value. Using zero gas and span gas with similar levels of oxygen as present in the stack gas will yield the most accurate results. This is recommended where oxygen levels in the stack gas is around 10 %.

When using this standard to calibrate AMS according to EN 14181, it is strongly recommended that zero gas and span gas contain similar levels of oxygen as present in the stack gas.

6.3 Calculations

6.3.1 TVOC mass concentration from volume concentration

The following formula shall be used to convert propane volume concentrations to total organic carbon mass concentrations.

$$C_{\mathrm{m}} = C_{\mathrm{v,C3H8}} \times \frac{3 \times M_{\mathrm{c}}}{V_{\mathrm{M}}} = C_{\mathrm{v,C3H8}} \times \frac{3 \times 12}{22{,}4} \qquad (1)$$

where

C_{m} is the mass concentration expressed in mg/m^3 as carbon at 273 K and 101,3 kPa;

$C_{\mathrm{v,C3H8}}$ is the volume concentration expressed in ppm (V/V) C_3H_8;

M_{c} is the molecular mass of carbon (= 12 g/mol);

V_{M} is the molar volume at 273 K and 101,3 kPa (= 22,4 l/mol).

6.3.2 TVOC correction to reference conditions

The results of the measurement shall be expressed in TVOC as a concentration at reference conditions in milligrams per cubic metre. The calculation of total organic mass concentration from the measured volume concentration is described in 6.3.1. The measured TVOC concentration shall be corrected to reference conditions using Formula (2) if required.

$$C_{\mathrm{n}} = C_1 \left[\frac{100}{100 - \%\mathrm{H_2O}} \right] \left[\frac{21 - \mathrm{O_{ref}}}{21 - \%\mathrm{O_m}} \right] \quad (2)$$

where

C_{n} is the TVOC concentration in milligrams per cubic metre stated at reference conditions of humidity (dry gas) and oxygen;

C_1 is the TVOC concentration in milligrams per cubic metre (273 K, 101,3 kPa) at flue gas conditions of humidity and oxygen;

$\%\mathrm{H_2O}$ is the measured percentage by volume of water in the flue gas according to EN 14790;

$\%\mathrm{O_m}$ is the measured percentage by volume of oxygen in the dry flue gas according to EN 14789;

$\%\mathrm{O_{ref}}$ is the percentage by volume of oxygen at the dry reference conditions.

If the moisture content is below 2 % volume, then the monitoring and correction to moisture is not required.

If no reference condition for oxygen is required, the monitoring and correction for oxygen is not required.

6.3.3 Uncertainty

The overall uncertainty of the method shall be calculated in accordance with EN ISO 14956 on the basis of the performance characteristics determined during the general performance test and shall meet the uncertainty required for the measurement objective.

The results from the test and calculations from Table 1 shall be included in the calculation of uncertainty.

6.4 Measurement report

The test report shall be in accordance with the requirements of EN 15259.

The following additional information relating to the FID test and performance shall be included: zero and span gases, with their composition and uncertainty.

Annex A
(normative)

Determination of the performance characteristics of a FID

A.1 General

Before determining the main performance characteristics of a FID, the instrument shall be set up according to the procedure detailed in 6.2.1.

Performance characteristics are also given in EN 15267-3.

A.2 Response time

Pass span gas into the FID.

The response time interval between first response of analyser, when span gas is introduced, and reaching 90 % of the span gas value, should be in accordance with EN ISO 9169.

A.3 Lack of fit (linearity check)

Five or six test gas concentrations (usually propane is used), distributed evenly over the measuring range, shall be used to demonstrate that the FID has a linear calibration curve.

A.4 Repeatability standard deviation at zero point

To determine the repeatability standard deviation at zero point (X_0), first adjust the zero point of the FID then carry out a minimum of 30 determinations within a period of about 1 h. This is done by feeding zero gas into the FID, noting the reading and calculating the result using the following formula:

$$X_0 = 2 \cdot s_{xo} \tag{A.1}$$

where

s_{xo} is the standard deviation, expressed as TVOC in mg/m^3, of the blank readings.

A.5 Repeatability standard deviation at span point

To determine the repeatability standard deviation at span point (X_{Sp}), first adjust the span point of the FID then carry out a minimum of 30 zero and span measurements within a period of about 1 h. This is done by feeding span gas and zero gas alternately into the FID, noting the reading during span gas feeding and calculating the result using the following formula:

$$X_{Sp} = 2 \cdot s_{Sp} \tag{A.2}$$

where

s_{sp} is the standard deviation, expressed as TVOC in mg/m^3, of the span readings.

A.6 Effect of oxygen

Oxygen can affect both the zero point and the span value. To demonstrate the effects of oxygen, pass into the FID the following test gases:

Zero gases:

a) 10 % oxygen and 90 % nitrogen (by volume);

b) 20 % oxygen and 80 % nitrogen (by volume).

Test gases:

c) span gas concentration in complementary gas of 10 % oxygen and 90 % nitrogen (by volume);

d) span gas concentration in complementary gas of 20 % oxygen and 80 % nitrogen (by volume).

Use the procedure specified in EN 15267-3:2007, 10.19.

NOTE The effect of oxygen interference can be reduced by using zero gas and span gas with the same oxygen concentration as the flue gas.

A.7 Other interference checks

Only those interferences shall be checked which have proven to be relevant during instrument performance testing. The determinations have to be carried out according to EN ISO 9169.

A.8 Response factors

To determine the response factors, comparative measurements shall be made between the organic components being investigated and propane.

$$f_{\mathrm{c}} = \frac{\frac{S_{\mathrm{i}}}{C_{\mathrm{c,i}}}}{\frac{S_{\mathrm{ref}}}{C_{\mathrm{c,ref}}}} \qquad \text{(A.3)}$$

where

f_{c} is the carbon-related response factor;

S_{i} is the reading of the FID (measurement signal) for substance *i*;

S_{ref} is the reading of the FID (measurement signal) for propane;

$C_{\mathrm{c,i}}$ is the carbon concentration of substance *i* in mg/m^3 (273 K, 101,3 kPa);

$C_{\mathrm{c,ref}}$ is the carbon concentration of propane in mg/m^3 (273 K, 101,3 kPa).

The carbon-related response factor can be calculated from the measuring apparatus readings when admitting a test gas with organic components being investigated.

The response factors for aliphatic and aromatic hydrocarbons shall be measured by determining the response factors of the individual compounds and taking the mean, as indicated in Annex B. The benzene and toluene test gases shall be equivalent to gravimetrically prepared gas standards traceable to primary standards.

Annex B
(informative)

Basic functionality of an FID

B.1 Principle

The sample gas to be measured is mixed with fuel gas and let into a combustion chamber, where the gas mixture is further mixed with combustion air and ignited (see 4.1, Figure 1).

During the combustion process, all hydro-carbons are being cracked. This results first in CH fragments which are then being oxidised with oxygen to form CHO^+ ions.

These ions are then measured using a detector which contains two electrodes. One electrode is negatively polarised by means of a precision power supply and the other electrode (the so-called “collector” is connected to a high impedance, low noise electronic amplifier. The two electrodes establish an electrostatic field.

When a gaseous sample is introduced to the burner, it is ionised in the flame and the electrostatic field causes the ions to migrate to their respective electrodes. The migration creates a small current between the electrodes. This current is measured by the precision electrometer amplifier and is directly proportional to the carbon concentration of the sample.

B.2 Influences on the measurement result

B.2.1 General

The reading of the FID analyzer is influenced by various parameters and can vary even if the concentration of the hydrocarbons in the sample gas remains constant.

B.2.2 Sample gas flow

It is obvious from the above description, that the sample gas flow through the flame nozzle has a direct and nearly proportional influence. If the sample gas flow increases, there will be more ions between the electrodes, and the current will increase.

Consequently, both the control and the monitoring of the gas flow in the instrument are very important. The sample gas and flue gas mixture is often controlled by a series of critical orifices, and the cleanliness of these is important. If the nozzles of the instrument are contaminated, the instrument will draw less sample gas, and the reading will decrease, leading to an underestimation of the concentration.

To keep the entire instrument clean, the sample gas is filtered before it enters into the instrument; and to avoid condensation in the instrument, the sample gas is heated before it enters the combustion chamber. If the particle filter is clogged, the sample gas flow will be reduced, the instrument will draw less sample and flue gas, and the reading will decrease, leading to underestimation of the concentration.

B.2.3 Combustion chamber

Contamination of the combustion chamber itself may also result in too low readings. If e.g. silicon containing compounds are present in the sample gas, the electrodes may, due to the high temperature in the combustion chamber, be glazed, leading to an increased insulation of the electrodes. This will reduce the current drawn from the combustion gas, and the reading will decrease, leading to underestimation of the concentration.

B.2.4 Combustion air

The ambient air, drawn from the surroundings of the analyser, may also contain hydrocarbons, especially if the analyser is placed in the vicinity of the ovens. With a required detection limit of a fraction of a ppm, the surrounding shall not contain high amounts of hydrocarbons, before the measurement results are “contaminated” (in citation marks, because the instrument measures correctly, it cannot distinguish hydrocarbons originating from either the sample gas or the ambient air).

To avoid this problem, a “synthetic combustion air” is often used, consisting of N_2 with 20,9 % O_2.

B.2.5 Cross sensitivities (interferences)

Cross sensitivities are components in the sample gas which will cause the FID analyser to change its reading, without having changed the concentration of the hydrocarbons in the sample gas.

Typical components showing a cross sensitivity are gases like SO_2, NO, NO_2. Cross sensitivities can show both positive as well as negative deviations. Furthermore, cross sensitivities do not necessarily show a linear behaviour. To a certain degree, they also depend on the construction of the instrument. This is why EN 15267-3 certifications require extensive testing of cross sensitivities against various chemical compounds.

B.2.6 Oxygen synergy

Another possible cross sensitivity is oxygen. The higher the concentration of oxygen in the sample and flue gas mixture, the shorter is the time, where the hydrocarbons are ionised before they are oxidised, and the reading will fall, leading to underestimation of the concentration. The cross sensitivity to oxygen can be reduced by the design of the instrument, but also depends on the various gas flow rates and the composition of the test gases.

The maximum cross sensitivity is stated in this standard and EN 15267-3.

B.2.7 Response factors

The ionic current in the FID flame is over a wide range proportional to the number of carbon atoms in the gas under investigation. However, the molecular structure (i.e. single or double bond, number and nature of hetero-atoms, chain length and ring structure) has a considerable influence on the oxidation properties of the carbon and thereby also on the strength of the detector signal. Consequently, organic compounds with oxygen as hetero-atom are generally indicated with far less sensitivity than pure hydrocarbons with the same number of carbon atoms per molecule. That means their response factors are lower than those of the pure hydrocarbons.

The following cases (criteria) have to be considered for the continuous measurement with FID:

a) Known VOC composition:

   If the VOC (volatile organic compounds) composition of the waste gas is known and not too complicated (not too many compounds), the response factors of the mixture or of the individual VOC compounds can be determined and the average carbon related response factor can be calculated according to Formula (A.3).

b) Single VOC compounds determination:

   If single VOC compound gases shall be investigated, the FID can directly be calibrated with this compound and the signal output would be a mass concentration of this compound. In this case, a test gas with the wanted compound has to be produced and used. If the FID shall be further checked with propane test gas, a mass related (not carbon related) response factor of the wanted compound can be determined and used.

c) Changing VOC composition:

If the FID shall be used for measuring waste gases with changing VOC composition over the time, carbon related response factors of a certain number of representative VOC compounds of the gas (e.g. six compounds) have to be determined and their average response factor should be used. The standard deviation of these different response factors should not exceed a limit of 15 %.

Instead of determination of single compound response factors, a control gas mixture could be used to check the FID response against changing VOC composition. The selection of representative VOC compounds or the composition of a control gas mixture should be designed according to the measuring task, e.g. for flue gas investigation of waste incineration plants or for solvent mixtures.

B.3 Special aspects — Measuring TVOC and not TOC

The FID analyser shall have a sample gas cleaning system, preventing contamination by particles and/or condensation inside the instrument, as described above.

This means that hydrocarbons of a higher order entering the analyser as solids, will be filtered, and consequently not measured. Although the directives prescribe the measurement of TOC (Total Organic Carbon), the FID analyser actually measures TVOC (Total Volatile Organic Carbons).

This is generally accepted in the industry and by competent authorities.

Such aerosols could however lead to a pollution of the sampling system with uncontrolled absorptions and desorptions causing memory effects. That means that it takes a long time until the FID shows zero when fed with zero gas.

Nevertheless, if there are aerosols in the waste gas which are retained in the filter or agglomerated in the sampling line and the filter or sampling line temperature is higher than the evaporation temperature of these aerosols, these compounds will change into the gas phase and be measured by the FID.

Therefore,, aerosol-containing waste gases, or the presence of high molecular VOCs, can cause undefined uncertainties of the measurement. This fact should have be kept in mind when measuring such gases.

Annex C
(informative)

Measurement uncertainty and associated statistics

C.1 General

The original validation trials were carried out in 1996 for the original standards EN 12619 and EN 13526. The following are details of the results obtained.

C.2 Validation tests for EN 12619:1999

The measurement procedure was tested on a hazardous waste incinerator using a variety of commonly available FIDs and the results are as shown in Table C.1. *s* is the mean standard deviation of between five and eight instruments calculated from 10 min sampling periods; it represents the sum of the variances due to each source of uncertainty. The TVOC concentration emitted by the hazardous waste incinerator was such that only a limited number of measurements were obtained at higher concentrations. The uncertainty, *U*, of the measurement results of all of the following tables was calculated using Formula (C.1), where *t* is the student *t* value for a confidence level of 95 %; *s* is the standard deviation within the concentration range.

$$U = t_{n-1} \cdot s \qquad \text{(C.1)}$$

By comparison, typical results from a paired test using two identical instruments, approximating to the minimum performance requirements of this standard, operating on a municipal waste incinerator are shown in Table C.2.

Table C.1 — Field test results from several instruments of different types operating on a hazardous waste incinerator

Range mg/m^3	Mean value mg/m^3	Mean standard deviation mg/m^3	No. of values	Uncertainty 95 % confidence level mg/m^3
< 1	0,33	0,55	88	1,1
1 to 5	2,52	1,09	29	2,2

Table C.2 — Results of a test with one FID model (double test with two devices) operating on a municipal waste incinerator

Range mg/m^3	Mean value mg/m^3	Standard deviation mg/m3	No. of values	Uncertainty 95 % confidence level mg/m^3
< 1	0,55	0,14	174	0,28
1 to 5	1,99	0,18	31	0,35
5 to 10	6,88	0,19	68	0,38
10 to 15	13,04	0,21	22	0,42

On the basis of the data in Table C.1 and Table C.2, the likely uncertainty of measurements performed on instruments manufactured to meet the requirements of this standard will be as shown in Table C.3.

Table C.3 — Approximate uncertainty

TVOC range mg/m^3	Uncertainty for 95 % confidence level mg/m^3	Relative Uncertainty in %
< 1	± 1,0	± 200
1 to 5	± 1,3	± 50
5 to 10	± 2,3	± 30
10 to 20	± 3,0	± 20

C.3 Validation tests for EN 13526:2001

This measurement procedure was tested on a thermal oxidiser operating on a solvent using process, using a variety of commonly available FIDs. The results, calculated according to ISO 5725-1, are shown in Table C.4.

Table C.4 – Field test results from a thermal oxidiser using several FID analyser models operated by two teams

Range of measured values	Mean TVOC Concentration		Standard deviation	No. of values	No. of instruments	Uncertainty 95 % confidence level
	Prior to the oxidiser	After the oxidiser				
mg/m^3	mg/m^3	mg/m^3	mg/m^3			mg/m^3
< 10	–	8,1	0,4	39	6	0,8
10 to 20	–	12,1	0,9	12	6	2,0
above 200	592	–	14,2	44	2	28,9

Annex D
(informative)

Safety measures

When using the FID, attention should be given to the general working environment and any associated local safety instructions.

The flame should be controlled using a temperature sensor in the analyser. In case of malfunction, leading to flame failure or a decrease of the flame temperature, a valve should automatically close the fuel gas flow upstream of the burner.

In the case of indoor use, laboratory safety rules should be applied. In addition, it is advisable that the FID is fitted with a safety system to automatically shut down the gas flow in case of a pressure drop after the pressure regulator.

All exhaust fumes from the FID, both burner and bypass (if fitted), should be vented to an external safe area.

The manufacturer's instructions should be followed.

Annex E
(informative)

Significant technical changes

1) The revision of this standard has combined EN 12619:1999 and EN 13526:2002 into one standard.

2) The overall range was increased to 1 000 mg/m^3.

3) This standard is not applicable for permanently installed AMS. For permanently installed AMS refer to EN 15267-3.

4) The sampling strategy has been aligned with EN 15259. This standard has become a normative reference.

5) The FID sampling system and performance requirements have been aligned with EN 15267-3. This standard has become a normative reference.

6) Information on the effect of oxygen has been added (refer to 6.2.4).

7) The requirement for the annual use of a control gas, has been removed (refer to Annex B).

8) Annex B on basic functionality of an FID has been added.

Bibliography

[1] EN 14181, *Stationary source emissions — Quality assurance of automated measuring systems*

[2] EN 14789, *Stationary source emissions — Determination of volume concentration of oxygen (O2) — Reference method — Paramagnetism*

[3] EN 14790, *Stationary source emissions — Determination of the water vapour in ducts*

[4] ENV 13005, *Guide to expression of uncertainty in measurement*

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

[6] Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control)

[7] CEN/TS 14793, *Stationary source emission — Interlaboratory validation procedure for an alternative method compared to a reference method*

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

bsi.

...making excellence a habit.™