

Australian/New Zealand Standard™

Methods for sampling and analysis of ambient air

Method 17: Determination of gaseous compounds in ambient air—Direct-reading cavity ring-down spectroscopy instrumental method

AS/NZS 3580.17:2016

PREFACE

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

In preparing this Standard, sections of the Foreword and Clause 4 were reproduced with permission from the United States Environmental Protection Agency Handbook: *Optical Remote Sensing for Measurement and Monitoring of Emissions Flux* and Figure 1 is reproduced with permission from the Royal Society of Chemistry.

The objective of this Standard is to provide regulatory and testing bodies with a standard method for the determination of the concentrations of gaseous compounds in ambient air using instrumentation based on cavity ring-down spectroscopy.

FOREWORD

Most small molecules (e.g. nitrogen dioxide, ammonia, carbon dioxide, water, methane) have unique near-infrared absorption spectra consisting of sharp well resolved lines. Traditional absorption spectroscopy techniques measure the absolute change in light intensity after passing through a sample relative to the original intensity of the light. Cavity ring-down spectroscopy (CRDS) techniques measure the rate of decay of light intensity exiting from a high-finesse optical cavity. Using the rate of decay rather than the change in light intensity makes the CRDS technique less sensitive to fluctuations in light intensity or variations in ambient conditions (such as humidity). The reflectivity of the closed optical (or ring-down) cavity yields much longer effective sample path lengths for greater detection sensitivity. CRDS applications are most often used for measurements of weakly-absorbing or highly dilute atmospheric samples.

METHOD

1 SCOPE

This Standard sets out a method for determining gaseous compounds in ambient air using a direct-reading cavity ring-down spectroscopy instrument. This Standard also has application for instrumentation based on other cavity enhanced absorption spectrometric methods such as off-axis integrated cavity output spectroscopy. The method applies to the determination of gaseous compounds within the concentration ranges typically found in ambient air.

2 REFERENCED DOCUMENTS

The following documents are referred to in this Standard:

AS/NZS

3580 Methods for sampling and analysis of ambient air

3580.1.1 Part 1.1: Guide to siting air monitoring equipment

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

ISO/IEC

Guide 98 Uncertainty of measurement

Guide 98-3:Part 3: Guide to the expression of uncertainty in measurement (GUM:1995) 2008

California Environmental Protection Agency Air Resources Board

Standard Operating Procedures, Picarro G-1301 Methane, Carbon Dioxide, Water Vapor Analyzer

Environment Protection and Heritage Council

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

United States Environmental Protection Agency

EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux

3 DEFINITIONS

For the purpose of this Standard, the definitions below apply.

3.1 Drift

The percentage change in instrument response over a 24 h period of continuous unadjusted operation.

3.2 Full scale (FS)

The nominated maximum concentration for which an instrument has been calibrated.

3.3 Level 1 calibration

A simplified, two-point analyser calibration used when analyser linearity does not need to be checked or verified.

3.4 Level 2 calibration

A simple check of an analyser's response. These checks may be performed using non-certified test atmospheres (e.g. expired test cylinders).

3.5 Linearity

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

3.6 Lower detectable limit

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

3.7 Noise

Spontaneous, short duration deviations in instrument output, about the mean output, 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.

3.8 Parts per billion (p.p.b.)

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.

3.9 Parts per million (p.p.m.)

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.

3.10 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.

3.11 Proficiency audit

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

3.12 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 20.0 p.p.m.

3.13 Rise time

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

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.

4 PRINCIPLE

Cavity ring-down spectroscopy is a form of laser absorption spectroscopy. A general schematic of the essential components of a CRDS instrument is shown in Figure 1. At the heart of this technique is a sample cell (cavity) which is bounded by highly reflective concave mirrors (traditionally two mirrors as shown in Figure 1, but often three or more mirrors are employed to improve measurement quality). Light is injected into the cavity until a threshold level is reached, at which point the light source is switched off. Within the closed optical cavity the light reflects off the mirrors, with a known amount defined by the mirrors' reflectivity, leaking from the cavity on each reflection.

If the optical cavity is empty, this rate of light intensity decay is characterized by a steady, exponential decrease to zero. If a gaseous species that absorbs light corresponding to that of the laser source is present in the cavity, then the light intensity decay rate will increase depending on the concentration of the absorbing species, as shown in Figure 2.

The difference in the decay (ring-down) time with and without laser absorption is proportional to the concentration of the absorbing gas species in the sample.

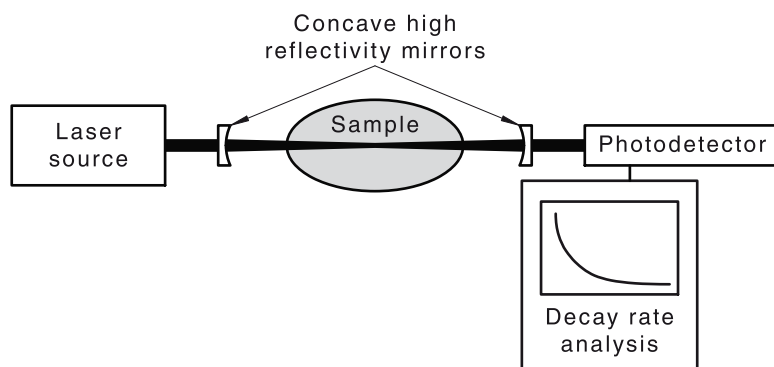


FIGURE 1 SCHEMATIC OF A CRDS INSTRUMENT

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See <http://dx.doi.org/10.1039/B206699H>.)

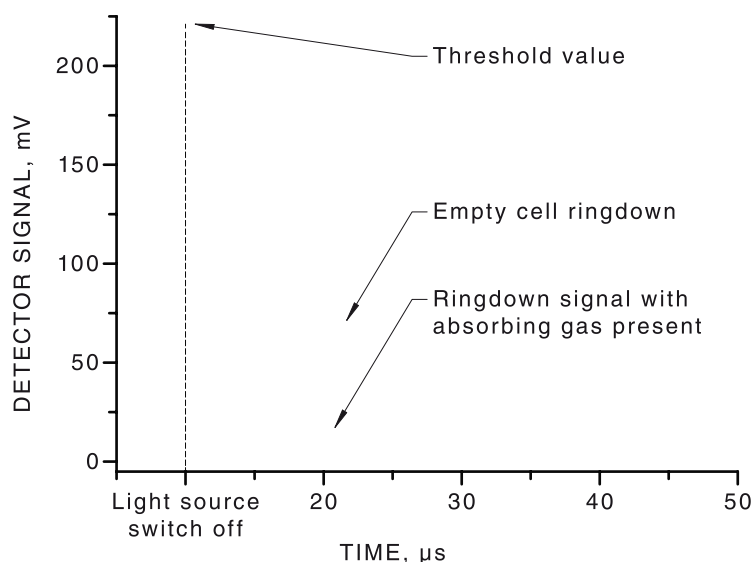


FIGURE 2 SCHEMATIC REPRESENTATION OF LIGHT INTENSITY AS A FUNCTION OF TIME IN A CRDS SYSTEM

By incorporating multiple lasers, or tuning the laser to different wavelengths, that correspond to different spectral absorption lines, it is possible for a single CRDS instrument to measure different gaseous species.

It is possible to simulate the ring-down time for the empty cavity by using light of a wavelength that does not match an absorption feature of any gas in the cavity rather than evacuating the cavity.

5 SAFETY

CRDS instruments emit Class 3B invisible laser radiation when open. Avoid direct exposure to the beam. Do not open any enclosures within the instrument. Failure to do so could result in exposure which can permanently damage eyes and skin.

The inlet bulkhead fitting on some CRDS instruments can be extremely hot when the instrument is operating, or after it has been shut down. In such circumstances, care should be taken when connecting gas lines or working at the rear of the instrument to avoid contact with these surfaces or to wear protective gloves.

6 APPARATUS

6.1 Instrument

Typical CRDS instruments consist of a laser source, a high-precision wavelength monitor, a high-finesse optical cavity containing two or more mirrors, a photodetector, and a data processing computer.

The full scale of the instrument should be selected to cover the normal range of values expected in the sampling environment. The instrument may be used over any range within the limits of the Standard but shall be calibrated in accordance with Clause 8.1.

Table 1 provides typical measurement capabilities for the gases generally available on current commercially available CRDS instruments. 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 CRDS AMBIENT AIR QUALITY MEASUREMENT CAPABILITIES

Parameter	CO ₂	CO	CH ₄	NH ₃
Range	0–1500 ppm	0–1000 ppm	0–20 ppm	0–8 ppm
Measurement interval	<5 s	<5 s	<5 s	<5 s
Lower detectable limit	<200 ppb	<150 ppb	<1 ppb	<1 ppb
Rise/fall (90%)	<5 s	<5 s	<5 s	<1 min
Drift (24 hr)	<150 ppb	<100 ppb	<1 ppb	<0.15 ppb (zero)
Precision	<50 ppb	<2 ppb	<0.7 ppb	<1 ppb
Operating temperature	10–35°C	10–35°C	10–35°C	10–35°C
Operating humidity	<99%, non-condensing	<99%, non-condensing	<99%, non-condensing	<99%, non-condensing

6.2 Zero air

Zero air shall be free from contaminants likely to cause a detectable response on the test analyser. The concentration of O₂ in the zero air shall be within $\pm 2\%$ v/v of the normal composition of air (20.9% v/v).

NOTES:

- 1 Specific attention should be given to the preparation of zero air as the lower detectable limits of CRDS instruments is generally well below that of normally available zero air sources.
- 2 As an alternative to zero air, ultra-high purity nitrogen can be used provided this matrix does not interfere with normal instrument response.

6.3 Reference test atmosphere

Reference test atmospheres of gaseous target compounds shall be produced in accordance with AS/NZS 3580.2.2, using zero air as a diluent gas. Alternately, the target compound atmosphere can be supplied direct to the instrument without dilution where certified calibration gas cylinders containing the appropriate concentrations of the target compound are available.

6.4 Level 1 span and zero calibrations

Level 1 span and zero calibrations shall be performed using reference test atmospheres produced in accordance with AS/NZS 3580.2.2, using zero air as a diluent gas, or from certified cylinders. Adjustments to the analyser span or zero settings shall only be made when performing Level 1 calibrations.

6.5 Level 1 span and zero checks

Level 1 span and zero checks shall be performed using reference test atmospheres produced in accordance with AS/NZS 3580.2.2, using zero air as a diluent gas, or from certified cylinders. These checks are often performed automatically and are used to check the analyser response to a known test atmosphere. Adjustments to the analyser gain or zero settings shall not be made when performing checks.

6.6 Level 2 span and zero checks

Level 2 span and zero checks may be performed using non-certified test atmospheres (e.g. permeation tubes, expired gas cylinders) and are intended as quick, inexpensive and convenient checks to be used in between Level 1 span and zero calibration/checks to identify possible analyser malfunctions or calibration drift. Whenever a Level 2 check indicates a possible calibration problem, a Level 1 span and zero calibration shall be performed.