



Withdrawn

Gas analysis — Determination of sulphur dioxide — Part 1 : General guidance for the choice of methods

Analyse des gaz — Dosage du dioxyde de soufre — Partie 1 : Directives pour le choix des méthodes

Technical Report 6566/1 was drawn up by Technical Committee ISO/TC 158, *Analysis of gases*, and was submitted to the member bodies in August 1977.

0 Introduction

This Technical Report constitutes the first part of a future International Standard concerning the determination of sulphur dioxide in gases. Each of the other parts will describe in detail one of the methods of determination.

Pending finalization of a certain number of parts describing the available methods for the determination of sulphur dioxide, it was considered preferable to publish this first part, which gives a rapid comparison of the methods, as a Technical Report. This type of publication will better draw the attention of users to the fact that further studies are being carried out on methods for the determination of sulphur dioxide.

1 Scope and field of application

This Technical Report gives a non-exhaustive list of methods that can be used to determine the sulphur dioxide content of gases and explains a certain number of analytical criteria, pertaining to each of them, in order to enable users to select judiciously the method for the application being considered.

The user should understand, however, that the criteria given in this Technical Report are not sufficient to perform the analysis and reference should be made to the specific part of the International Standard which describes in detail the particular method chosen.

2 Available methods

The various methods of analysis compared in clause 3 are the following :

- non-dispersive infrared absorption;
- infrared spectrometry using cells of long path length;
- gas chromatography, with detection by catharometry or flame photometry;
- colorimetry using pararosaniline;

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- electrical conductimetry;
- coulometry;
- detector tubes;
- flame photometry;
- mass spectrometry;
- ion-specific electrode;
- electrochemical cell : coulometry using a membrane;
- non-dispersive ultraviolet absorption;
- ultraviolet fluorescence;
- correlation spectrometry;
- second derivative spectrometry;
- measurement of gaseous acid pollution index.

Other methods for the determination of sulphur dioxide are available but are not considered here.

3 Comparison of characteristics of the methods

The fourteen characteristics given below have been chosen to enable a comparison to be made between the methods considered. However, there are other characteristics of the analytical methods that the user should take into account when considering the determination.

Characteristics 1 to 11 are presented in tabular form for easy and rapid comparison. Characteristics 12 to 14, which require longer explanations, are described in clause 4.

The characteristics mentioned in the table are only given for guidance as they depend upon a number of particular measuring conditions which cannot be taken into consideration in this general document which has to be concise to enable a first rapid comparison of the methods.

The list of characteristics considered is as follows :

- 1 — Detection threshold¹⁾²⁾
- 2 — Maximum measurable concentration²⁾
- 3 — Nature of output signal
- 4 — Response time (or analysis time for a discontinuous method)
- 5 — Repeatability (as a relative value)³⁾
- 6 — Possibility of re-use of the sample
- 7 — Method of measurement : automatic or manual⁴⁾

1) The **detection threshold** is a purely qualitative concept defined as follows : The smallest variation of the sample concentration of the gas being analysed which produces a significant change in the output signal.

This should not be confused with **measuring threshold** for which the value is related to repeatability and can be close to the detection threshold.

2) Values in columns 1 and 2 of the table are not correlated and generally cannot both be obtained with the same set of operational conditions.

3) The value indicated gives only an order of magnitude of repeatability for usual measuring conditions.

4) The characteristics given in the other columns of the table correspond to the automatic or manual method (that considered is underlined if both are mentioned). Automatic refers to a method in current use where one or more of the steps are automated.



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Gas analysis — Determination of sulphur dioxide — Part 1 : General guidance for the choice of methods

MODIFICATION IN THE TITLE

On first page, modify the title in French as follows :

Gas analysis — Determination of sulphur dioxide — Part 1 : General guidance for the choice of methods

Analyse des gaz — Dosage du dioxyde de soufre — Partie 1 : Guide pour le choix des méthodes

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- 8 — Degree of portability¹⁾ (ease of use of the method during or after transport of the equipment)
- 9 — Frequency of use¹⁾
- 10 — Costs¹⁾
- 11 — Operator qualifications¹⁾ (for apparatus in normal use)
- 12 — Sampling
- 13 — Calibration
- 14 — Possible application of the method to other components, and interferences.

4 Comparison of characteristics 12 to 14

4.1 Sampling (characteristic 12)

4.1.1 General precautions

Certain precautions to be taken during sampling are inherent in the determination of sulphur dioxide, and are thus applicable to all the methods of analysis :

- it is advisable to avoid any loss of sulphur dioxide by dissolution in condensed water from the gas;
- it is advisable to ensure that pressure and temperature do not vary in order to avoid errors due to adsorption and desorption phenomena;
- the sample should be adjusted to a temperature close to ambient temperature (except for continuous mass spectrometry where it is not necessary).

4.1.2 Specific precautions

In addition, the following precautions and characteristics should be considered for each method of analysis.

4.1.2.1 Non-dispersive infrared absorption

- a) eliminate water and particulates before measurement;
- b) carry out continuous sampling to minimize memory effects;
- c) keep the pressure constant, and in general close to atmospheric pressure;
- d) keep the temperature of the sample constant; ensure that the sample is compatible with the cell materials; take into account the calibration temperature.

4.1.2.2 Infrared spectrometry using cells of long path length

- 1) For discontinuous sampling :
 - a) eliminate water and particulates before measurement;
 - b) memory effects may occur, owing to sorption phenomena; it is, therefore, recommended to evacuate the cell or to purge it with an inert gas and then to verify the absence of sulphur dioxide.
- 2) For continuous sampling : see 4.1.2.1.

1) Criteria 8 to 11 are difficult to evaluate in detail and therefore the increasing number of crosses gives only an element of comparison between methods (one cross represents low cost or low qualification; four crosses represent high cost or high qualification).

Table — Comparison of some characteristics of the various methods available

Characteristics	1	2	3	4	5	6	7	8	9	10	11	Comments*
Method	Detection threshold	Maximum measurable concentration	Nature of output	Response time	Repeatability (relative value) of the order of	Possibility of re-use of the sample	Method of measurement	Degree of portability	Frequency of use Concentration C $C < 10^{-6}$ $10^{-6} < C < 10^{-3}$ $C > 10^{-3}$	Purchase Costs	During use	
Non-dispersive infrared absorption	10^{-5} (V/V)**	10^{-4} to 1 (V/V)**	Continuous	1 to 10 s**	1 %	YES	Automatic	XX	XX	XX	X	1 This threshold corresponds to the use of a cell of 20 cm optical path length. 2 Depends on the geometry of the cell.
Dispersive infrared spectrometry using cells of long path length	5×10^{-8} (V/V)**	5×10^{-4} (V/V)**	Continuous**	Dead time : seconds to a few minutes Rise time : 2 to 3 min	5 %	YES	Automatic or manual	XXXX	XX	XXX	XX	1 For an optical path length of 20 m at 10 bar. 2 For an optical path length of 1 m at 1 bar. 3 Used with a compressor at low concentration.
Gas chromatography with detection by catharometer	5×10^{-5} (V/V)	10^{-1} (V/V)	Discontinuous	Duration of analysis : 4 to 40 min**	5 %	NO	Automatic or manual	XXXX	X	XX	XXX	4 As the method is essentially sequential, no value can be given for response time.
Gas chromatography with detection by flame photometer	10^{-9} (V/V)	10^{-1} (V/V)**	Sequential	Duration of analysis : 4 to 40 min**	5 %	NO	Automatic or manual	XXX	X	XXX	XXXX	2 With a reduced sample. 4 As the method is essentially sequential, no value can be given for response time.
Colorimetry using perarosaniline	10^{-9} (V/V)**	4×10^{-7} (V/V)**	Continuous	Dead time : 10 min Rise time : a few minutes	5 %	NO	Automatic or manual	XX	XXX	XXX	XXXX	1 This threshold corresponds to the sampling of 30 litres of gas. The level can be increased by taking a larger volume of gas. 2 This value can be increased by sampling over short durations (30 min) and according to the volume of the absorbing solution (50 ml).
Electrical conductivity**	5×10^{-4} (V/V) (discontinuous sampling)	1 (V/V)	Discontinuous	Between 1 and 5 min**	5 %	NO	Automatic or manual**	XXX	X	XX	XX	** This is not a very specific method, but is used in ambient air in urban and industrial areas. 4 Varies with concentration. 7 Is, however, generally used in laboratories in the non-automatic version.
Coulometry	10^{-9} (V/V)	10^{-5} (V/V)	Continuous	A few minutes	1 %	NO	Automatic	XXX	—	XXX	XX	1 Depends on tube used. 2 Depends on concentration.
Detector tubes	10^{-7} (V/V)**	5×10^{-3} (V/V)**	Discontinuous	10 s to a few minutes	10 %	NO	Manual	XXXXX	XX	X	X	
Flame photometry	10^{-9} (V/V)	10^{-1} (V/V)	Continuous	Dead time : ≈ 5 s Rise time : ≈ 30 s	1 %	NO	Automatic	XXX	X	XX	XXX	
Mass spectrometry	10^{-5} (V/V)	1 (V/V)	Discontinuous (or continuous)	A few minutes (or a few seconds)	5 % (Automatic : 1 %)	NO	Automatic or manual	X	—	XXXXX	XXXXX	

Ion-specific electrode	10^{-7} (V/V)	10^{-3} (V/V)	Discontinuous	30 s to 4 min	5 %	NO	Automatic or manual	XXX	X	X	XX	X	1 Depends on the purity of the water used.
Electrochemical cell coulometry using a membrane	10^{-8} (V/V)	5×10^{-3} (V/V)	Continuous	A few minutes	5 %	NO	Automatic	XXXX	X	X	XX	X	
Non-dispersive ultra-violet absorption	10^{-6} (V/V)**	2×10^{-3} (V/V)**	Continuous	30 s**	5 %	YES	Automatic or manual	XX	X	X	XXX	X	1 Depends on cell length. 2 } 4 }
Ultraviolet fluorescence	10^{-8} (V/V)**	10^{-1} (V/V)**	Continuous	Of the order of 1 min	5 %	NO	Automatic or manual	XXXX	X	X	XXX	X	1 Depends on detection system. 2 }
Correlation spectroscopy	5×10^{-5} **	10^{-3} **	Continuous	1 to 30 s	10 %	—	Automatic or manual	XXXX	**	**	XXXX	XXX	1 } 2 } 9 X for concentration range 5×10^{-5} to 10^{-3} .
Second derivative spectroscopy	10^{-8} (V/V)	10^{-5} (V/V)	Continuous	5 min	5 %	YES	Automatic or manual	XXX	X	X	XXXX	XX	
Measurement of gaseous acid pollution index**	10^{-8} (V/V)	2×10^{-6} (V/V) to 10^{-2} (V/V)**	Sequential	30 min	5 %	NO	Automatic	XX	XXX	—	XX	X	** This is a non-specific method but is used in ambient air in urban and industrial areas. 2 Depends on the nature and concentration of the solution used for the analysis.

* The numbers preceding the comments refer to the characteristic concerned.

** See column "Comments".

4.1.2.3 Gas chromatography

- a) eliminate particulates which may have a mechanical influence on the sampling apparatus and may be retained by adsorption;
- b) sampling should be discontinuous;
- c) the sampling line should be maintained at constant pressure and temperature;
- d) the flow rate has no influence provided that it does not affect the pressure in the sampling valve.

4.1.2.4 Colorimetry using pararosaniline

- a) eliminate interferences;
- b) sampling may be continuous or discontinuous;
- c) the mass rate of flow should remain constant for the gas and for the reagent.

4.1.2.5 Electrical conductimetry

- a) eliminate interferences;
- b) eliminate particulates using a filter;
- c) sampling may be continuous or discontinuous;
- d) in the case of continuous sampling, the mass rate of flow should remain constant;
- e) in the case of discontinuous sampling, pressure and temperature should remain constant.

4.1.2.6 Coulometry

- a) as far as possible, eliminate oxidizing or reducing interferences;
- b) sampling should be continuous;
- c) the mass rate of flow should remain constant.

4.1.2.7 Detector tubes

- a) to be used generally at ambient temperature;
- b) these tubes generally have a limited shelf life.

4.1.2.8 Flame photometry

- a) eliminate interferences;
- b) sampling should be continuous;
- c) the mass rate of flow should remain constant.

4.1.2.9 Mass spectrometry

- a) sampling may be continuous or discontinuous;
- b) in the case of continuous sampling, particulates should be eliminated;
- c) in the case of discontinuous sampling, operation at reduced pressure may facilitate elimination of condensation;
- d) pressure and temperature should remain constant.

4.1.2.10 Ion specific electrode

- a) eliminate interferences;
- b) sampling should be discontinuous;
- c) pressure and temperature should remain constant;
- d) the gas volume should be known.

4.1.2.11 Electrochemical cell : coulometry using a membrane

- a) eliminate particulates;
- b) sampling should be continuous;
- c) pressure and temperature have to remain constant.

4.1.2.12 Non-dispersive ultraviolet absorption

- a) eliminate particulates;
- b) sampling should be continuous;
- c) pressure and temperature should remain constant.

4.1.2.13 Ultraviolet fluorescence

- a) eliminate particulates;
- b) eliminate water;
- c) sampling should be continuous;
- d) pressure should remain constant.

4.1.2.14 Correlation spectroscopy

No control of the sample is possible

4.1.2.15 Second derivative spectroscopy

- a) eliminate particulates;
- b) sampling should be continuous;
- c) pressure should remain constant.

4.1.2.16 Measurement of gaseous acid pollution index

- a) eliminate particulates;
- b) sampling should be continuous.

4.2 Calibration (characteristic 13)

For all these methods, calibration is usually carried out using calibration gas mixtures.

It should be carried out under conditions as similar as possible to those of the determination.

In order to avoid, in particular, the effect of different viscosities on the sampling rate, it is recommended that the analyser is calibrated with a calibration gas mixture having a composition similar to that of the sample gas.

It is, however, to be noted that :

- in the case of the non-dispersive infrared absorption method, a matrix effect may occur, due to the thermal properties of other components and this should be avoided;
- in the case of the method by infrared spectrometry using cells of long path length, calibration should be made with a calibration gas mixture having a sulphur dioxide (SO_2) concentration as close as possible to the concentration to be measured; this calibration gas mixture should be prepared with a complementary gas as similar as possible to the gas mixture to be analysed. All precautions should be taken to ensure that calibration is carried out under the same conditions of temperature and pressure as the sampling;
- in the case of the method by electrical conductimetry with continuous gas sampling, calibration can also be carried out using standard sulphuric acid solutions provided that the calibration circuit and, in particular, the flow rate and reaction efficiency in the apparatus are closely controlled;
- in the case of the determination of gaseous acid pollution index, no calibration is generally made since a standard solution is available.

4.3 Possible application of the methods to other components, and interferences (characteristic 14)

4.3.1 Non-dispersive infrared absorption

a) Application to other components

CO , CO_2 , NO , NO_2 , C_xH_n , NH_3 , N_2O , etc., provided that the detector is changed.

b) Interferences

Mainly CO_2 but also H_2O and most organic compounds. This method is used only with samples which remain fairly constant in composition (for example air, combustion gases).

4.3.2 Dispersive infrared spectrometry using cells of long path length

a) Application to other components

The method applies to many other components.

b) Interferences

These depend on the spectrometric resolution of the apparatus and the bands which are adjacent to the SO_2 absorption band.

4.3.3 Gas chromatography

— with detection by catharimetry

a) Application to other components

CO , CO_2 , NO , N_2O , hydrocarbons, etc.

(Most gases can be analysed using this method if they are stable under the conditions of measurement and provided suitable columns are used.)

b) Interferences

None, if the column is suitable.

— with a flame photometer detector

a) Application to other components

All sulphur compounds and, provided the optical filter is changed, phosphorus compounds.

b) Interferences

None if the column is suitable.

4.3.4 Colorimetry using pararosaniline

- a) Application to other components

The method is applicable only to the determination of SO_2 .

- b) Interferences

O_3 , NO_x , Cl_2 , HCl , H_2S , mercaptans, aldehydes and heavy metals.

4.3.5 Electrical conductimetry

- a) Application to other components

CO_2 , H_2S , Cl_2 , NO , NO_x , O_3 , etc., provided that the reagents are changed.

- b) Interferences

Cl_2 , HCl , NH_3 , NO_2 and to a lesser degree NO , O_3 , H_2S , CO_2 , CH_4 and H_2O . The method has very little selectivity.

4.3.6 Coulometry

- a) Application to other components

H_2S , sulphides, mercaptans and, generally, oxidizing or reducing compounds, provided that an appropriate redox couple is chosen.

- b) Interferences

O_3 , H_2S , Cl_2 , NO , NO_2 . The method has little selectivity but it is used with selective absorbents which mitigate this inconvenience.

4.3.7 Detector tubes

- a) Application to other components

The tube selected for the determination of SO_2 is obviously specific and does not permit determination of other components.

- b) Interferences

These depend on the reagents used (for example H_2S , NO and NO_2 may interfere).

4.3.8 Flame photometry

- a) Application to other components

H_2S and total sulphur and, provided that the optical filter is changed, phosphorus derivatives.

- b) Interferences

All sulphur and phosphorus derivatives in high concentrations.

4.3.9 Mass spectrometry

- a) Application to other components

All volatile components.

- b) Interferences

Only a few possibilities of interference.