

Australian/New Zealand Standard™

Methods for sampling and analysis of ambient air**Method 11.1: Determination of methane and non-methane organic compounds in ambient air—Direct-reading instrumental method**

AS/NZS 3580.11.1:2013

PREFACE

This Standard was prepared by the Joint Standards Australia/Standards New Zealand Committee EV-007, Methods for Examination of Air, to supersede AS 3580.11.1—1993, Method 11.1: *Determination of volatile organic compounds—Methane and non-methane volatile organic compounds—Direct-reading instrumental method*.

This Standard incorporates Amendment No. 1 (March 2016). The changes required by the Amendment are indicated in the text by a marginal bar and amendment number against the clause, note, table, figure or part thereof affected.

This Standard has been developed as a performance-based standard, which may include direct-reading instrumental methods other than FID detection.

FOREWORD

Hydrocarbons are minor constituents of ambient air, with methane the dominant species, typically being present at a level of approximately 1.8 p.p.m.C. The major natural sources of organic compounds are the production of methane by bacteria under anaerobic conditions, e.g. swamps, ruminant animals and the emission of terpenes by leaves. The major anthropogenic sources are motor vehicles (often contributing 40% to 50% or more of the non-methane organic compounds), solvent evaporation (such as from surface coatings, printing and adhesives), and petroleum refining and distribution.

Non-methane volatile organic compounds in the atmosphere are active in the production of photochemical smog, which is characterized by the presence of elevated concentrations of ozone. In the presence of sunlight, organic compounds, nitrogen and oxygen undergo complex chemical reactions, which ultimately lead to the formation of ozone and other oxidized species. Ozone is an irritant to the respiratory system and elevated concentrations of the gas have a deleterious effect on the lung function.

METHOD

1 SCOPE

This Standard sets out a method for determining methane and non-methane organic compounds in ambient air using a direct-reading instrument. The method applies to the determination of hydrocarbons in ambient air within the concentration range 0 to 20 p.p.m.C. by volume.

The methane and non-methane organic compound content of the air is most commonly measured using an automatic or intermittent sampling direct-reading instrument containing a flame ionization detector (FID) and the results obtained are reported as a methane equivalent response. The analysis is sensitive to all hydrocarbons, but will also respond to almost all organic compounds and will yield responses more or less depending on the number of carbon to hydrogen bonds in the compound. Empirical data generally show that the relative sensitivity to various hydrocarbons is approximately equal on a carbon mass basis. Unsaturated, oxygenated and halogenated compounds give a lower response.

2 REFERENCED DOCUMENTS

The following documents are referred to in this Standard:

AS

3580 Methods for sampling and analysis of ambient air

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

AS/NZS

3580 Methods for sampling and analysis of ambient air

3580.1.1 Part 1.1: Guide to siting air monitoring equipment

ISO/IEC

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

ISO/TR

15916 Basic considerations for the safety of hydrogen systems

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.

Global Environment Centre Foundation. September 1998

Technology of Air Pollution Continuous Monitoring in Japan

3 DEFINITIONS

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

3.1 Full scale (FS)

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

3.2 Level 1 calibration

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

3.3 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).

3.4 Linearity

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

3.5 Lower detectable limit

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

3.6 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.

3.7 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.

3.8 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.

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

A ratio expressing the volume of equivalent gaseous carbon pollutant contained in 1 000 000 volumes of atmosphere. Alternatively, it is one million times the ratio of the partial pressure of gaseous carbon pollutant to the pressure of the atmosphere in which it is contained. For a specific compound, p.p.m.C. is equivalent to parts per million by volume (p.p.m) multiplied by the number of carbon atoms in the compound.

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 Span drift

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

3.15 Test atmosphere

A reference test atmosphere containing a known concentration of pollutant.

3.16 U_{95}

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

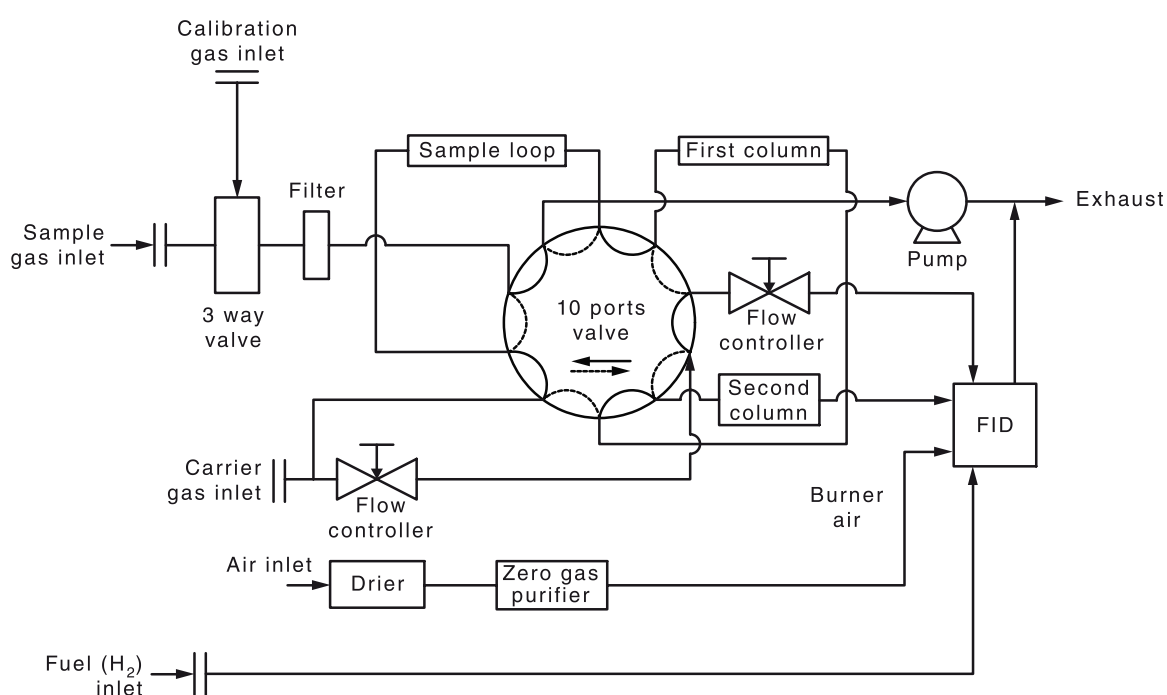
3.17 Zero drift

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

4 PRINCIPLE

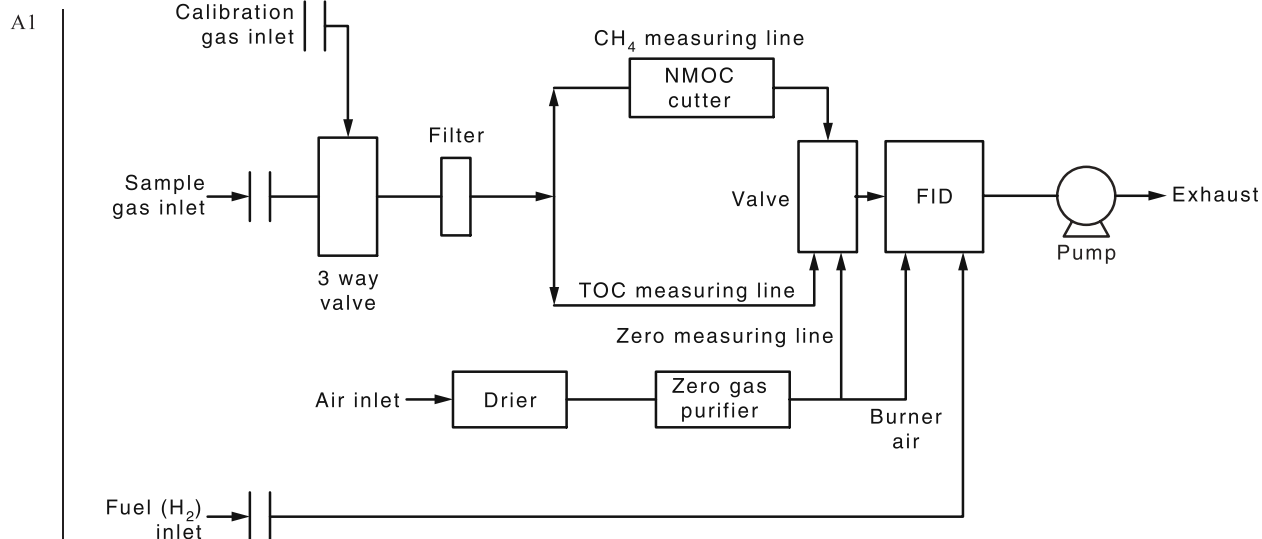
Flame ionization detection is the principal method for the determination of hydrocarbons in ambient air. The two analytical methods used to separate methane from other hydrocarbons are gas capillary columns with chromatography (GC) and selective non-methane combustion. Using gas capillary columns, the air sample is injected into a carrier gas and passed through an analytical column where methane is separated from other non-methane organic compounds (NMOC). The methane is passed to the FID and the remaining non-methane organic compounds are back-flushed for detection; see Figure 1.

Using selective combustion methods, the air sample is divided into two streams. In one stream, the sample is passed through a catalytic non-methane oxidizer to remove all non-methane compounds and then on to an FID to measure methane content. The sample in the second stream is passed directly to an FID for determination of total organic compounds (TOC); see Figure 2. The difference between the two readings gives the non-methane organic compound concentration.



(ADAPTED FROM: 'Technology of Air Pollution Continuous Monitoring in Japan',
Global Environment Centre Foundation, September 1998)

FIGURE 1 SCHEMATIC OF GAS CHROMATOGRAPH METHOD
(MEASUREMENT MODE)



(ADAPTED FROM: 'Technology of Air Pollution Continuous Monitoring in Japan',
Global Environment Centre Foundation, September 1998)

FIGURE 2 SCHEMATIC OF SELECTIVE COMBUSTION METHOD

5 APPARATUS

5.1 Instrument

A continuous direct-reading instrument is required, which shall meet or exceed those specifications given in Table 1. The FS 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 7.1. The manufacturer's published performance specifications shall be deemed as acceptable evidence of conformance to the given requirements. Direct-reading instruments and methods are constantly evolving and, for this reason, this Standard does not restrict measurement to FID methods alone. Providing the instrument's performance is within the specifications given in Table 1, alternate methods may be used within the context of this Standard. It should be noted, however, that methods employing photo ionization detection alone cannot comply with this Standard. Light hydrocarbons such as methane are unable to be ionized by photolytic methods and as such will not be detected. Likewise, methods employing optical analysis techniques, such as ultraviolet or infra-red spectrometry, are not suitable as the contribution of every possible organic hydrocarbon in the sample cannot be assured.

TABLE 1
INSTRUMENT PERFORMANCE
SPECIFICATIONS

Parameter	Requirements
Range	0–20.0 p.p.m.C.
Noise	≤0.025 p.p.m.C.
Lower detectable limit	≤0.06 p.p.m.C.
Response times	≤90 s
Rise (90%)	
Zero drift	1% FS
24 h	
Span drift	2% FS
24 h	
Precision	1% FS
Linearity	2% FS
Operating temperature	20–30°C
Humidity	10–80%

5.2 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 ±2% v/v of the normal composition of air (20.9% v/v).

Sufficiently purified air can be obtained by passing dry ambient air through a heated hydrocarbon oxidizer at greater than 520°C. As any hydrocarbons present in the zero air will produce an elevated zero response, the removal of methane and other organic compounds from ambient air requires considerable attention. A periodic zero check, using a cylinder of hydrocarbon-free air (<0.1 p.p.m.) as a cross check, is recommended to verify the quality of the zero air.

5.3 Hydrogen

FIDs require a flame to ionize the sample. This flame is generated from the combustion of hydrogen and zero air. Hydrogen is a flammable, colourless and odourless gas. It poses an immediate fire and explosive hazard when concentrations exceed 4%. It is much lighter than air and burns with an invisible flame. High concentrations that will cause suffocation are within the flammable range and must not be inhaled. Refer to technical report ISO/TR 15916.

Hydrogen with a minimum purity of 99.999% and a hydrocarbon content of less than 1 p.p.m. shall be used. Hydrogen in cylinders or hydrogen produced by a hydrogen generator, free from moisture, particles and other impurities that will measurably affect the determination, is suitable. For reasons of safety, the use of hydrogen generators is preferred to gas cylinders.

5.4 Carrier gas

Carrier gas with a minimum purity of 99.999% and a hydrocarbon content of less than 0.5 p.p.m. shall be used. The carrier gas shall be free from moisture, particles and other impurities which will measurably affect the determination.

NOTE: Silica gel driers may be used as desiccants in gas lines; however, a filter should be installed downstream to protect gas regulators from particles.

5.5 Reference test atmosphere

Reference test atmospheres of methane and non-methane organic compounds shall be produced in accordance with AS 3580.2.2, using zero air as a diluent gas.

NOTE: Propane is commonly used to generate the non-methane organic reference atmosphere. Other single component gases such as isobutylene can also be used, provided their FID response factor is well defined and taken into account when calculating the p.p.m.C value of the reference concentration.

5.6 Level 1 span and zero calibrations

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

5.7 Level 1 span and zero checks

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

5.8 Level 2 span and zero checks

Level 2 span and zero checks may be performed using non-certified test atmospheres (e.g. 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.

When Level 2 checks are implemented, a 'reference' response for the check shall be obtained immediately following a Level 1 span and zero calibration while the analyser's response is accurately known. Subsequent Level 2 checks can then be compared to this 'reference' response to determine whether a change has occurred.

If Level 2 checks are implemented, then the frequency of such checks shall be daily. When daily Level 2 checks are performed, the frequency of Level 1 checks can be extended to a maximum of 31 days. Table 2 summarizes frequencies for checks.

TABLE 2
INSTRUMENT RESPONSE
CHECK FREQUENCY

Level 1 check interval	Level 2 check frequency
1–7 days	Not required
8–31 days	Daily