

Australian/New Zealand Standard™

AS/NZS 3580.16:2014

Methods for sampling and analysis of ambient air

Method 16: Determination of polycyclic aromatic hydrocarbons (PAH)

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/m³ to several hundred ng/m³, 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 U_{95}

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 m^3 , 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 $\pm 1\%$ U_{95} . 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.

NOTE: If the ambient air temperature or barometric pressure changes, a mass flow controlled high volume sampler changes the volumetric flow to achieve a constant mass flow rate, whereas the volumetric flow controlled sampler maintains a constant volumetric flow rate, independent of temperature changes.

A typical sampler is illustrated in Figure 1 and a typical filter holder and sorbent cartridge in Figure 2.

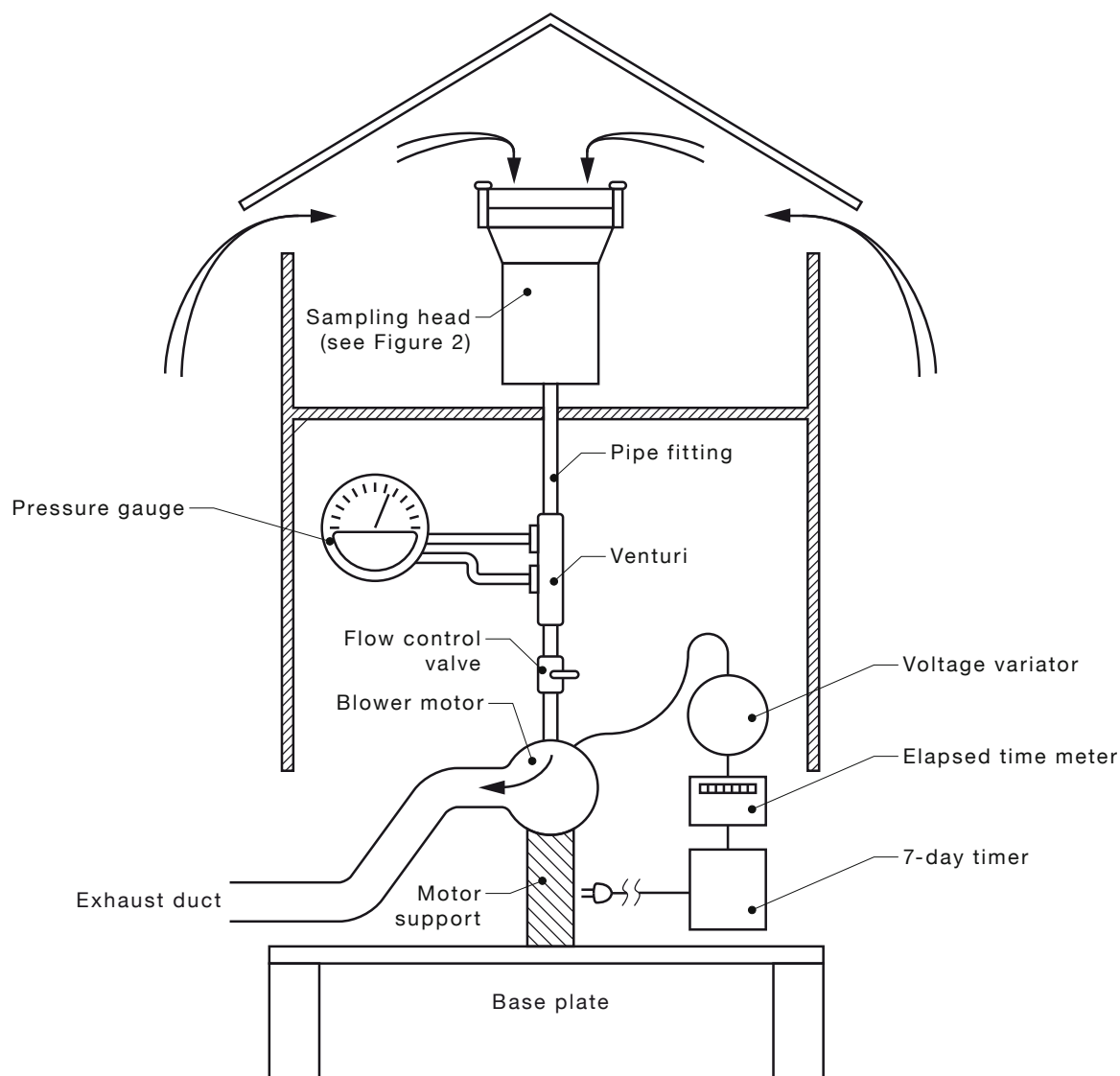


FIGURE 1 TYPICAL PAH HIGH VOLUME SAMPLER

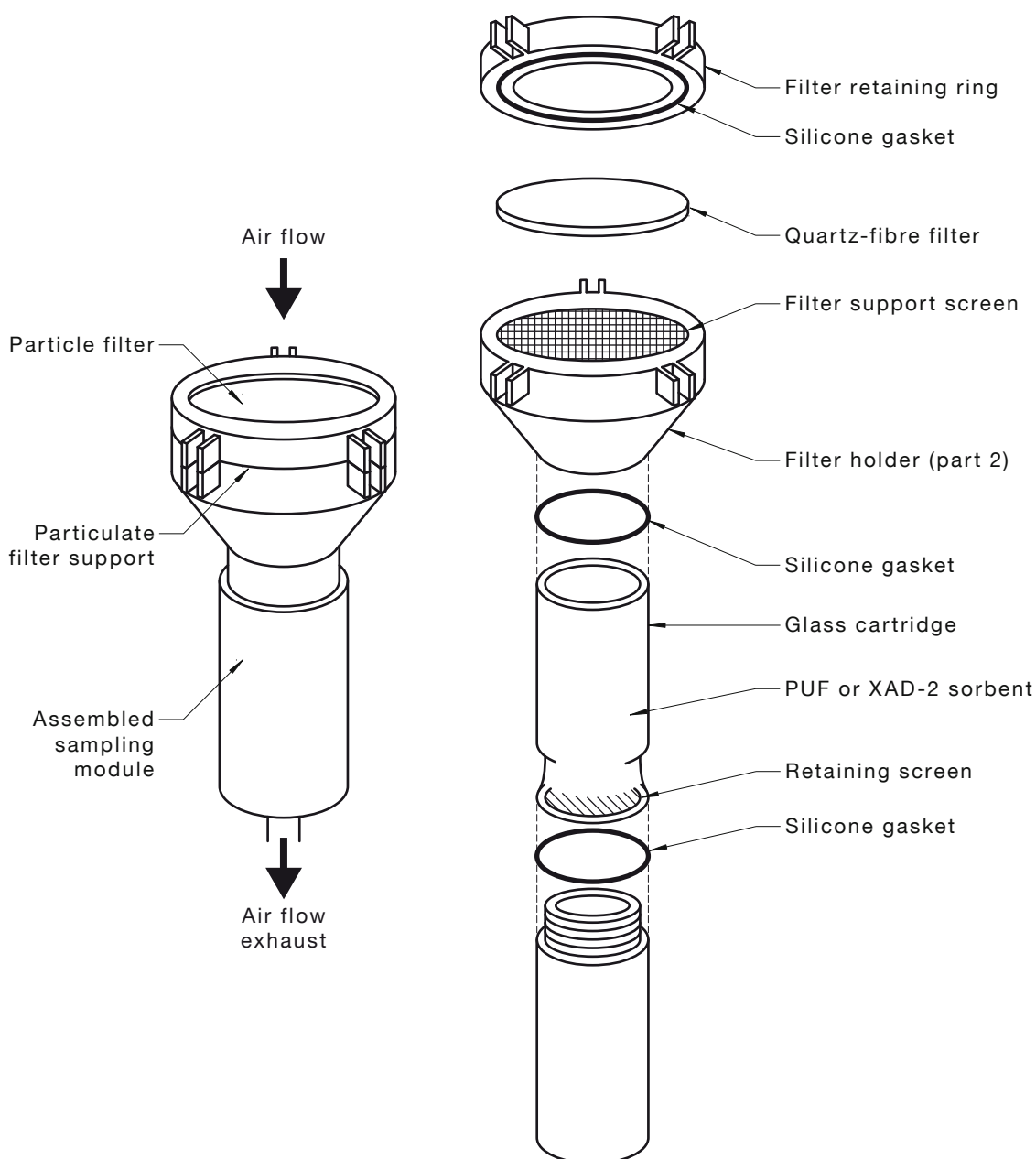


FIGURE 2 FILTER HOLDER AND SORBENT CARTRIDGE

The sampler shall be capable of passing ambient air at all times during the sampling period through an approximately 8000 mm² portion of a clean filter (nominal filter diameter 100 mm) at a constant flow rate ($\pm 10\%$) within the range 100 L/min to 250 L/min.

The motor shall be capable of continuous operation over the range of expected environmental conditions for periods of at least 24 h. The shelter and TSP inlet shall be constructed of materials capable of withstanding extremes of temperature, relative humidity and the air pollutants to which they will be exposed.

The filter shall be installed in a filter holder (Figure 2). The filter holder shall be horizontally mounted in the high volume sampler so that the sample air is drawn downwards through the filter. The filter holder shall be clamped firmly to provide an air-tight seal against the high volume sampler.

The high volume sampler and its installation shall comply with relevant statutory electrical requirements. As the instrument is operating outdoors under all weather conditions, it is recommended that regular electrical safety inspections are conducted. It is recommended that a residual current device (RCD) be installed in the electrical supply circuit and tested according to the manufacturer's instructions at regular intervals.

An exhaust muffler or other noise reducing technique should be used where noise pollution is of concern (for example in residential areas).

The exhaust from the sampler shall be dispersed to minimize re-entrainment of filtered air and to prevent dust being stirred up from the ground.

The high volume sampler shall be firmly secured to prevent the sampler from being blown over.

The high volume sampler's air flow measuring device shall be capable of being calibrated, and providing the basis for measuring the flow rate through the filter, and subsequent calculation of the air volume sampled.

NOTES:

- 1 Typical devices include a mass flow meter, or an orifice located in the sample air stream or a bypass flow meter.
- 2 The air flow measuring device may provide feed-back to the automatic flow control system.

5.2 Flow rate calibration unit

For the purpose of calibration, it is necessary to have a means of varying the flow rate through the high volume sampler. The high volume sampler may have this flow rate set-point adjustment capability built in. This may be achieved by varying the speed of the motorized fan, by throttling the flow with a valve, or by some other means. If the high volume sampler is not provided with flow rate set-point control, internal resistance (multi-holed plates) may be used to give differing air flows for a complete calibration range.

The flow rate calibration unit provides a means of calibrating the high volume sampler flow measuring device in the field. It is a transfer standard that shall itself be calibrated against a certified flow meter (refer to Appendix A) or provided with a certified calibration chart. It shall be capable of temporary connection to the high volume sampler during calibrations. Either one of the following flow rate calibration units shall be used:

- (a) *An orifice flow rate calibration unit* This shall consist of an orifice unit incorporating an adaptor plate that connects to the inlet of the high volume sampler and a differential manometer to measure the differential pressure across the orifice. The differential manometer connects to the side tapping on the orifice unit via a suitable length of flexible tubing with air-tight connections at each end.

NOTE: The differential manometer may be a water filled U-tube manometer or an electronic manometer. A water filled U-tube manometer should have a graduated scale.

The manometer shall have a total range of at least 300 mm of water, graduated in 2 mm divisions or less. An electronic manometer shall have a range equivalent to at least 3.0 kPa (approximately 300 mm of water), with 0.02 kPa (approximately 2 mm of water) resolution or less. If an electronic manometer is used to measure the differential pressure across the orifice, it shall be calibrated against a primary standard differential manometer (such as a water filled U-tube manometer) at an interval not exceeding every twelve months. The manometer shall be zeroed prior to connection to the orifice flow rate calibration unit. The water manometer shall be secured in a vertical position during use.

NOTE: The differential pressure is the total difference in the level of water in the two halves of the U-tube and is measured in millimetres of water.

The orifice unit shall itself be calibrated in accordance with Appendix A. It shall at all times be handled with care to prevent damage, which could jeopardize the accuracy of the unit. The orifice flow rate calibration unit shall be inspected for damage prior to each use. Any visible damage to the area around the orifice shall necessitate recalibration or replacement of the unit.

The dimensions of the orifice flow rate calibration unit shall be as defined in Appendix A.

- (b) *A calibrated volumetric flowmeter* This shall be capable of measuring flow rates of between 100 L/min and 250 L/min with negligible pressure drop.

5.3 Filters

Binderless, acid-washed quartz fibre filters of a minimum diameter of 100 mm shall be used. The filters shall have a specified collection efficiency of at least 99% for particles of 0.3 µm EAD and shall permit a minimum air flow rate of 250 L/min. The filters shall be free from pinholes and other defects (see Clause 5.8). The filter shall be able to withstand folding.

5.4 Polyurethane foam

Polyurethane foam with a density of 22 ± 1 g/L, cut into cylinders with minimum dimensions of 76 mm long by 62 mm diameter shall be used.

For initial clean-up, the PUF plug is placed in a Soxhlet apparatus and extracted with acetone for 14 h to 24 h at approximately 4 cycles per h, followed by a second Soxhlet extraction for 14 h to 24 h at approximately 4 cycles per h with a mixture of 10% v/v of diethyl ether in n-hexane (or other appropriate solvent used in the sample extraction step as validated by the user).

NOTE: Pressurized fluid extraction apparatus may be used instead of Soxhlet apparatus.

The PUF plug may be reused if properly cleaned after each use. The number of possible uses before significant deterioration of performance occurs has not been determined, but it should not be used more than six times without verifying that the performance is unchanged.

NOTE: If the PUF plug is reused, 10% v/v of diethyl ether in n-hexane (or the optional extraction solvent, if appropriate) may be used as the solvent for clean-up.

The extracted PUF plug is placed in a vacuum oven connected to a high purity nitrogen gas stream and dried at room temperature for approximately 2 h to 4 h (until the plug is no longer swollen).

5.5 XAD-2 resin

Spherical beads of precleaned XAD-2 resin, 500 µm in diameter, shall be used.

For initial clean-up, a batch of XAD-2 (60 g to 100 g) is placed in a Soxhlet apparatus and extracted with dichloromethane for 16 h at approximately 4 cycles per hour (or other appropriate solvent used in the sample extraction step as validated by the user). At the end of the extraction, the used dichloromethane is discarded and replaced with fresh reagent. The XAD-2 resin is once again extracted for 16 h at approximately 4 cycles per h.

The XAD-2 resin is removed from the Soxhlet apparatus, placed in a vacuum oven connected to a high purity nitrogen gas stream and dried at room temperature for approximately 4 h to 8 h (until the resin particles flow freely).

NOTE: The XAD-2 resin may be dried quicker using a fluidized bed suspension system with dry nitrogen.

The XAD-2 resin may be reused if properly cleaned after each use. The number of possible uses before significant deterioration of performance occurs has not been determined, but it should not be used more than six times without verifying that the performance is unchanged.

5.6 Sample cartridge and stainless steel screen

A glass sample cartridge and stainless steel screen are used to contain the PUF and/or XAD-2 resin.

If the sorbent is removed from the cartridge prior to extraction, the cartridge and stainless steel screen shall be cleaned prior to reuse. Clean them with acetone and n-hexane, and then wash with hot water and detergent. Rinse with tap water and distilled water and allow them to drain and dry.

Once dry, rinse again with n-hexane and store inverted or capped with n-hexane rinsed aluminium foil.

5.7 Sample containers

Wide mouth, airtight and screw capped glass jars with PTFE lined lids are used to hold filters and cartridges during transport to the analytical laboratory.

5.8 Light-table

A light-table is used to check filters for pinholes or other defects.

5.9 Reference barometer

A reference barometer—traceable to national standards, with an uncertainty of ± 0.5 kPa U_{95} —is required for the calibration of any pressure transducers that form part of the flow control and measurement system.

5.10 Reference thermometer

A reference thermometer—traceable to national standards, with an uncertainty of $\pm 0.5^\circ\text{C}$ U_{95} —is required for the calibration of any temperature sensors that form part of the flow control and measurement system.

6 REAGENTS

6.1 General

This method utilizes reagents and standards that are either potentially hazardous or carcinogenic if not handled appropriately. Refer to material safety data sheets for handling instructions and personal protective equipment requirements.

6.2 Acetone

Chromatography grade.

6.3 Compressed gases

Chromatographic carrier gas (e.g. ultra-high purity helium) and nitrogen for sample concentration (high purity).

6.4 Cyclohexane

Chromatography grade.

6.5 Dichloromethane

Chromatography grade.

6.6 Diethyl ether

Reagent grade, preserved with 2%v/v ethanol.

6.7 Extraction efficiency standards

Fluorene-d10, pyrene-d10, benzo(k)fluoranthene-d12, or other appropriate deuterated standards, of purity 98%w/w or better. Alternatively or additionally, 2,2'-dibromobiphenyl and 2,2',3,3',4,4',5,5',6,6'-decafluorobiphenyl or ¹³C-labelled PAH may be used as extraction efficiency standards. Spiking solutions of the standards are made up in n-hexane or dichloromethane, as appropriate, to a concentration of 50 ng/μL.

6.8 n-Hexane

Chromatography grade.

6.9 Internal standards

Naphthalene-d8, acenaphthene-d10, perylene-d12, chrysene-d12, of purity 98% w/w or better.

6.10 Pentane

Chromatography grade.

6.11 Silica gel

High purity grade, type 60, grain diameter 75 μm to 200 μm.

6.12 Sodium sulfate

Anhydrous, reagent grade (purified by washing with dichloromethane followed by heating at 450°C for 4 h in a shallow tray).

6.13 Toluene

Chromatography grade.

7 CALIBRATION

7.1 General

Checks and calibrations shall be carried out in accordance with the frequencies specified in Table 1.

7.2 Flow calibration

High volume samplers used for PAH measurements shall have automatic flow control to maintain a constant flow. Commonly used high volume samplers have either a mass flow sensor or a volumetric flow sensor. The operator shall determine whether the high volume sampler being used controls mass flow rate or volumetric flow rate and the sampler shall be calibrated accordingly.

Calibration shall be carried out in accordance with the manufacturer's instructions, using either a volumetric flow meter [5.2(b)] or an orifice flow rate calibration unit [5.2(a)] and a different filter and sample cartridge to that used for sampling. Appropriate correction formulae for mass flow or volumetric flow shall be provided with the orifice flow rate calibration unit. The correction formulae shall also provide a means of adjusting for actual calibration conditions of temperature (T_{AC}) and pressure (P_{AC}). They shall take the following forms:

- (a) Equation relating volumetric flow rate ($Q_{VOLUMETRIC}$) to differential pressure (ΔP) across the orifice:

$$\Delta P = \left(\frac{Q_{VOLUMETRIC}}{c} \right)^2 \times \frac{P_{AC}}{T_{AC}} \quad \dots 7.2(1)$$