International Standard

ISO 19702

Sampling and analysis of toxic gases and vapours in fire effluents using Fourier Transform Infrared (FTIR) spectroscopy

Échantillonnage et analyse des gaz et des vapeurs toxiques dans les effluents du feu par spectroscopie infrarouge à transformée de Fourier (IRTF)

Third edition
2024-12

Reference number
ISO 19702:2024(en)

© ISO 2024



COPYRIGHT PROTECTED DOCUMENT

© ISO 2024

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword ..... **v**
Introduction ..... **vi**
1 Scope **1**
2 Normative references **2**
3 Terms and definitions **2**
4 Principles **3**
5 Sampling **3**
5.1 General 3
5.2 Temperature of the sampling system 4
5.3 Filter systems 4
5.4 Sampling probes 6
5.4.1 General 6
5.4.2 Single-hole probes 7
5.4.3 Multi-hole probes 7
5.4.4 Probe positioning 7
5.5 Sampling line 8
5.6 Pump selection, position, and flow rate 9
5.7 Response time of the sampling system 10
5.8 Optical cell 10
6 The FTIR spectrophotometer **11**
6.1 Spectrophotometer environment 11
6.2 Detector 11
6.3 IR-source 11
6.4 Mirror alignment and cleanliness 11
6.5 Spectrophotometer compartment 11
6.6 Spectral range limits 12
6.7 Resolution 12
7 Calibration **12**
7.1 Background noise 12
7.2 Limits of detection and of quantification (L_D and L_Q) 12
7.3 Calibration methods 12
7.4 Acquiring and collecting calibration standards 13
8 Measurement procedure **13**
8.1 General 13
8.2 Daily setup, checks and controls 13
8.2.1 General 13
8.2.2 Control of calibration method 13
8.2.3 Spectrophotometer sensitivity measurements 14
8.2.4 Sampling system tests 14
8.2.5 Control of the sampling flow rate 14
8.3 Preparation for sampling and analysis 15
8.4 Initial procedures immediately before a test 15
8.5 Procedures during sampling from a test 15
8.6 Procedures after a test 16
8.7 Data reduction 16
9 Test report **16**
10 Precision and accuracy **17**
10.1 General 17
10.2 L_D and L_Q 17
10.3 Repeatability and reproducibility 17

© ISO 2024 – All rights reserved

Annex A (informative) **FTIR theory** **18**
Annex B (informative) **FTIR sampling systems** **20**
Annex C (informative) **Analysis of filter(s), the sampling line and probe for effluent retention** **24**
Annex D (normative) **Response time determination of the complete FTIR sampling system** **25**
Annex E (informative) **Considerations for FTIR optical cell selection** **27**
Annex F (normative) **Verification of FTIR optical cell performance** **29**
Annex G (informative) **Spectrophotometer** **31**
Annex H (normative) **Verification of spectrometer performance** **34**
Annex I (informative) **Reference gases** **37**
Annex J (informative) **Calibration methods** **42**
Annex K (informative) **Recording reference spectra and building a calibration set** **45**
Annex L (informative) **Repeatability and reproducibility** **55**
Annex M (informative) **Historical examples of equipment and parameters** **56**
Bibliography **67**

© ISO 2024 – All rights reserved

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 19702:2015), which has been technically revised.

The main changes are as follows:

— Clause 3 has been updated;

— Annex K has been expanded.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

© ISO 2024 – All rights reserved

Introduction

Sampling and analysis of fire effluents is required for a variety of applications in life threat assessments[4][11][26] and environmental impact from fires assessments.[6] The end result of these analyses is a list of chemical species and their concentrations in the effluent at a specific time or over a time interval, and at a specific location, during (and possibly after) the period of generation of the effluents. Depending on the end use of these data, the requirements can range from a highly detailed, time-resolved, quantified and validated list of chemical species to a simple estimate of a single compound or small range of compounds.

Although methods used in other fields are occasionally employed (e.g. atmospheric pollution), obtaining relevant data often requires specialized sampling and analysis techniques. This is due to the complexity, reactivity and generally "hostile" nature of typical fire effluents, as well as the commonly observed rapid changes in concentrations with time and distance from the fire source.

The following typical properties of fire effluents render more "traditional" methods of sampling and analysis inappropriate:

— high temperatures of 1 000 °C or higher;

— presence of aerosols (i.e. solid and liquid particulates) with a wide range of particle sizes and distribution, together with adsorbed and absorbed chemical species;

— presence of condensable organic and inorganic vapours (e.g. water);

— high turbulence, with spatially and temporally variable concentrations;

— a very wide range of species and their concentrations, typically varying rapidly with time and location with respect to the fire source (or heating zone in the case of a "bench-top" physical fire model);

— presence of acidic/corrosive species;

— presence of water-soluble species and/or or highly reactive species resulting in sampling losses.

The identification of these factors has led to the development of new methods or the adaptation of existing methods for the sampling and analysis of the gases and vapours in the effluent from fires and physical fire tests.

Common sampling and analysis methods have emerged in recent years, and in some cases, International Standards, such as ISO 19701, have been published for selected gases and vapours. Much of this information is provided in ISO 19701, which presents a variety of methods for the sampling and analysis of individual gases of toxicological importance. Several methods are often needed to determine all the species of interest for fire hazard analysis.

Fourier Transform Infrared (FTIR) spectroscopy offers an improved procedure, principally through:

— single-method measurements of gases and vapours relevant to fire toxicology;

— time-resolved measurements over relatively short periods (i.e. concentrations of chemical species of interest), enabling the monitoring of chemical species development and decay throughout the fire or physical fire test; and

— revisiting the stored FTIR spectra to potentially obtain relevant data concerning the presence of a toxicant which is identified as important.

While ISO 19701 summarizes the technique and some applications of FTIR in fire gas analysis along with many other common methods, this document provides details of the established requirements and best practices for obtaining reliable sampling and analysis results using the FTIR method.

FTIR spectroscopy can be used to analyse fire effluents using these two methods:

a) open path analysis, where the infrared beam is directed across the effluent within and/or outside the fire test apparatus;

© ISO 2024 – All rights reserved

b) extractive analysis, where a fraction of the effluent from a fire test apparatus is drawn continuously through a heated sampling system through the gas cell of the FTIR instrument, enabling remote measurement (e.g. IMO Resolution MSC 61(67), Part 2: Toxicity analysis[9]).

Both procedures (and variants) have been successfully applied, although the extractive analysis technique is far more common in fire effluent analysis.

Of particular relevance in the development of FTIR as a practical tool in fire gas analysis is the Smoke Gas Analysis by Fourier Transform Infrared Spectroscopy or SAFIR, a European Union-funded project[18][19] which focused on the testing and validation of an extractive FTIR method when used in a variety of situations. The results of the SAFIR project formed the basis of the first edition of this document (ISO 19702:2006). The second edition of this document (ISO 19702:2015) was based on subsequent updates e.g. References [8], [15], [21], [25] and [27].

Any chemical analysis is selective in terms of chemical species determined and the accuracy and precision of quantitative measurements. Some chemical analytical methods can be appropriate for accurate determination of some species but less appropriate for other species. Thus, despite the ability of FTIR spectroscopic analysis to measure a wide range of chemical species of interest in the field of life threat from fire, additional methods can also be necessary to determine all the species of interest for a particular application. However, the use of FTIR analysis alone can provide data of sufficient quality to identify and calculate the concentrations of many of the chemical species that are important in toxic hazard assessment.

© ISO 2024 – All rights reserved

Sampling and analysis of toxic gases and vapours in fire effluents using Fourier Transform Infrared (FTIR) spectroscopy

1 Scope

This document specifies requirements and makes recommendations for sampling systems for use in small-scale and large-scale fire tests, for the selection of parameters and use of the FTIR instrument, and for the collection and use of calibration spectra.

The primary purpose of the methods outlined in this document is to measure the concentrations of chemical species in fire effluents which can be used to:

a) provide data for use in combustion toxicity assessment without requiring biological studies;

b) allow the calculation of yield data in fire characterization studies;

c) provide data for use in mathematical modelling of hazard to life from the fire effluent by characterizing the effluent composition generated by physical fire models;

d) characterize the effluent composition of small-scale physical models and larger-scale fires for comparative purposes;

e) assist in the validation of numerical fire models;

f) set the conditions for exposure in biological studies if required;

g) monitor biological studies where used; and

h) assist in the interpretation of biological studies where used.

This document specifies principles of sampling and methods for the individual analysis, in fire effluents, of airborne volume fractions of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen cyanide (HCN), hydrogen chloride (HCl), hydrogen bromide (HBr), nitric oxide (NO), nitrogen dioxide (NO_2) and acrolein (CH_2CHCHO).

NOTE Depending on the optical path length, there can potentially be some saturation of certain spectral lines at high concentration, leading to incorrect volume fractions.

In most common cases, a wide concentration range can be measured by an FTIR instrument. Typically, it is in the range of a few µl/l to thousands of µl/l for HCl, HBr, HF, SO_2, NO_x, and HCN, and up to a few per cent for CO, CO_2 and H_2O. These mentioned species are only indicative, and many other species could be added.[27] Although not specifically defined in this document, as they were not specifically studied in the SAFIR project,[18] the method presented is also suitable for analysis of other gaseous species, including e.g. hydrogen fluoride (HF) and sulfur dioxide (SO_2) with appropriate sampling methods.

Calibration methods are provided in this document. Guidance is also given on the recommended cleaning, servicing and operating checks and procedures to be carried out on the FTIR instrument and the sampling systems which are considered essential for maintaining the instrument in a suitable condition for use in fire effluent analysis.

Sampling is considered to be an integral part of the whole FTIR measurement methodology and recommendations are made for the design, maintenance and operation of suitable systems.

© ISO 2024 – All rights reserved

This document provides general recommendations for the sampling and analysis of fire effluents based on best practice as determined from a wide variety of small-scale and large-scale standard and ad hoc fire test studies. This document is not necessarily applicable for use in specific published fire test methods where FTIR is specified as a requirement for effluent sampling and analysis in that particular test. In these cases, the specific requirements for the sampling and analysis by FTIR within the published standard test procedures are followed. However, if such specific requirements have not been published, this edition of this document can be used as a basis for acceptable results.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 12828-1, *Validation method for fire gas analysis — Part 1: Limits of detection and quantification*

ISO 13344, *Estimation of the lethal toxic potency of fire effluents*

ISO 13571, *Life-threatening components of fire — Guidelines for the estimation of time to compromised tenability in fires*

ISO 13943, *Fire safety — Vocabulary*

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

3 Terms and definitions

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

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

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

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

3.1
apodisation
mathematical process to correct deviations from the theoretical interferogram obtained in Fourier Transform Infrared (FTIR) spectroscopy

Note 1 to entry: This process widens absorption bands and therefore lowers the resolution.

3.2
interferogram
pattern of variable radiation intensity resulting from the interaction of (usually) two beams of monochromatic electromagnetic radiation of the same wavelength when the beams have travelled over a different path length before combining

3.3
resolution
capacity of a spectrophotometer to distinguish between two adjacent frequencies (or wavenumbers), mathematically defined as that separation which produces two bands which are separated by at least half the intensity of one of them

Note 1 to entry: In infrared spectroscopy, two consecutive bands often have a different intensity. Resolution is generally expressed as the width at half height of a single absorption band recognized as “isolated and thin”.

Note 2 to entry: This is commonly expressed in units of cm^{-1} and is the smallest spacing between absorption peaks that can be resolved.

© ISO 2024 – All rights reserved