

Australian/New Zealand Standard™

Methods for sampling and analysis of ambient air

Method 15: Determination of gaseous pollutants in ambient air using differential optical absorption spectrometry (DOAS)—Direct-reading instrumental method

AS/NZS 3580.15:2014

PREFACE

This Standard was prepared by the Joint Standards Australia/Standards New Zealand Committee EV-007, Methods for Examination of Air, as a Joint Australian/New Zealand Standard.

The objective of this Standard is to provide regulatory and testing bodies with a method for monitoring gaseous ambient air pollutants with open-path monitoring equipment utilizing the differential optical absorption spectrometry (DOAS) technique.

The requirements for instruments specified in this Standard were derived from those given in the European Standards for air quality monitoring instruments—EN 14212:2012 (SO₂), EN 14211:2012 (NO/NO₂), EN 14625:2012 (O₃). European Standards have developed extensive performance testing procedures for criteria ambient pollutants such as those covered by this Standard. This ensures that instruments which are used in the application of this Standard will demonstrate a performance suitable for this application.

METHOD

1 SCOPE

This Standard sets out the method for the determination of nitrogen dioxide (NO₂), sulfur dioxide (SO₂) and ozone (O₃) found in ambient air using the open-path differential optical absorption spectrometry (DOAS) technique. This Standard sets out performance criteria for these gases, however, the DOAS measurement technique is applicable to other gases. This method can provide a measure of multiple gases integrated over an open-path length of between 100 and 1000 metres.

2 REFERENCED DOCUMENTS

The following documents are referred to in this Standard:

AS

3580 Methods for sampling and analysis of ambient air

3580.1.1 Method 1.1: Guide to siting air monitoring equipment

3580.2.2 Method 2.2: Preparation of reference test atmospheres—Compressed gas method

EN

- 14211 Ambient air—Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence
- 14212 Ambient air—Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence
- 14625 Ambient air—Standard method for the measurement of the concentration of ozone by ultraviolet photometry
- 16253 Air Quality—Atmospheric measurements near ground with active Differential Optical Absorption Spectroscopy (DOAS)—Ambient air and diffuse emission measurements

ISO/IEC

Guide 98 Uncertainty in measurement,

Guide 98-3 Part 3: Guide to the expression of uncertainty in measurement (ISO GUM 2008)

US EPA

Environmental Protection Agency (1995). "Federal Register" Vol. 60, No. 58, 2 May 1995, pp. 21518-21520

40 CFR 58 Code of Federal Regulations, Title 40, Protection of Environment, Part 58, Ambient Air Monitoring Reference and Equivalent Methods, Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring

Environment Protection and Heritage Council, Peer Review Committee (PRC)

National Environment Protection (Ambient Air Quality) Measure, Technical Paper No. 5, Data Collection and Handling, 2001.

CASANZ

Clean Air Society of Australia and New Zealand, Air Pollution Measurement Manual, Volume 1, Open-path Monitoring of Air Pollutants by Differential Optical Absorption Spectrometry (DOAS), M. Dawson, D. Neale, 5th edition, 2000

3 DEFINITIONS

For the purposes of this Standard the definitions below apply:

3.1 Full scale (FS)

The nominated maximum concentration for which an instrument has been calibrated. The full scale should be selected to cover the normal range of values expected in the sampling environment.

3.2 Interferent

Component of the air sample—excluding the measured constituent—that affects the output signal.

3.3 Linearity

The deviation of an instrument's output from a straight line of best-fit line when subjected to varying test atmospheres.

3.4 Lower detectable limit

The minimum pollutant concentration that produces a signal of exactly twice the noise level.

3.5 Noise

Spontaneous, short duration deviations in instrument output, about the mean, which are not caused by input concentration changes. Noise level is determined as the standard deviation about the mean and is expressed in concentration units.

3.6 Parts per billion (ppb)

A ratio expressing the volume of gaseous pollutant contained in 1 000 000 000 volumes of atmosphere. It may be expressed in terms of microlitres per cubic metre since the values are identical. Alternatively, it is one thousand million times the ratio of the partial pressure of gaseous pollutant to the pressure of the atmosphere in which it is contained.

3.7 Parts per million (ppm)

A ratio expressing the volume of gaseous pollutant contained in 1 000 000 volumes of atmosphere. It may be expressed in terms of millilitres per cubic metre as the values are identical. Alternatively, it is one million times the ratio of the partial pressure of gaseous pollutant to the pressure of the atmosphere in which it is contained.

3.8 Precision

Variation about the mean of repeated measurements of the same pollutant concentration on the same instrument, expressed as one standard deviation about the mean.

3.9 Proficiency audit

An evaluation process used to measure the performance or effectiveness of a measurement system including analysis and validation.

3.10 Range

Nominal minimum and maximum concentrations that a method is capable of measuring.

NOTE: The nominal range is specified by the lower and upper range limits in concentration units, e.g. 0 to 500 ppb.

3.11 Repeatability

Closeness of the agreement between the results of successive individual measurements of gas carried out under the same conditions of measurement.

3.12 Rise time

The time interval, after a step increase in input concentration, between initial instrument response and 90 per cent of final instrument response.

3.13 Span drift

The percentage change in instrument response to an on-scale pollutant concentration over a 24 hour period of continuous unadjusted operation.

3.14 Test atmosphere

A reference test atmosphere containing a known concentration of pollutant.

3.15 U_{95}

A measurement of uncertainty at a confidence interval of 95% according to ISO/IEC Guide 98-3.

3.16 UV-visible spectrum

The section of the electromagnetic spectrum with wavelengths between approximately 200 and 800 nanometres.

3.17 Zero drift

The change in instrument response to zero pollutant concentration over a 24 hour period of continuous unadjusted operation.

4 PRINCIPLE

4.1 Principle of measurement

The DOAS technique is based on the Beer-Lambert Law, which relates the absorption of light as a function of the concentration of the absorbing species, the absorption characteristics of that species, and the length of the absorption path. In contrast to traditional UV-visible laboratory measurements (which typically use a relatively high concentration of absorbing species, a single wavelength and a short optical path length), the open-path DOAS technique uses a relatively low concentration of absorbing species, differential absorption spectra over a range of 200 to 800 nanometres and an optical path length typically between 100 and 1000 metres. Figure 1 shows the absorption wavelength intervals for a variety of gaseous species that are commonly monitored using DOAS technology.

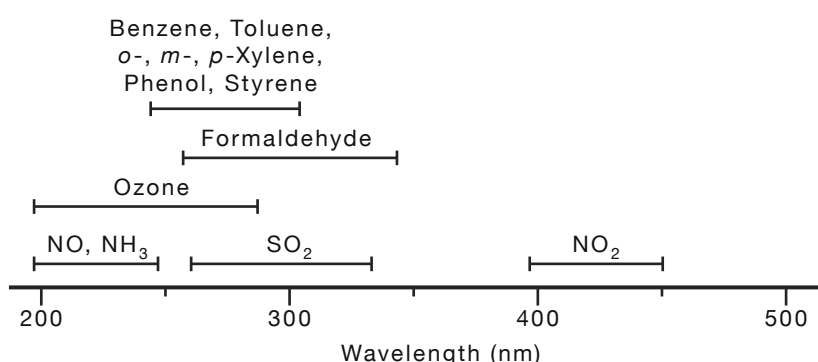


FIGURE 1 ABSORPTION WAVELENGTH INTERVALS FOR A VARIETY OF GASEOUS SPECIES

The Beer-Lambert Law can be expressed mathematically as follows:

$$I(\lambda) = I_0(\lambda) e^{-\sum c_i a_i(\lambda) L} \quad \dots 4(1)$$

where

$I(\lambda)$ = measured light intensity at specific wavelength λ

$I_0(\lambda)$ = light intensity at specific wavelength λ without any absorption

c_i = concentration of gaseous species i

$a_i(\lambda)$ = absorption cross-section at wavelength λ for gaseous species i (quantifies the probability for light absorption at each wavelength; units are m² per molecule, m² per µg, or similar, depending on the unit of concentration)

L = the optical path length

As $I_0(\lambda)$ —the light intensity without any absorption—is not measurable, the DOAS technique is used to study specific, and quite narrow, features within the overall absorption spectrum. DOAS is based on measuring the difference between absorbance at certain wavelengths where the pollutant of interest has distinct absorption peaks and other wavelengths on either side of these peaks. This is illustrated in Figure 2.

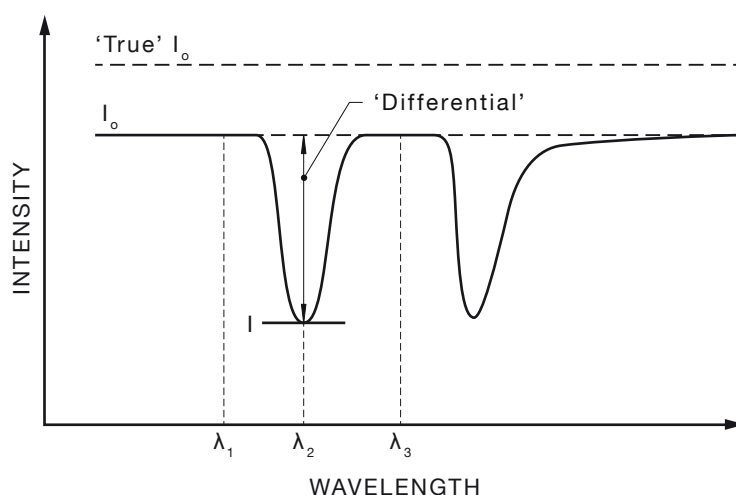


FIGURE 2 BASIS OF DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY

When using the DOAS technique, Equation 4(1) becomes:

$$\Delta I(\lambda) = \Delta I_0(\lambda) e^{-\sum c_i \Delta a_i(\lambda) L} \quad \dots 4(2)$$

With $\Delta I(\lambda)$, $\Delta I_0(\lambda)$ the differential light intensities and $\Delta a_i(\lambda)$ the differential cross section.

By knowing the cross-sections of the molecules supposed to be present in the atmosphere as well as the optical path length, this differential approach then allows for the determination of the concentration of the target gases.

4.2 Applicable gases

DOAS is most commonly used for monitoring of nitric oxide, nitrogen dioxide, sulfur dioxide, ozone, benzene, toluene, xylene and formaldehyde, but it is possible to use the technique to monitor other gases with narrow absorption features in the UV and visible spectrum. With some instrumentation it is also possible to monitor a range of infrared absorbing gases through the use of optional infrared detection hardware in conjunction with the UV–visible detection system, however, the measurement of infrared absorbing gases is not within the scope of this Standard.

Table 1 provides typical measurement capabilities for the gases generally available on current commercially available DOAS equipment. This information has been compiled from manufacturer's technical specifications and is intended as a general guide only. Manufacturers' documentation should be consulted for a detailed assessment of the capabilities of individual instruments.

TABLE 1
TYPICAL DOAS AMBIENT AIR QUALITY MEASUREMENT CAPABILITIES

Gas	Measurement range ¹ (ppb)	Lower detection limit ¹ (ppb)	Recommended optical path length ² (m)
Nitric oxide	0–1500	1.2	100–300
Nitrogen dioxide	0–500	0.6	300–1000
Sulfur dioxide	0–500	0.3	300–1000
Ozone	0–500	0.9	300–800
Benzene	0–150	0.9	300–800
Toluene	0–150	0.8	300–800
o-Xylene	0–150	1.5	300–800
m-Xylene	0–150	0.6	300–800
p-Xylene	0–150	0.8	300–800
Formaldehyde	0–400	1.1	300–800
Phenol	0–500	0.3	300–800
Styrene	0–450	1.0	300–800
Ammonia	0–650	2.5	100–300

NOTES:

- 1 Based on five minute averaging and a 500 metre optical path, except nitric oxide and ammonia (250 metre optical path).
- 2 Optical path lengths outside these ranges may be selected, but at the potential expense of instrument sensitivity and overall performance (i.e. detection limit). When monitoring multiple gases, the lowest recommended optical path length range should be used.

5 APPARATUS

5.1 General

A typical DOAS open-path field installation consists of the following components:

- (a) Transmitter.
- (b) Receiver.
- (c) Spectrometer.
- (d) Data processing system.

A schematic layout diagram illustrating the key features of a DOAS system is shown in Figure 3.

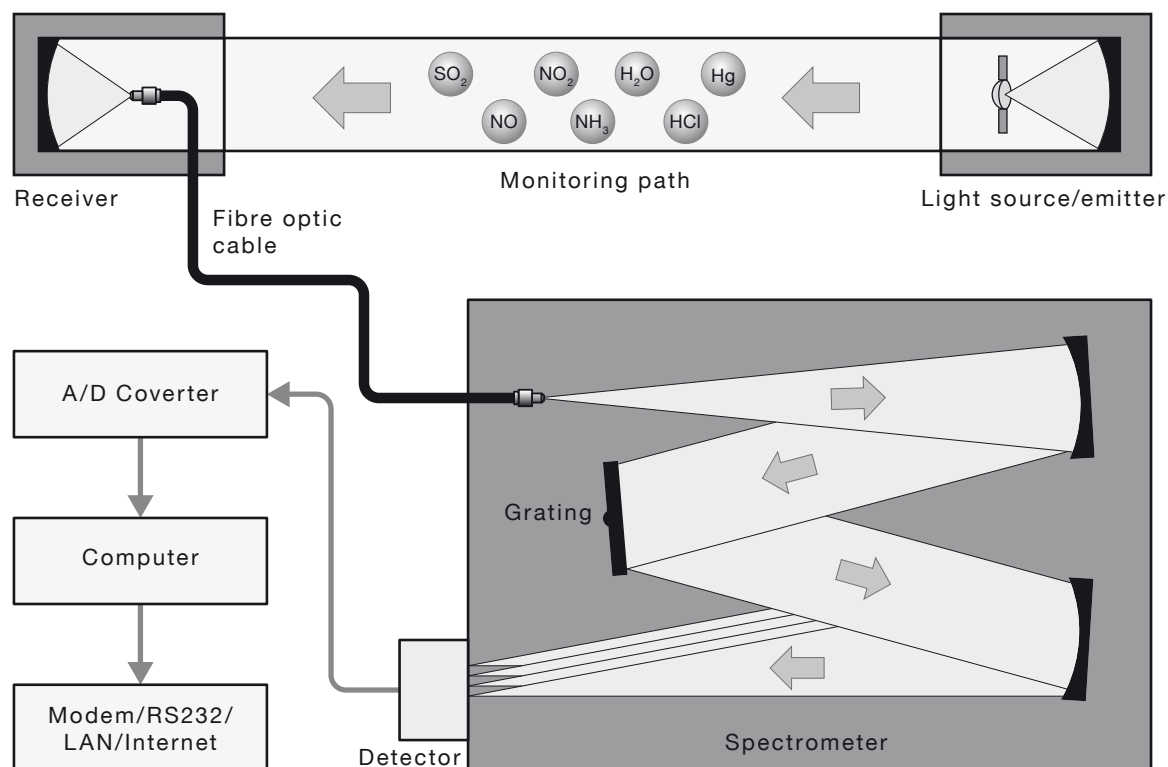


FIGURE 3 SCHEMATIC LAYOUT DIAGRAM ILLUSTRATING THE KEY FEATURES OF A TYPICAL DOAS SYSTEM
(Courtesy of Opsis AB)

5.2 Transmitter

Most transmitters use a xenon lamp, which produces a continuous spectrum in the approximate range 200 to 800 nanometres. Two types of xenon lamps are commonly used, depending on the lower spectrum range required for the gases being monitored. Measurement of nitric oxide and ammonia requires a xenon lamp capable of generating wavelengths down to 200 nanometres. This lamp is also capable of converting oxygen in the air inside the transmitter to ozone, necessitating continuous ventilation of the transmitter to prevent ozone accumulation and consequent artificial elevation of ozone measurement results. The light from the lamp is focused by the optics of the transmitter into a narrow beam of essentially parallel light which is directed to a receiver located up to 1000 metres away (typical optical path length is 400 to 500 metres). Other types of lamps may be used provided they conform to manufacturers' recommendations for the types of gases being measured.

5.3 Receiver

The receiver collects the light from the transmitter and focuses it to a narrow beam a few millimetres in diameter. This focused beam is then passed by fibre-optic cable or other optical device to the spectrometer. Monitoring of gases in the range 200 to 240 nanometres, such as nitric oxide, requires the use of a special fibre optic cable that has high transmission in the UV range.

Some instruments use a coaxial telescope arrangement, where both the transmitting and receiving optics are contained in the same housing, and a passive reflector (a quartz mirror or reflector array) is placed at the remote end of the optical path. In this situation the optical path length is twice the physical separation between the transmitter/receiver and the passive reflector. With some instrumentation it is possible to sequentially measure over multiple optical paths using a single spectrometer through the use of a multiplexer or other device to switch between light paths.

5.4 Spectrometer

5.4.1 General

Two types of spectrometer are currently used in commercially available equipment.

5.4.2 Photosensor array system

One type of system uses a broadband spectrometer operating in the range 200 to 375 nanometres, equipped with a flat field holographic grating coupled to a photosensor array system. Such a system captures a spectrum of around 160 nanometres at a resolution typically less than 0.5 nanometres over the entire spectrum. Exposure time varies between one and a few seconds according to atmospheric transmission fluctuation, and is adjusted automatically.

By acquiring the entire spectrum over a broad wavelength range, the photosensor array system can determine the concentrations of different pollutants from the same spectrum. The system is also mechanically simple, featuring no moving parts. However, the recorded spectrum may be affected by inhomogeneous illumination or noise in the photosensor array system. The more mechanically complex grating spectrometer (Clause 5.4.3) avoids such noise problems.

5.4.3 Grating system

The second type of spectrometer uses a reflection grating (Czerny-Turner principle) coupled with a photomultiplier detector. Light entering the spectrometer through a fibre-optic cable is diffracted by the grating so that a 40 nanometres or less section of the absorption spectrum is scanned by the detector. To overcome light variations caused by atmospheric turbulence, which would otherwise destroy the key differential spectral information, a very short scan time of 30 milliseconds or less is employed. This can be achieved by the use of a rotating disc containing radially placed slits located in front of the detector. At each pass of a slit in front of the photomultiplier the spectrum is recorded. The photomultiplier current is converted into digital signals, and the signals stored and accumulated in a multi-channel register. Measurement times—and therefore the number of individual spectra accumulated prior to spectral analysis—is user-selectable, but is typically between 30 seconds and three minutes.

NOTE: The United States Environmental Protection Agency equivalent method designation stipulates that the total cycle time for measurement of all gases using an open-path system should be less than 200 seconds.

If the instrument is measuring several gases with different optimum evaluation spectrum regions, the grating will move to the next wavelength region upon completion of measurements in one region. This means that gases whose absorption peaks are not in the same wavelength region cannot be measured simultaneously.

5.5 Data processing system

The process of deriving pollutant concentrations from the raw absorption spectrum obtained from the spectrometer is as follows. To obtain differential absorption spectra for the atmospheric gases, it is necessary to remove spectral features due to variations in lamp output or other optical components and broadband atmospheric influences such as scattering and absorption. Firstly, the ambient air spectrum is divided by a system reference spectrum (i.e. a lamp spectrum which is pre-recorded under conditions where no absorption for the measurement gases was present) to produce a spectrum consisting of only broadband and narrowband absorption features. This eliminates any effects due to the lamp, the fibre-optic cables, the detector or other optical components in the system.