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Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Performance characteristics of automated measuring methods

Émissions de sources fixes — Détermination de la concentration en masse de dioxyde de soufre — Caractéristiques de performance des méthodes de mesurage automatiques

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Contents

Annexes

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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.

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.

International Standard ISO 7935 was prepared by Technical Committee ISO/TC 146, *Air quality*, Sub-Committee SC 1, *Stationary source emissions*.

Annex A forms an integral part of this International Standard. Annexes B and C are for information only.

Introduction

Sulfur dioxide can arise in considerable quantities from combustion of fossil fuels used for energy generation, industrial activities processing sulfur or sulfur containing material, and from combustion of sulfur containing waste. The waste gas from these processes, containing sulfur dioxide, is usually discharged into the ambient atmosphere, via a duct or a chimney.

For evaluating the mass concentration of sulfur dioxide present in the waste gas of stationary source emissions, a number of highly developed methods of integrated sampling and subsequent determination by chemical analysis and automated measuring systems are available. Considerable experience exists on their application under plant conditions. One of these methods is standardized as ISO 7934.

ISO 7934 is used for example in comparative measurements, where the automated measuring methods are involved. The automated technique is capable of continuous measurement of the mass concentration of sulfur dioxide.

For methods where performance characteristics are given, the values of performance characteristics are used to decide whether a method is suitable for a given measuring task (see ISO 6879:1983, clause 1). Values of the main performance characteristics of automated measuring systems, capable of determining the mass concentration of sulfur dioxide present in waste gas stationary emission sources, are given in clause 5.

Additional performance characteristics are given in informative annex B.

The procedure for evaluating the values of the performance characteristics listed in clause 5, is described in normative annex A.

Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Performance characteristics of automated measuring methods

1 Scope

This International Standard specifies a complete set of values of performance characteristics for automated measuring systems for the continuous measurement of the mass concentrations of sulfur dioxide in stationary source emissions.

NOTE 1 If the performance characteristics of an automated measuring system are listed according to table 1, this ensures that the automated measuring system is reliable and gives satisfactory continuous results.

The set of data listed in table 1 refers to the performance characteristics of measurement methods, including all steps from sampling to recording and, if necessary, storage of data.

This International Standard is applicable to extractive and non-extractive automated sulfur dioxide measuring methods. For both methods it implies the applicability of zero and calibration gas and the availability of comparable samples. The automated measuring system can be calibrated with calibration gases, by applying the manual method described in ISO 7934, or by applying an automated measuring system previously verified according to this International Standard using a different principle of detection. The value of the integral performance (3.7) is determined by using ISO 7934 or an automated measuring system verified according to this International Standard with a different principle of detection. At present, the range over which this specification applies is between 0 g/m^3 to 0,1 g/m^3 and 0 g/m^3 to 8 g/m^3 (see table 2 for details).

NOTE 2 Although it is impossible to give precise testing details, the requirements and testing principles are also applicable to non-extractive systems.

Table 1 — Main performance characteristics

Performance characteristics	**Numerical value**	**Test methods** (see annex A)
Detection limit	2 % 1)	A.4.2.1.1
Effect of interfering substances	± 2 % 1) 2)	A.4.2.1.2
Response time	⩽ 200 s 3)	A.4.2.1.3
Integral performance (s_A)	± 2,5 % 1) 4)	A.4.2.2

1) Related to the upper limit of measurement.

2) The main interfering substances in the flue gas from combustion plants are CO_2, CO, NO, H_2O and, in smaller concentrations, NO_2 and NH_3. If the water vapour is not removed from the flue gas of coal and waste fired incinerators, HCl and HN may also interfere. In special cases there may be other interfering substances (e.g. cyanide).

3) Assuming an integration time of 30 min.

4) See 3.7.

The facilities at which the values of the performance characteristics given in table 1 have been verified according to this International Standard in the appropriate ranges are listed in table 2.

Table 2 — Facilities and measuring ranges

Facility	Measuring range g/m^3 of SO_2 1)
Furnaces for hard coal	0 - 1 to 0 - 8
Furnaces for hard coal with stack gas desulfuration plant	0 to 0,1
Furnaces for brown coal	0 - 0,1 to 0 - 3,0
Furnaces for heavy fuel oil	0 - 0,1 to 0 - 5,0
Refuse incinerator	0 - 0,4 to 0 - 1,0
Coke oven	0 to 1
Calcar with heavy fuel oil	0 to 5
Sulfuric acid recovery plant	0 to 1

1) Related to 101,3 kPa, 273 K and dry gas.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6879:1983, *Air quality — Performance characteristics and related concepts for air quality measuring methods.*

ISO 7934:1989, *Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Hydrogen peroxide/barium perchlorate/Thorin method.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 automated measuring system (AMS): A complete system that may be attached to a chimney to continuously measure and record the mass concentration of sulfur dioxide passing through the chimney.

3.2 analyser: Analytical part in an extractive AMS.

3.3 verified AMS: AMS previously verified in ISO 7935.

3.4 calibration gas: A gas of known and reliable composition that may be used to check the response of an AMS.

3.5 comparative measurements: Measurements that are performed in the same chimney in the same sampling plane for the same period of time.

3.6 manual method: The test method defined in ISO 7934 for the manual sampling and analysis of stationary source emissions containing sulfur dioxide.

3.7 integral performance, s_A**:** The integral performance is a measure of the working accuracy of the AMS. It is calculated according to the formula for standard deviations.

The integral performance is derived from the difference in the pairs of measured values of sulfur dioxide by the AMS under investigation, and by an ISO manual method or a verified AMS of different measuring principle on the basis of a sufficient number of comparative measurements spread over the period of unattended operation (see annex A).

NOTES

3 It is not possible to determine the standard deviation of an AMS under repeatable working conditions because

- commercially available calibration gas mixtures containing sulfur dioxide do not have all the properties of actual waste gas and do not cover all possible influences;
- the mass concentration of sulfur dioxide in waste gas usually varies with time;
- it is not possible to maintain the properties of a waste gas present in the waste gas flue when it is transferred into a vessel.

4 The reason that the integral performance is defined as a measure of the working accuracy, is that it contains, in addition to random errors, all the effects of interfering substances, changes in temperature and power line as well as zero drifts and span drifts. It also includes the standard deviation of the ISO manual method or the verified AMS using a different principle of detection, which can be determined separately and eliminated if necessary. Furthermore, it includes the effects, for the different methods, of a different response time to variations in the composition of the waste gas.

The integral performance defined in this subclause is an upper limiting value for the AMS. Relevant systematic errors of the measured values of the ISO manual method, or the verified AMS using a different principle of detection, have to be known and taken into account.

3.8 chimney: Stack or final exit duct on a stationary process used for the dispersion of residual process gases.

3.9 mass concentration: The concentration of a substance in an emission, expressed in milligrams per cubic metre or grams per cubic metre.

3.10 stationary source emissions: Those waste gases that have been emitted from a stationary plant or process and are exhausted to a chimney for dispersion into the atmosphere.

4 Description of the automated measuring systems

4.1 Introduction

There are two types of automated measuring systems:

— extractive methods;

— non-extractive methods, known as in-situ or cross-duct measuring methods.

Examples of the components of these systems are given in figures 1 and 2.

Using the extractive method, the representative gas sample is taken from the stack with a sampling probe and conveyed to the analyser through the sample line and sample gas conditioning system. The values determined are often recorded or stored by means of electronic data processing.

The non-extractive method does not require any sample processing. In addition, it takes into consideration a larger part of the waste gas. Most of the methods described in 4.2 and 4.3 are able to determine sulfur dioxide specifically. Methods which rely on conductometry determine total sulfur oxides.

4.2 Extractive methods

The extractive methods enable separation of the sampling and analysis parts, thereby facilitating maintenance operations.

The main parts are

— a sample probe;

— a sample line;

— a gas conditioning system;

— an analytical part.

Certain extractive methods also include sample dilution.

The sample probe is placed inside the duct containing gaseous effluents. The choice of locations may sometimes be difficult, since the measurement to be made needs to be representative and calibration should be possible.

The design of the sample probe and the gas conditioning system essentially depends on physico-chemical characteristics (composition of the gaseous phase, particle concentration, temperature, water dew point, etc.) of the effluents to be analysed and the principle of the analyser used. Since particulate matter and humidity may influence the measurement, the line contains a particulate filter and a humidity elimination device.

In order to limit sulfur dioxide losses and inconsistent readings, the line is frequently heated.

The analytical detection methods most commonly used are absorption, using infrared or ultraviolet radiation, fluorescence, using ultraviolet radiation, interferometry and conductometry.

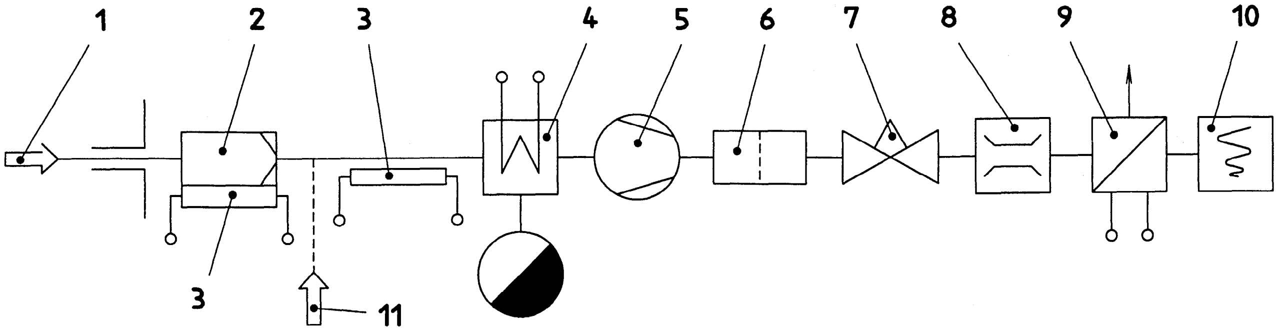
4.3 Non-extractive methods

For in-situ or cross-duct methods, an optical device is used which is positioned directly in the duct of gaseous effluents. It consists of two modules, one being a radiation emittor, the other a receptor of the radiation which has passed through the gases containing sulfur dioxide.

Installation of these two modules, in relation to the duct, depends on the apparatus used.

The signals from the receptor are subsequently processed, in order to convert the data into concentration, expressed as V/V or in milligrams per cubic metre.

NOTE 5 When comparing the results from dry extractive methods and non-extractive methods, it is necessary to know the water content of the flue gases for correction of the in-situ value to a value on a dry gas basis.

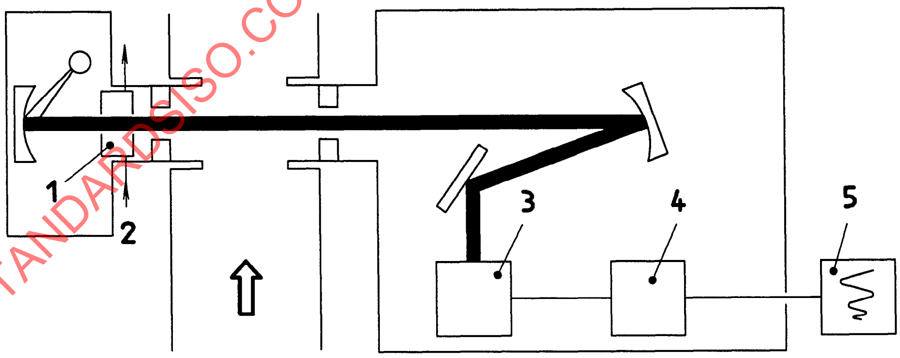


Key

1	Gas sampling probe
2	Particulate filter
3	Heating jacket or heating bandage
4	Cooler with condensate-separator
5	Sampling pump
6	Filter
7	Needle valve
8	Flowmeter
9	Analyser
10	Recorder
11	Inlet for

a) calibration gas mixtures containing sulfur dioxide
b) zero samples

Figure 1 — Example of the components for the extractive method



Key

1	Absorption-cell for calibration gas mixtures
2	Inlet for calibration gas mixtures
3	Optical receiver
4	Electronic module
5	Recorder

Figure 2 — Example of the components for the non-extractive method

5 Numerical values of performance characteristics and their applicability

When measured in accordance with the respective methods given in annex A, the performance characteristics shall meet the requirements given in table 1.

Together with the measuring ranges from table 2, the values of table 1 show the state of the art of source emission measurement of sulfur dioxide.

NOTES

6 Table B.1 gives additional performance characteristics that serve as a guideline to facilitate meeting the performance characteristics given in table 1. Table 2 gives facilities at which the values of the performance characteristics given in table 1 have been applied and verified, as well as the applicable measuring range.

7 The values of the performance characteristics specified in table 1 result in an inaccuracy of the result less than ± 10 %, related to the upper limit of measurement, if the automated measuring system is handled and maintained properly. Checks with calibration gas mixtures containing sulfur dioxide are carried out and the interfering effect of changes in atmospheric pressure are taken into account.

8 The performance characteristics given in tables 1 and B.1 are based on many measurements carried out with complete extractive measuring systems under plant conditions using the non-dispersive infrared (NDIR), non-dispersive ultraviolet (NDUV) and conductometric methods and on results obtained with non-extractive methods. The value of the integral performance was obtained on the basis of 50 comparative measurements performed according to ISO 7934.

9 The response time, $t \leqslant 200$ s, indicated in table 1 ensures a sufficient resolution of the changes in mass concentration of sulfur dioxide existing in practice, and avoids long sampling times when carrying out comparative measurements. If a response time of $t > 200$ is applied, this should be reported with the results.

10 When sufficient experience is available for new types of plant and/or different measuring ranges, the ranges listed in table 2 and the applications may be extended.

Annex A
(normative)

Determination of main performance characteristics of automated measuring systems

A.1 Scope

This annex describes methods for determining the main performance characteristics of the AMS. At present, the range over which this specification applies is between 0 g/m^3 to 0,1 g/m^3 and 0 g/m^3 to 8 g/m^3 for stack gases.

The performance characteristics established after installation of the AMS require validating in the event of a change in operation which could affect the AMS performance, e.g. a change in the type of fuel burned.

NOTE 11 For the determination of the main performance characteristics, the calibration of the measuring system is the first step. In A.4.1 the different methods of setting, checking and calibration are explained in detail. These are methods employing calibration gases and also comparative methods. The methods employing only calibration gases are applicable in plants where the flue gas composition is well known. They are also applicable when the comparative method is considered to be too costly and time consuming, e.g. in the event of intermittent use of the plant.

A.2 Principle

Three of the performance characteristics, namely detection limit, response time and effect of interfering substances, are determined either on site or in the laboratory using gases of known concentration. In the case of an extractive system, these gases are introduced at the beginning of the sampling line. An extractive AMS is provided by the manufacturer, with a basic calibration and a calibration curve of the analyser. A non-extractive AMS is precalibrated.

The integral performance of the AMS is then determined on site, by comparison with measurements performed according to ISO 7934 or a verified AMS with different principle.

A.3 Reagents

A.3.1 Zero gas

The zero gas shall be a gas containing no sulfur dioxide, for example technically pure nitrogen or sulfur dioxide-free air.

A.3.2 Calibration gases

The calibration gases shall have certified concentrations and be traceable to a national standard.

A.4 Test procedures

A.4.1 Calibration checks

In the event of continuous use, the setting of the analyser (A.4.1.1) shall be checked at regular intervals given by the period of unattended operation (usually seven days). In the event of intermittent use, the setting of the analyser shall be checked before each use. The calibration function (A.4.1.3) shall be checked at longer intervals (e.g. yearly) or after the analyser is repaired.

A.4.1.1 Setting of the analyser

Set up the analyser according to the manufacturer's instructions. Feed the zero gas (A.3.1) into the analyser and set the zero. Subsequently, feed in a calibration gas (A.3.2) that has a known concentration corresponding to approximately 70 % to 80 % of the full scale deflection of the analyser and set the scale reading accordingly. Next, feed the zero gas into the analyser once more and check that the reading returns to zero; if not, re-adjust the zero and repeat.

NOTE 12 For non-extractive devices, the setting of the analyser does not apply as it is part of the AMS.

A.4.1.2 Checking of the setting of the AMS

Carry out the procedures described in A.4.1.1 again, but this time use the complete AMS. For extractive AMS, the zero gas and the calibration gas are fed into the measuring equipment directly behind the sampling probe (if possible before the filter) at ambient pressure. In this way, the influence of the sampling system is taken into account.

For a non-extractive AMS, follow the manufacturers' instructions. For example, feed the zero and calibration gas into a tube matching the length of the measuring distance between the radiation emittor and the radiation receptor, or use absorbing devices provided by the manufacturer.

A.4.1.3 Checking of the entire scale of the analyser

In order to check the entire scale for measuring equipment that normally has a linear response function, carry out the procedure given in A.4.1.1 but using five uniformally distributed calibration gas concentrations (20 %, 40 %, 60 %, 80 %, 90 % of the full scale). To obtain these concentrations gradually dilute the calibration gas (A.3.2) used for setting purposes (see A.4.1.1). In the case of a non-linear calibration function, a minimum of ten concentrations is required.

A.4.1.4 Calibration using comparative measurements in the stack

For comparative measurements, take additional gas samples with a separate probe.

For an extractive AMS, the inlets of both gas sampling probes shall be separated by a distance not exceeding 30 cm, to ensure that the composition of the samples is as similar as possible.

For a non-extractive AMS, check whether the use of a sampling grid for the comparative measurement is necessary or whether a single sampling point will suffice.

Calibrate, as specified in ISO 7934 or with an AMS previously verified according to this International Standard using a different principle of detection.

Carry out 20 pairs of measurements immediately one after another.

The sampling period for each of the pairs of comparative measurements shall be 30 min. Take the mean of the instrument readings of the AMS over the sampling period.

If possible, change the values of the concentration of sulfur dioxide between each pair of measurements.

Calculate the calibration function by linear regression. Report the confidence limit with the results.

If the calibration of the AMS according to A.4.1.2 differs by more than 4 % of full scale from the calibration by linear regression, investigate the cause and take remedial measures. As a consequence, the calibration resulting from the comparative measurements is usually adopted.

NOTE 13 For extractive AMS, the check according to A.4.1.1 is always the first step for the determination of the performance characteristics. Subsequently, the installation of the complete AMS needs to be checked according to A.4.1.2. Differences of corresponding values may be produced by leaks. A dilution failure of the gas probe has to be smaller than 0,5 % of full scale. Measurement errors caused by absorption, adsorption and solubility of the measuring gas are normally due to neglect. Checking of the entire scale of the analyser according to A.4.1.3 is necessary if the given drift values in table B.1 are exceeded frequently, or after longer intervals (e.g. yearly). Differences greater than 1 % of full scale have to be incorporated in the evaluation to maintain the values of the performance characteristics; if the differences are greater than 3 %, there is a fault in the analyser.

Calibration by comparative measurement according to this subclause is required when, for example, installing continuous monitoring equipment at large sources. This may be performed at the time of installation of a system and again after several years of operation.

Comparative measurements can also be applied, to investigate the reason for exceeding the limit value of the integral performance (see also A.4.2.2).

A.4.2 Determination of performance characteristics

A.4.2.1 Tests using calibration gases

Perform the tests with calibration gases on the complete AMS, either in the laboratory or on-site with the sampling line installed in a duct.

For an extractive system, feed zero gas (A.3.1) and calibration gases (A.3.2) directly into the sampling line, as near as practicable to the sampling head (see figure 1) and at such a pressure that the same sample flow is obtained through the analyser as in A.4.1.2. If the sampling head is installed in a duct, take measures, for example by closing any valve immediately adjacent to the sampling head, to ensure that the calibration gases are not contaminated with the gas from the duct.

For non-extractive systems, special arrangements are necessary for the measurements with test gases as follows:

> The test equipment shall include mechanical components to feed test gases into the measurement path at the appropriate temperature and pressure. For in-situ type AMS, this may be a sealed end-cap for the probe, with appropriate gas connections. This entire assembly can be placed in a furnace.

For cross-duct measuring equipment, a large optical cell is required, with windows transparent to the wavelengths used by the analyser. This optical cell shall be of sufficient diameter to accomodate the analyser beam width and of sufficient length to simulate the highest test gas concentrations required.

NOTE 14 The necessary devices are provided by the manufacturers.

A.4.2.1.1 Detection limit

Carry out a minimum of 30 determinations by feeding zero gas (A.3.1) into the AMS as described in A.4.2.1 and note the reading. Carry out these readings in the shortest period of time possible, in order to minimize the zero drift and the temperature responsive zero deviation (see annex B).

Assuming a confidence level of 95 %, calculate the detection limit x, in milligrams per cubic meter, using the formula

$$x = \bar{x}_0 + 2s_{x0}$$

where

$\bar{x}_0$ is the mean, in milligrams per cubic meter, of the blank readings;

s_{x0} is the standard deviation, in milligrams per cubic meter, of the blank readings.

A.4.2.1.2 Evaluation of the effect of interfering substances

Pass into the AMS, as described in A.4.2.1, test gases containing various known concentrations of the interfering gas, y_i, that correspond to typical values. Note the measured values, x_{si}, expressed as milligrams of sulfur dioxide per cubic meter, as well as the mass concentrations, ρ_{si}, of the interfering gas.

In gases where the change in measured value is linear with increasing mass concentration of a substance, the effect of the substance may be given by x_{si}/ρ_{si}. If the change in measured value is not linear with increasing mass concentration of a substance, the interfering effect of the substance has to be determined separately.

Determine the effect of each interfering substance separately and also the combined effect of a mixture of all the interfering substances.

NOTE 15 A typical picture of interfering substances of flue gas from combustion plants contains

CO_2: 275 g/m^3

CO: 100 mg/m^3

NO: 400 mg/m^3

NO_2: 30 mg/m^3

rest, N_2

Calculate the interfering effect, S, of a typical mixture of substances from the obtained individual effect, x_{xi}/ρ_{si}, of the interfering substances, y_2, using the formula

$$S = \frac{1}{\rho_{FS}} \times \sum_{i=1}^{n} \frac{x_{si}}{\rho_{si}} \times \rho_{mi} \times 100$$

where

ρ_{mi} is the mass concentration of the interfering substance in the moisture, in milligrams per cubic metre;

ρ_{FS} is the measuring range, in milligrams per cubic metre;

n is the number of interfering substances.

Compare the calculated value with the measured value of the mixture. If the two values agree to within 2 %, the effect of combination can be neglected and the interfering effects for other mixtures can be calculated.

NOTES

16 The value given in table 1 is the sum of interfering effects caused by the maximum interfering substance concentrations in the measuring sample.

17 The composition of the flue gas depends greatly upon the type of plant.

Generally, valid maximum interfering substance concentrations cannot be given.

A.4.2.1.3 Determination of response time

Pass into the AMS, as described in A.4.2.1, a calibration gas containing a concentration of sulfur dioxide corresponding to between 50 % and 90 % of the upper limit of measurement of the detector.

Consider the response time as the average time interval between feeding in the calibration gas mixture and reaching 90 % of the recorded mass concentration (see 4.2.2.13 of ISO 6879:1983).

A.4.2.2 Determination of integral performance

Determine the integral performance of the AMS on site only. Obtain the integral performance by carrying out a minimum of 30 measurements using the AMS under test according to A.4.1.4. Compare the results with those obtained using ISO 7934 or another AMS previously verified according to this International Standard using a different measurement principle.

NOTE 18 Because the inaccuracy of the measuring results of the AMS, which depends on the quality of the (complete) automated measuring system, is judged over the period of unattended operation, a sufficient number of comparative measurements (as described in this subclause) is carried out throughout the period.

Calculate the integral performance, s_D, and the known standard deviation, s_M, for the measured values of the ISO manual method (see ISO 7934) using the formula

$$s_A = \sqrt{s_D^2 - s_M^2}$$