

Australian/New Zealand Standard™

Methods for sampling and analysis of ambient air

Method 16: Determination of polycyclic aromatic hydrocarbons (PAH)

AS/NZS 3580.16:2014

PREFACE

This Standard was prepared by the joint Standards Australia/Standards New Zealand Committee EV-007, Methods for Examination of Air. This Standard deals with the method for the determination of polycyclic aromatic hydrocarbons (PAH) utilizing a modified high volume sampler and quartz filter, together with a sorbent bed containing polyurethane foam (PUF), styrene/divinylbenzene polymer resin (XAD-2) or a combination thereof.

The objective of this Standard is to provide regulatory and testing bodies with a standard method for the determination of PAH in ambient air.

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

For the purposes of this standard, PAH consist of two or more fused aromatic rings, with vapour pressures ranging from 10^{-2} kPa to 10^{-13} kPa at 25°C. PAH with vapour pressures greater than 10^{-8} kPa may be distributed between the gas and particle phases. During summer, volatilization from the filter is reported to be as high as 90% for PAH with vapour pressures greater than 10^{-6} kPa. At temperatures of 30°C and above, as much as 20% of benzo(a)pyrene and perylene have been found in the sorbent bed. Consequently, separate analyses of the filter and PUF/XAD-2 resin will not reflect the phase distribution in the atmosphere.

PAH in the environment principally result from the incomplete combustion of organic material, mainly fuel and waste, or emissions to air from industrial processes. Important anthropogenic sources include domestic solid fuel burning, motor vehicles, coal fired power stations, petroleum refineries, coal-tar production plants, coking plants, bitumen and asphalt production plants, paper mills, wood product manufacturers and aluminium smelters.

PAH concentrations in urban environments typically range from low ng/m^3 to several hundred ng/m^3 , depending on the compound.

A number of PAH have been classified by the International Agency for Research on Cancer as human carcinogens, probable human carcinogens or possible human carcinogens.

Historically, Australian and New Zealand studies have utilized a range of techniques to measure PAH in ambient air making it difficult to compare results.

This Standard describes the test procedures to be followed when measuring PAH in ambient air, together with appropriate quality control measures.

METHOD

1 SCOPE

This Standard specifies a high volume sampling method for the determination of both gas phase and particle phase polycyclic aromatic hydrocarbons (PAH) in ambient air. The method provides a measure of the mean concentration of PAH over the sampling period employed.

Due to their relatively high vapour pressures, naphthalene and acenaphthene may not be efficiently collected by this method. The sampling efficiencies for the PAH of interest may be estimated by determining the dynamic retention efficiency of the sorbent bed. Mean concentrations of 0.05 ng/m³ and greater may be determined using a 24 h sampling period.

NOTE: Sampling is normally of 24 h duration to average diurnal variations in PAH concentrations and enable the collection of sufficient PAH mass for subsequent laboratory analysis.

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 Method 1.1: Guide to siting air monitoring equipment
- 3580.9.3 Method 9.3: Determination of suspended particulate matter—Total suspended particulate matter (TSP)—High volume sampler gravimetric method

ISO

- 12884 Ambient air—Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons—Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses

ISO/IEC

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

3 DEFINITIONS

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

3.1 Equivalent aerodynamic diameter (EAD)

The diameter of a spherical particle of unit density 1 g/cm³ that exhibits the same aerodynamic behaviour as the particle in question.

3.2 Dynamic retention efficiency

The ability of the sorbent to retain a given PAH when air is drawn through the sampler under normal conditions for a period equal to or greater than that required for the intended use.

3.3 Measurement uncertainty

A variable associated with the result of a measurement that characterizes the dispersion of the values that could be reasonably attributed to the measurand.

NOTE: The variable may, for example, be a standard deviation (or given multiple of it), or the half width of an interval having a stated level of confidence. ISO/IEC Guide 98-3 provides a basis for evaluating the uncertainty in the output of a measurement system.

3.4 Total suspended particulate matter (TSP)

Atmospheric suspended particulate matter having an approximate EAD of less than 50 µm.

3.5 U₉₅

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

4 PRINCIPLE

Ambient air is drawn at a constant flow rate through a filter and sorbent bed containing polyurethane foam (PUF), styrene/divinylbenzene polymer resin (XAD-2), or a combination thereof, via a TSP inlet. The TSP inlet effectively acts as a hood to prevent precipitation and debris from falling onto the filter.

NOTE: Although sampling is not conducted at the flow rate specified for TSP in AS 3580.9.3, ISO 12884 reports the collection of all airborne particulate matter up to at least 40 µm. Particle phase PAH are concentrated on fine particles in ambient air, consequently the sampler inlet design is not considered critical.

The filter and sorbent (or sorbent cartridge) are subsequently extracted, concentrated and analysed by gas chromatography/mass spectrometry (GC/MS) to determine the PAH mass.

NOTE: Alternative analytical techniques may be used, provided the PAH identification, limits of detection and quality assurance measures achieved (see Clause 12) can be demonstrated to be equal to, or exceeding, the requirements of this Standard.

The PAH concentration is determined by dividing the PAH mass by the sample volume, which is calculated from the sample duration and either the average or totalized flow rate. The results represent the combined gas phase and particle phase concentrations of each PAH analysed.

Sampling times may be varied depending on monitoring needs and the detection limits required. However, the total volume of air sampled shall not exceed 350 m³, unless deuterated PAH or other suitable materials are added to the PUF or XAD-2 sorbent before sampling to validate the dynamic retention efficiency.

5 APPARATUS

5.1 High volume sampler

The high volume sampler shall consist of a TSP inlet, filter holder, sorbent cartridge, motorized fan, shelter, air flow measuring device and an elapsed time meter that measures the actual sample duration to within ±1% U₉₅. Samplers shall have a programmable time clock capable of controlling operation of the sampler to within 2% of the selected time period.

NOTE: A seven-day time clock is useful for operating the sampler on pre-set days in unattended locations. A six-day time clock may be used when the sampler is required to operate on a six-day cycle (sampling 24 h every sixth day). Battery backup for the programmable time clock is preferable to avoid incorrect sample times or the installation of an hour run meter to verify the sample duration.

Automatic flow controlled samplers shall be designed to maintain fixed flow despite a build-up of particles on the filter by either—

- (a) adjustable flow control and a method for automatic flow adjustment to maintain a constant flow rate; or
- (b) be constructed in such a way that only a constant and known air flow rate can pass through the filter and sorbent cartridge, irrespective of variations in power supply voltage, power supply frequency or filter resistance normally experienced on a routine basis.