

Australian Standard®

Methods for sampling and analysis of ambient air

Method 11.1: Determination of volatile organic compounds—Methane and non-methane volatile organic compounds—Direct-reading instrumental method

PREFACE

This Standard was prepared by the Standards Australia Committee on Methods for Examination of Air as a further part of the AS 3580 series of methods for the sampling and analysis of ambient air.

During the preparation of this Standard, the Committee paid special attention to the work of ASTM Committee D-22 on Sampling and analysis of atmospheres in D 3416, *Total hydrocarbons, methane, and carbon monoxide in the atmosphere (Gas chromatographic method)* and to *Code of Federal Regulations, Protection of Environment*, Title 40, Part 50, Appendix E.

FOREWORD

Hydrocarbons are minor constituents of pristine air, with methane the dominant species, typically being at a level of around 1.5 p.p.m. The major natural sources of volatile organic compounds are the production of methane by bacteria under anaerobic conditions, e.g. in swamps, in ruminant animals, and the emissions of terpenes by leaves. In urban air some hundreds of types of volatile organic compound species are usually present with about fifty major species having significant concentrations.

In urban areas, the total level of volatile organic compounds is typically 2 p.p.m. to 3 p.p.m., with about half being methane. The major anthropogenic sources are motor vehicles (often contributing 40% to 50% or more of the non-methane hydrocarbons), 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, volatile 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 affect on the lung function. Public health and pollution control authorities (NH&MRC and USEPA) recommend that ozone concentrations should not exceed 0.12 p.p.m. (1 h average). The composition and concentration of hydrocarbons emitted into the air are major determinants of the rate of the photochemical smog-forming process. The various hydrocarbon species have a wide range of smog-forming activities, some acting to produce smog at a much faster rate than others. Methane however is notably less reactive than the rest and does not play a major role in smog formation.

METHOD

1 SCOPE This Standard sets out a method for determining methane and non-methane volatile organic compounds in ambient air. The volatile organic compound (VOC) content of the air is 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 it 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 about equal on a carbon mass basis. Unsaturated, oxygenated and halogenated compounds give a lower response.

2 APPLICATION The method will detect those components in ambient air which yield an FID response. The FID response factors of the individual atmospheric volatile organic compounds vary widely, in particular oxygenated and chlorinated species yield significantly lower response factors than those hydrocarbons containing the same number of carbon atoms. The FID response factors for the volatile organic compounds are also dependent on the particulars of the instrument design and operating conditions. The volatile organic compounds content of the air measured by this method is expressed in the unit of p.p.m. C equivalents which denotes the equivalent concentration of methane in parts per million (by volume) in air which would produce the same FID response as that observed for the sample. The method is applicable to ambient air with a volatile organic compound content in the range 0 to 10 p.p.m. C equivalents.

3 REFERENCED DOCUMENTS The following documents are referred to in this Standard:

AS

- 2850 Chemical analysis—Interlaboratory test programs—For determining precision of analytical method(s)—Guide to the planning and conduct
- 2922 Ambient air—Guide for the siting of sampling units
- 3580 Methods for sampling and analysis of ambient air
- 3580.2.2 Method 2.2: Preparation of reference test atmospheres—Compressed gas method
- 3580.4.1 Method 4.1: Determination of sulfur dioxide—Direct reading instrumental method

4 DEFINITIONS For the purpose of this Standard, the definitions given in AS 3580.4.1 apply.

5 PRINCIPLE Ambient air is sampled on either a continuous or semicontinuous basis. For methane and non-methane volatile organic compound determination, the air sample is injected into a carrier gas and passed through an analytical column where methane is separated from other non-methane volatile organic compounds. The methane is passed to the detector and the remaining non-methane volatile organic compounds are back-flushed for detection (see Figure 1(a)).

For methane and total volatile organic compounds, the air sample is divided into two streams. In one stream the sample is passed through a catalytic non-methane cutter to remove all non-methane compounds and then on to an FID to measure methane content. The air sample in the second stream is passed directly to an FID for determination of total volatile organic compounds. Sequential detection uses a single detector whereas continuous detection uses a two-detector system (see Figures 1(b) to (d)).

6 REAGENTS

6.1 Hydrogen Either high purity grade hydrogen in cylinders or hydrogen produced by a hydrogen generator, free from moisture, particles and other impurities which will measurably affect the determination. Because hydrogen is a very flammable gas it is essential that precautions be taken to avoid fire or explosion. For reasons of safety, the use of hydrogen generators is preferred to gas cylinders.

6.2 Carrier gas Purified air containing less than 0.5 p.p.m. volatile organic compounds. The carrier gas shall be free of moisture and particles.

NOTE: Silica gel driers may be used as desiccants in gas lines however a 10 μm filter should be installed downstream to protect gas regulators and to reduce the loading on the 1 μm filter.

7 APPARATUS

7.1 Filter assembly An in-line filter of approximately 1 μm pore size shall be used to protect the instrument pressure regulator diaphragms (see Figures 1(a) to (d)).

7.2 Analyser One of the following analyser arrangements shall be used:

- (a) For methane and non-methane volatile organic compounds—an instrument designed to automatically sample air at a minimum frequency of 10 times per hour. The instrument shall be fitted with a gas sampling valve, a chromatographic column to separate methane from other volatile organic compounds, a single FID and a recorder. An automatic back-flushing device shall be provided to flush non-methane components from the column to the detector (see Figure 1(a)). The sample valve and back-flushing valve may be combined.
- (b) For methane and total volatile organic compounds—
 - (i) an instrument designed to continuously sample air, fitted with a single FID and a recorder. Sample air is split into two separate streams. One stream shall pass to a non-methane cutter and then to the FID (via a switching arrangement which alternates each of the two streams to the FID). The second stream shall pass directly to the FID via the switching arrangement to determine total volatile organic compounds (see Figure 1(b));
 - (ii) an instrument designed to continuously sample air, fitted with dual FIDs and a recorder. After compression by an internal pump the air sample shall be pressure regulated and split into two separate streams. One stream shall pass to a non-methane cutter and then to the first detector to determine methane. The second stream shall pass the sample directly to the second detector to determine total volatile organic compounds (see Figure 1(c)); or
 - (iii) an instrument designed to automatically sample air at a minimum frequency of 10 times per hour fitted with a gas sampling valve, a single FID and a recorder. The air sample shall be split into two separate streams. One stream is passed directly to the detector for determination of total volatile organic compounds. The other stream is passed sequentially through a non-methane cutter, i.e. a molecular sieve 5A column, to the same detector for determination of methane (see Figure 1(d)).

NOTE: A data logger has been found to be a suitable recorder.

WARNING: THESE ANALYSERS ARE NOT DESIGNED FOR OPERATION IN AN EXPLOSIVE ATMOSPHERE.