

Australian/New Zealand Standard™

Methods for sampling and analysis of ambient air

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

PREFACE

This Standard was prepared by the Joint Standards Australia/Standards New Zealand Committee EV-007, Methods for Examination of Air as an Australian/New Zealand Standard to supersede AS/NZS 3580.2.2:2009. The Standard deals with the preparation of reference test atmospheres for ambient air analysers utilizing compressed gas Certified Reference Materials (CRMs). The objective of this revision was to re-write the procedure to reflect current practice.

The term ‘normative’ has been used in this Standard to define the application of the appendix to which it applies. A ‘normative’ appendix is an integral part of a Standard.

FOREWORD

The calibration and verification of ambient air analyser response is principally carried out utilizing a compressed gas CRM and associated dilution apparatus. This has resulted in a need to standardize the procedures followed.

METHOD

1 SCOPE

This Standard sets out a method for the preparation of reference test atmospheres containing known concentrations of determinand(s), using a calibration gas dilution method.

The method is applicable to components that do not react with each other, the cylinder walls or the dilution gas, and that remain totally vaporized in the cylinder at all pressures and temperatures anticipated during the preparation and use of the reference test atmosphere.

2 REFERENCED DOCUMENTS

The following documents are referred to in this Standard:

AS

2030 Gas cylinders

2030.1 Part 1: General requirements

2473 Valves for compressed gas cylinders

2473.1 Part 1: Specifications, type testing, and manufacturing tests and inspections

ISO/IEC

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

3 DEFINITIONS

For the purpose of this Standard the following definitions apply:

3.1 Certified Reference Material (CRM)

Reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a reference material certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability. The reference material certificate to be provided by a laboratory accredited by signatories to the International Laboratory Accreditation Cooperation (ILAC) through their Mutual Recognition Arrangement (MRA) and/or produced by National Metrology Institutes (NMIs) and included in the Bureau International des Poids et Mesures (BIPM) key comparison database (KCDB).

NOTE: In Australia, ILAC (MRA) accredited bodies include National Association of Testing Authorities (NATA) and in New Zealand they include International Accreditation New Zealand (IANZ).

3.2 Full scale

The nominated maximum concentration for which an instrument has been calibrated. Selected to cover the normal range of values expected in the sampling environment.

3.3 Linearity

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

3.4 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.

3.5 Reference material

Material sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.

3.6 Test atmosphere

A reference test atmosphere containing a known concentration of pollutant.

3.7 U_{95}

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

3.8 Zero air

Air free from contaminants likely to cause a detectable response on the test analyser.

4 PRINCIPLE

The reference test atmosphere is produced by the dilution of a compressed gas CRM utilizing zero air.

5 APPARATUS

5.1 Certified reference material cylinder

A gravimetric or volumetric standard compressed gas CRM that serves as a source of determinand of known concentration.

5.2 Zero air

A supply of regulated zero air from either a cylinder or other suitable supply source. The concentration of oxygen in the zero air shall be within $\pm 2\%$ v/v of the normal composition of air (20.9% v/v).

5.3 Dilution apparatus

A device capable of blending zero air with CRM at known concentrations.

5.4 Gas transfer lines

Tubing or manifold used to transport zero air, CRM and the blended product.

5.5 Reference flow meter

A reference (working standard) flow meter(s), traceable to national standards, is required for the calibration of the dilution apparatus flow controller(s). The reference flow meter uncertainty shall be greater of $\pm 2\%$ U_{95} at any flow controller test point or $\pm 1\%$ U_{95} of flow controller full scale.

5.6 Reference thermometer

A traceable thermometer of $\pm 0.5^\circ\text{C}$ U_{95} and a resolution of 0.1°C . The thermometer shall be checked against a reference standard thermometer at 0°C (ice point), or at one point in the working range, on a six-monthly basis.

5.7 Reference barometer

A traceable barometer of ± 0.5 kPa U_{95} . The barometer shall be checked on a six-monthly basis, at one point against barometric pressure measured at an appropriately located meteorological station.

Alternatively, barometric pressure may be determined from measurements taken at an appropriately located meteorological station, with the pressure corrected for differences in elevation between the sampling site and the meteorological station.

6 USE OF APPARATUS

6.1 General

Gas cylinders shall comply with the requirements of AS 2030.1. Gas regulators shall comply with the requirements of AS 2473.1.

6.2 Certified Reference Material (CRM)

6.2.1 General

The CRM shall not contain any foreign component(s) that would invalidate the reference test atmosphere, e.g. oil in a mixture of methane in air to be used for the calibration of a total hydrocarbon analyser, oxygen contamination in a mixture of nitric oxide in nitrogen.

6.2.2 Low temperature

The gas cylinder could potentially be exposed to low temperatures during storage and transportation. For gas mixtures containing condensable components, (e.g. high molecular weight hydrocarbons), it is important that the cylinder is not stored or transported at temperatures below those recommended by the CRM provider. If the mixture is exposed to temperatures below the stated range, some components may condense and this will change the composition of the mixture. If the mixture has been exposed to temperatures lower than those recommended by the CRM provider, the certificate from the CRM provider may be no longer valid. Homogenizing and checking the mixture before usage may be required.

6.2.3 Elevated temperature

Elevated temperatures may result in decomposition of thermally unstable species. Avoid direct exposure to sunlight as this may also heat the cylinder. Avoid high temperatures (heating) close to the cylinder, e.g. from welding flames, blowlamps, ovens or other intense heat sources. High temperatures will result in higher pressures leading to potentially hazardous situations. Cylinders shall not be heated above 45°C.

6.2.4 Water

Gas cylinders shall be protected from excessive humidity during transport. Transportation by boat may result in the cylinder being sprayed with water; this and/or excessive humidity may cause corrosion of the cylinder valve. The cylinder shall be protected from precipitation to prevent corrosion. If the cylinders are stored outdoors, they should be protected by a roof and the cylinder base should also be protected from water accumulating on the floor by raising it above the ground.

6.2.5 Storage and handling

Cylinders shall be stored in a secure manner to prevent rolling and/or falling. For safety reasons, cylinders containing flammable gases shall be separated from cylinders containing oxidizing components. Mixtures containing condensable components may require rehomogenization if stored for extended periods of time and if exposure to temperatures below the condensation point cannot be excluded. This may be done by equilibrating the cylinders to ambient temperature and rotating them in a horizontal position for an appropriate period of time, which will depend on the matrix gas and the components. Homogenizing and checking the mixture before usage may be required.

6.2.6 Minimum pressure

The information attached to the cylinder indicates the pressure below which the gas shall not be used. It has been reported that in some cases gas molecules adsorbed to the cylinder wall desorb when the cylinder pressure drops below a certain pressure, resulting in a higher mole fraction. With the following exception, cylinders shall not be used when the gas pressure falls below 700 kPa, or in accordance with the manufacturer's specifications. This does not apply in the case of certain hydrocarbon mixtures that contain condensable components. In these cases the minimum pressure shall not be less than 10% of the initial cylinder pressure as manufactured, or in accordance with the manufacturer's specifications.

6.2.7 *Storage life*

Compressed gas mixtures have a limited storage life. The usable life of the mixture has been reached when the expiry date on the certificate has lapsed or the cylinder pressure has fallen below the minimum pressure (Clause 6.2.6), unless the cylinder composition has been revalidated. The revalidation procedure shall be in accordance with Appendix A.

6.2.8 *Pressure reduction and flow*

Normally, the withdrawal of gas from a cylinder is regulated by a pressure reducer and/or flow controller (needle valve, mass flow controller, capillary, etc.). Due to the reversible adiabatic expansion of the gas when withdrawing the gas from the cylinder, cooling of the gas in the cylinder will occur. Furthermore, Joule-Thomson cooling and/or heating will change the temperature of the transported gas. Again, especially with mixtures containing condensable components, condensation might occur due to these temperature effects. Temperature equilibration of the gas could help to minimize this. The pressure drop across flow controllers shall be minimized. Flow characteristics of flow controllers are normally specified by the manufacturer and give sufficient information to judge whether the required flow can be controlled by the chosen flow controllers. In calculating the pressure drop, tube sizing (inside diameter and length) shall also be considered.

Variations in compressed gas CRM flow may affect the composition of the reference gas. The pressure reduction and flow control system selected shall be capable of providing a constant pressure supply at the required flow rate.

6.3 **Regulators, transfer lines and dilution apparatus materials**

Materials used for surfaces with which the gases may come into contact (e.g. regulators, valves, tubing, mass flow controllers, mixing chamber, manifold) shall not promote changes in chemical composition of the gases. All devices shall be leak tight.

Gas regulators shall be thoroughly purged before use to minimize potential contaminants and adverse reactions with the CRM. For example, oxygen in ambient air will react with nitric oxide to form nitrogen dioxide.

Where polymers come into contact with the CRM, their permeability to certain gases and water vapour should be considered. For example, PTFE is very inert and suitable for a large range of gases; however, the permeability of this material makes it unsuitable for use with water-soluble gases, as water vapour can easily permeate into the transfer line. It is also strongly recommended not to use rubber-based materials or polymers of unknown composition.

For some gases, particularly reactive gases such as sulfur dioxide and ozone, it is recommended transfer lines be conditioned by flushing a high concentration gas mixture through the system to ensure passivation of all internal surfaces.

Examples of material compatibility with various gases are provided in Table 1.

TABLE 1
MATERIAL COMPATIBILITY

Gas	Material																	
	Stainless steel			Copper			PTFE			PEEK			Glass/quartz			Silica-lined stainless steel		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
Inert gas	+	+	+	+	+	+	+	o*	–	+	+	o	+	+	+	+	+	+
O ₂	+	+	+	+	+	+	+	o	–	+	+	o	+	+	+	+	+	+
CO ₂	+	+	+	+	+	+	+	+	o	o	o	–	+	+	+	+	+	+
CO	o	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+
Alkanes	+	+	+	+	+	+	+	+	o	+	+	o	+	+	+	+	+	+
Alkenes	+	+	+	+	+	+	+	o	–	+	+	+	+	+	+	+	+	+
Aromatics	+	+	+	–	–	–	+	o	–	+	+	+	+	+	+	+	+	+
NO	+	+	+	+	+	+	o	o	o	+	+	+	+	+	+	+	+	+
NO ₂	+	+	+	–	–	–	o	o	o	***	+	+	+	+	+	+	+	+
Cl ₂	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
HCl	o**	o**	o**	o	o	o	+	+	–	***	***	***	+	+	+	+	+	+
NH ₃	+	+	+	–	–	–	–	–	–	+	+	+	+	+	+	+	+	+
H ₂ S	+	+	–	–	–	–	o	o	o	o	o	o	+	+	+	+	+	+
SO ₂	+	+	+	o	o	o	+	+	o	o	o	o	+	+	+	+	+	+

LEGEND:

- a = Mole fraction >1% (10 000 ppm)
 b = Mole fraction ≥0.001% ≤1% (≥10 ppm ≤10 000 ppm)
 c = Mole fraction <0.001% (<10 ppm)
 + = suitable
 o = of limited suitability
 – = not suitable
 * = not suitable for helium
 ** = suitable only after passivation
 *** = no experience available, usage not recommended for safety reasons

6.4 Zero air

Zero air used for zero response checks or for dilution of the compressed gas CRM shall be clean, dry air containing no detectable concentration of the pollutant of interest. The zero air shall also contain no contaminant that causes a detectable response on the analyser or that suppresses or enhances the analyser's response at the flow rate used during operation.

Variations in the zero air flow may affect the composition of the reference gas. The zero air supply system selected shall be capable of providing a constant pressure supply at the required flow rate.

If ambient air is used as zero air, it shall be treated to remove the pollutants of interest. Some of the commonly used treatment methods are given in Table 2.