

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

QSM Approval: _____

Analytical Method for the Determination of Selected PACs in Ambient Air Samples

1. INTRODUCTION

The analytical methodology described in the following method is applicable to the determination of polycyclic aromatic hydrocarbons (PAH) and Total C1 to C4 alkylated PAHs, dibenzothiophene (DBT) and Total C1 to C4 alkylated dibenzothiophenes (DBTs) in ambient air samples. Note from this point forward any reference to C1 to C4 alkylated PAHs also includes DBT and C1 to C4 alkylated DBTs. Samples are collected using a modified high-volume sampler which draws air (typically 700-1000 m³) through a Teflon-coated glass fibre filter followed by a pair of polyurethane foam (PUF) plugs to collect both gas phase and particulate bound PAH.

2. PRINCIPLE OF THE METHOD

Prior to extraction samples are spiked with a solution containing isotopically- labelled PAH at a concentration that is similar to the level in the samples. The samples are then extracted by Soxhlet apparatus for a period of 16 to 20 hours with cyclohexane. The raw sample is dried through anhydrous sodium sulphate if required and concentrated.

Target analytes are isolated from the sample matrix by fractionation using silica gel column chromatography. The first fraction, collected using hexane, contains the aliphatic hydrocarbons. The second fraction, containing the selected polynuclear aromatic compounds (PAC) including the parent PAHs and the C1 to C4 alkylated PAHs, is collected by elution with benzene. If required, a third fraction may be collected containing the more polar nitrated and oxygenated PAH by eluting with a mixture of dichloromethane/benzene. The PAC fraction is further concentrated and spiked with a known quantity of recovery standard. PAH and C1 to C4 PAHs are analyzed separately by capillary column gas chromatography / low-resolution mass spectrometry (LRMS). The mass spectrometer is operated using electron impact ionization in the selected ion-monitoring mode (SIM). A minimum of two characteristic ions are monitored per target analyte. Target compound identification is confirmed when the analyte's characteristic ions are present in the right ratio at the appropriate retention times.

This method has been developed in-house and is fit for its intended use.

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

3. INTERFERENCES

Sources of interference will include but not be limited to, impurities in the reagents, solvents or glassware, high levels of background in the sample matrix and cross-contamination. Reagents and glassware must be vigorously cleaned following the protocols established and the purity closely monitored to reduce any potential contamination source. Care must be taken during all sample processing steps to minimize the occurrence of cross-contamination.

During the preparation of polyurethane foam, care must be taken to minimize its exposure to air currents. PACs are inherently present in air and freshly prepared PUFs will readily absorb PAC. Background levels of PAC in clean PUFs will directly reflect the amount of exposure to air; especially to high mass flow rates (i.e. in fumehood).

4. SAMPLE REQUIREMENTS

Samples are wrapped in aluminum foil to reduce exposure to light and stored in a freezer at a temperature of -10°C or less. Samples should be analyzed within 6 months.

5. APPARATUS AND EQUIPMENT

5.1 Sample Preparation

- 5.1.1 Beakers: Assorted volumes
- 5.1.2 Boiling flasks: 200 mL to 1000 mL range
- 5.1.3 Calibrated Centrifuge Tubes: 10 to 15 mL capacity
- 5.1.4 Cleanup Columns: 20 to 30 cm length x 1.0 to 1.4 cm ID for silica gel cleanup
- 5.1.5 Evaporative concentrator: Rotary evaporator and nitrogen blow down device.
- 5.1.6 Oven: Temperature range up to 240-260°C for activating silica gel and up to approximately 110°C for drying reagents.
- 5.1.7 Pasteur pipettes: 22 cm, disposable
- 5.1.8 Pipettes: Electronic or mechanical pipettes with capacities from 10 µL to 1000 µL
- 5.1.9 Powder funnels: 7 cm diameter or 10 cm diameter short stem
- 5.1.10 Soxhlet extractor apparatus: 500 mL and 1000 mL capacity Soxhlet extractors and appropriate condensers
- 5.1.11 Tweezers and forceps: Stainless steel
- 5.1.12 Vials: Assorted capacities from 1.5 mL to 40 mL amber glass, screw cap with Teflon-faced septum.

5.2 Sample Analysis

- 5.2.1 Gas Chromatograph/mass spectrometer: Agilent 6890N or 7890A GC

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

interfaced directly to Agilent 5973N, 5975 or 5975C. Samples were injected using an Agilent 7683, 7683B or 7693 autosampler.

- 5.2.2 GC column: 30m DB-XLB fused silica capillary column, 0.25 mm ID, and 0.25 µm film thickness (or equivalent or better).
- 5.2.3 Syringes: 5 µL capacity for injecting samples into GC (for cool-on column or splitless injection)
- 5.2.4 Autosampler Vials and caps: 1.5ml with 200ul conical inserts and 1.5 mL amber vials with autosampler caps.

6. REAGENTS AND MATERIAL

- 6.1 Benzene, Toluene: distilled in glass, chromatographic quality
- 6.2 Cyclohexane, Dichloromethane: distilled in glass, chromatographic quality
- 6.3 Compressed gases: Helium, Ultra high purity (GC carrier gas) and nitrogen high purity or better for sample concentration
- 6.4 Hexane: distilled in glass, chromatographic quality
- 6.5 Filter: Pallflex Emfab Teflon coated glass fibre (8" x 10")
- 6.6 Glasswool: pyrex fiberglass, 8 µm
- 6.7 Recovery Standard: fluoranthene-d₁₀, purity 98% or better. Spiking solution of the recovery standard is made up in toluene at a concentration of 10 ng/µL
- 6.8 Methanol: distilled in glass, chromatographic quality
- 6.9 Polyurethane Foam: Density = 22.4 kg/m³, compression = 1531, open cell type (7.5 cm x 7.5 cm diameter)
- 6.10 Reference material: Urban dust reference material available from NIST.
- 6.11 Silica gel: high purity grade 923, mesh size 100-200
- 6.12 Sodium sulphate: anhydrous, granular, reagent grade
- 6.13 Surrogate standards: naphthalene-d₈, acenaphthylene-d₈, acenaphthene-d₁₀, fluorene-d₁₀, dibenzothiophene-d₈, phenanthrene-d₁₀, anthracene-d₁₀, pyrene-d₁₀, benzo(a)anthracene-d₁₂, triphenylene-d₁₂, chrysene-d₁₂, benzo(b)fluoranthene-d₁₂, benzo(e)pyrene-d₁₂, benzo(a)pyrene-d₁₂, perylene-d₁₂, indeno(123-cd)pyrene-d₁₂, dibenzo(ah)anthracene-d₁₄, and benzo(ghi)perylene-d₁₂ (purity 98% or better). Spiking solution of the surrogate standards is made up in toluene at a concentration of 10 ng/µL.
- 6.14 Standard Preparation and Storage: Refer to SOP 3.09/*.*/*S
- 6.15 Prepared reagents have an expiry date of 90 days from the date of preparation (refer to SOP 3.13/*.*/*S).

7. PROCEDURE

7.1 Glassware and Material Preparation

7.1.1 Glassware

All glassware is washed in an automatic washer with hot detergent solution and sequentially rinsed with hot water and deionized water. It is then

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

manually rinsed with three portions each of acetone and hexane. Glassware is air-dried in a fumehood or oven dried and then stored in a contaminant free area.

7.1.2 Glasswool

Glasswool is placed in a large column and eluted with two column volumes of dichloromethane followed by two column volumes of hexane. The clean glasswool is then placed in a pre-cleaned 1 L beaker, covered loosely with solvent rinsed foil and allowed to air dry overnight in a fumehood. The dry glasswool is kept in an oven at a temperature ranging from 110°C to 300°C until ready for use.

7.1.3 Sodium Sulphate

The sodium sulphate is poured into a pre-cleaned column (~ 8cm ID x 30 cm length) and eluted with two volumes of dichloromethane followed by two volumes of hexane. The dichloromethane and hexane are discarded. The clean sodium sulphate is poured into a pre-cleaned 1 L beaker, covered loosely with solvent-rinsed aluminum foil and allowed to air dry overnight in fumehood.

The sodium sulphate is further dried in an oven at approx. 110°C overnight and then stored in the oven at a temperature between 100°C and 300°C until ready for use.

7.1.4 Silica Gel

The silica is poured into a large pre-cleaned glass column and eluted with the equivalent of two volumes of methanol followed by dichloromethane. The methanol and dichloromethane are then discarded. The clean silica is poured into a pre-cleaned 1 L beaker, covered loosely with rinsed aluminum foil and allowed to air dry, overnight, in a fumehood. The silica is then dried in an oven at approx. 110°C overnight. Prior to use, the silica is activated at a temperature of 240°C to 300°C for a minimum of 24 hours. Care must be taken to ensure no traces of solvent are present prior to transferring to the 240°C oven. Store the activated silica in the oven (240°C to 300°C) in a properly labelled beaker that includes reagent name and date of preparation.

7.1.5 Polyurethane Foam (PUF)

See SOP 4.21/*.*S, Preparation of Polyurethane Foam Plugs (PUFs) for Ambient Air Monitoring, for information on the preparation of Polyurethane Foam Plugs.

7.2 Sample Preparation

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

7.2.1 Filter

Each filter is spiked with 1000 ng each of 18 isotopically-labelled PACs and placed inside a clean soxhlet apparatus. The sample is extracted with approximately 350 mL of dichloromethane (DCM) plus approx. 10% acetone for 16-20 hours. The raw extract is then filtered through Na₂SO₄ and concentrated to a volume of 3 to 5 mL by rotary evaporation at approx. 30°C for dichloromethane (refer to SOP4.22/*.*/*S). The solvent is exchanged to cyclohexane by adding 100 mL of cyclohexane and concentrating to 3-5 mL.

7.2.2 Polyurethane Foam (PUF)

PUFs are placed into clean soxhlet body using clean tweezers. After spiking with the surrogate mixture (1000 ng of 18 isotopically-labelled PACs) on the surface of the top PUF, PUFs are extracted overnight (16-20 hours) in DCM (~ 350 mL plus approx. 10% acetone for small soxhlet body or ~ 700 mL for large soxhlet body). The raw extract is then filtered through Na₂SO₄ if required and concentrated to a volume of 3 to 5 mL by rotary evaporation at approx. 30°C (refer to SOP4.22/*.*/*S). The extract may also be dried through sodium sulphate following concentration provided extra care is given to avoid bubbling in the rotary evaporator. The solvent is exchanged to cyclohexane by adding 100 mL of cyclohexane and concentrating to 3-5 mL.

7.2.3 Filter and PUF

The sample filter is folded in four and placed at the bottom of a large (500 mL capacity) clean soxhlet body followed by the PUFs. The surface of the top foam plug is spiked with 1000 ng each of 18 isotopically-labelled PACs. The sample is extracted for 16-20 hours in DCM (approx. 350 mL plus approx. 10% acetone for small soxhlet body or 700 mL for large soxhlet body). The raw extract is then filtered through Na₂SO₄ if required and concentrated to a volume of 3 to 5 mL by rotary evaporation at approx. 30°C (refer to SOP4.22/*.*/*S). The extract may also be dried through sodium sulphate following concentration provided extra care is given to avoid bubbling in the rotary evaporator. The solvent is exchanged to cyclohexane by adding 100 mL of cyclohexane and concentrating to 3-5 mL.

7.2.4 Samples analyzed for both PAC and Polychlorinated dibenzo-p-dioxin/polychlorinated dibenzofurans (PCDD/F)

In addition to spiking the sample with 1000 ng of the PAC surrogates, the sample is also spiked with 2-4 ng of the nine ¹³C₁₂ -labelled PCDD/F

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

compounds. The sample is extracted for 16-20 hours with a cyclohexane/toluene (80/20) mixture instead of DCM.

The sample is then concentrated to approximately 3 mL and the solvent is exchanged to cyclohexane by adding 100 mL of cyclohexane and concentrating to 3-5 mL. The extract is then transferred into a 12 or 15 mL centrifuge tube with 3 cyclohexane rinses of the flask and made up to a final volume of 12.0 mL. The sample extract is mixed well then split by removing 6.0 mL of the extract for PCDD/F analysis (see Section 7.3.2 for cleanup).

7.3 Sample Cleanup

7.3.1 For PAC extractions

A cleanup column is constructed using an open column (approx. 25 cm x 1.4 cm ID) plugged with clean glasswool. The column is filled to a pre-calibrated engraved marking (10 cc volume) with activated silica gel (approx. 7 g). Alternatively, a pre-cleaned 25 mL disposable pipette or glass column (approx. 25 cm x 1.4 cm ID) can be used by filling to the 15 mL mark (~ 7 g) with activated silica gel. The silica is poured into the column with gentle tapping to ensure uniform packing. The column is then topped with ~ 2 g (2 cc) of Na₂SO₄ and pre-washed with 10 mL of hexane. When the hexane has drained to bed level the raw extract is quantitatively transferred onto the column. The flask is rinsed with hexane three times (1 to 2 mL rinses) and each rinse is quantitatively transferred to the column.

The column is eluted with 5 mL of hexane, followed by 5 mL of benzene and the eluate is archived (aliphatic hydrocarbon fraction). The PAC is then eluted with two 5 mL aliquots of benzene into a calibrated centrifuge tube. If required, a third fraction may be collected containing the polar PAC which includes oxygenated and nitrated PAH compounds using 25mL of 50% DCM in benzene. The PAC fraction (benzene fraction) is concentrated to less than 0.9 mL by UHP nitrogen blow-down at ambient temperature in a fumehood. (Do not concentrate the sample extract to dryness, as significant analyte loss will be incurred). After addition of 100µL of d₁₀-fluoranthene (10 ng/µL), the purified sample extract is then reconstituted to a known volume (typically 0.5 or 1.0 mL) using benzene prior to GC/MS analysis.

7.3.2 For extracts from Section 7.2.4

The raw extract (6.0 mL) is applied to the silica column with 3 hexane rinses (1 mL each). The column is then eluted with 5 mL of hexane, followed by 5 mL of benzene and the eluate is archived (aliphatic hydrocarbon fraction). The PAC is then eluted with two 5 mL aliquots of

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

benzene into a calibrated centrifuge tube. If required, a third fraction may be collected containing the polar PAC which includes oxygenated and nitrated PAH compounds using 25 mL of 50% DCM in benzene. The PAC fraction is concentrated to less than 450 µL using UHP nitrogen. After addition of 50 µL of d₁₀-fluoranthene (10 ng/µL), the sample is then made up to a final volume of 500 µL prior to GC/MS analysis.

7.4 Analysis

7.4.1 The final purified extract is analyzed under the following operating conditions:

7.4.1.1 Instrument: Agilent 6890N or 7890A GC interfaced directly to Agilent 5973N, 5975 or 5975C MSD. Samples were injected using an Agilent 7683, 7683B or 7693 autosampler.

7.4.1.2 Injection: 1 µL to 2 µL cool on-column or splitless (280°C).

7.4.1.3 Column: 30 m DB-XLB fused silica, 0.25 mm ID and 0.25 µm film thickness (or equivalent or better).

7.4.1.4 Helium is utilized as the carrier gas with a constant flow of 2.0 mL/min.

7.4.1.5 Oven Temp for PAH: 90°C for 4 min, to 200°C at 20 C°/min, to 250°C at 2.5 C°/min, then to 283°C at 1.5 C°/min and hold for 6 min.

Oven Temp for C1 to C4 PAH: 90°C for 1 min., 5 °C/min to 320°C and hold for 10 minutes.

(Temperature programs may require modification for other column types or to improve resolution).

7.4.1.6 Detection Mode: Electron Impact Ionization @ 70 eV operated in the Selected Ion Monitoring (SIM) mode; Each PAC group (PAH and C1 – C4 PAH) has a 7-step program with one to three ions per compound, 15-100 msec dwell per ion.

7.4.1.7 Calibration: Calibration is performed using a standard PAH mixture containing 30 compounds at a concentration of 1 ng/µL of each compound (Table 1) and a standard containing at least 2 compounds whenever available for each of the C1 to C4 PAH (Table 2).

7.4.1.8 Quantitation: The internal standard quantitation method can be used for all PAH compounds. MS relative response factors determined for the standard mixture components on the same day are used to quantitate sample levels of target analytes. For C1 to C4 alkylated PAH the results are reported as total for each isomeric group. For C1 and C2 naphthalenes, C1-fluorenes, C1-DBTs, C1-phenanthrenes/anthracenes and C1-fluoranthenes/pyrenes each individual isomer is quantitated separately and then the concentrations totalled. For all other

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

isomeric groups the total is calculated as a single entity where the area used is the total area of the quantitation ion for all isomers in that group integrated as one and the relative response factor used is the average relative response factor of all isomers present in the standard and which are in that group. (See Section 8).

7.4.2 A minimum of three characteristic ions are monitored for each native PAC analyte. Two ions are monitored for each isotopically-labelled surrogate. Selected ion masses are listed in the attached tables. 7.4.3 The presence of a target compound in the final sample extract is confirmed when all of the following criteria are satisfied:

7.4.3.1 Response for the two most abundant characteristic ions must exceed the background noise level by a minimum ratio of 3:1.

7.4.3.2 The abundance ratio of the two major characteristic ions monitored must be within $\pm 40\%$ of the ratio for the corresponding compound in the calibration standard solution.

7.4.3.3 The third qualifying ion must be present unless the ion is masked by high background interference.

7.4.3.4 The peak maxima for the specified characteristic ions must be coincident within 2 scan units (3 seconds maximum).

7.4.3.5 Parent PAH analyte retention time relative to the closest eluting surrogate must be within 0.1 min of the relative retention time of the corresponding standard mixture components. The retention time windows for the C1 to C4 substituted PAHs were established by monitoring the parent and the qualifying ion from each group in fuel oils.

7.5 Calibration

The linear dynamic range is established using a minimum four-point calibration curve; constructed within the linear range of the instrument for every target analyte. If the coefficient of correlation (r) for each target analyte of the calibration curve (A_x / A_i vs C_x / C_i) is ≥ 0.995 or each coefficient of determination (r^2) is ≥ 0.990 , then linearity for the working range is established and the response factors of the daily calibration standard (1.0 ng/ μ L) are used to quantitate sample analyte concentrations. If these criteria are not met then instrument maintenance must be performed to correct the situation. The linear dynamic range must be successfully established prior to sample analysis.

Analysis is conducted within the range of the established calibration curve. Samples may need to be concentrated or diluted to bring concentrations within the calibration range.

7.5.1 Daily calibration check

A mid level calibration standard (typically 1.0 ng/ μ L) is analyzed daily to

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

monitor system performance. The standard is used to update the calibration table that is used to calculate the concentrations of the target analytes and the recoveries of the surrogates. The relative response factors (RRFs) must not vary by more than 30% from the previous updated calibration table, with no more than 4 compounds outside this limit. If RRFs vary by more than 30% then analysis is stopped until the problem is corrected (i.e. system may require recalibration).

7.5.2 Chromatographic Performance

The chromatographic resolution is verified daily with a mid-level calibration standard. Adequate resolution is demonstrated when the valley between phenanthrene and anthracene does not exceed 10% of the highest peak. The valley between benzo(b)fluoranthene and benzo(k)fluoranthene should not exceed 50% of the highest peak. Benz(a)anthracene, chrysene and triphenylene must be partially resolved. The valley between the benz(a)anthracene and triphenylene peaks must not exceed 30% of the highest peak and the valley between the chrysene and triphenylene peaks must not exceed 80% of the highest peak. The calibration check standard must demonstrate good overall peak shape for all target analytes. Chromatographic problems such as excessive peak tailing, split peaks, unsymmetrical peaks and poor sensitivity are corrected prior to further analysis.

The retention time windows for the C1 to C4 substituted PAHs are confirmed against a reference standard solution such as an extract from NIST Urban Dust 1649b at least monthly.

7.5.3 Surrogate and Recovery Standard Spiking Solutions

The sample spiking solutions, consisting of the recovery standard solution (fluoranthene-d₁₀) and surrogate standard solution, must be calibrated before use. These solutions must also be recalibrated periodically (at least every second batch of samples processed) against the daily calibration standard.

7.5.4 Standard Accuracy

The daily calibration standard must be verified against a certified PAC reference solution (i.e. NIST 1647, 1491a) at least every six months when samples are being analyzed. A dilution of the certified reference solution is analyzed as a sample. Calculated concentrations, for the majority of the compounds, must be within 15% of expected results, with no more than 20% of values falling outside of this range. Values outside of this range must fall within 50% of expected values. If these conditions cannot be met, a new standard solution will be prepared or corrections to the

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

concentrations applied.

7.5.5 Instrument Sensitivity

A standard with a concentration near detection limit (typically 0.0005 to 0.005 ng/uL for PAH and 0.05 ng/uL for alkylated PAHs) is analyzed regularly as sample analysis to verify system sensitivity.

8. CALCULATIONS

8.1 Native analyte RRF

Calculate the relative response factors for each native PAH analyte relative to the recovery standard (fluoranthene-d₁₀) according to the following equation:

$$RRF_x = (A_x / A_i) (C_i / C_x)$$

where:

RRF_x = Relative response factor for analyte (x) in standard

A_i = peak area of the quantitation ion for the recovery standard

A_x = peak area of the quantitation ion for the native PAH analyte (x) or for the average response of at least 2 native congeners of the alkylated PAH analyte whenever available.

C_i = concentration of the recovery standard, ng/μL

C_x = concentration of the native analyte (x), ng/μL

8.2 Surrogate RRF

Calculate the relative response factors for each surrogate relative to the recovery standard (fluoranthene-d₁₀) according to the following equation:

$$RRF_s = (A_s / A_i) (C_i / C_s)$$

where:

RRF_s = Relative response factor for surrogate (s) in standard

A_i = peak area of the quantitation ion for recovery standard

A_s = peak area of the quantitation ion for the surrogate analyte "s"

C_i = concentration of the recovery standard, ng/μL

C_s = concentration of the surrogate analyte "s", ng/μL

8.3 Analyte Concentration

8.3.1 The concentration of the native PAH analytes are not corrected for surrogate recovery and are calculated using the following equation:

$$C(X) = (A_x / A_i) (1 / RRF_x) (C_i \times V_{ext} / W)$$

The same equation is used to calculate the total concentration for each of the C1 to C4 PACs where:

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

RRF_x = Relative response factor for analyte (x) in standard
 A_i = peak area of the quantitation ion for recovery standard
 A_x = peak area of the quantitation ions for the native PAH analyte(x))
 or for the sum of the peak areas of the quantitation ions for the congeners within the retention time window of the alkylated PAH analyte.
 C_i = concentration of the recovery standard, ng/μL
 V_{ext} = volume of sample extract, μL
 W = sample size, m³

8.3.2 It is also possible to calculate the concentration of the native PAH analyte in the sample corrected for surrogate recovery, C(X) expressed in ng/m³, as follows:

$$C(X) = (A_x / A_i)(1 / RRF_x) (C_i \times V_{ext} / W) / (\text{Surrogate Percent Recovery} / 100)$$

where:

V_{ext} = volume of sample extract, μL
 W = sample size, m³

8.3.3 Where no corresponding isotopically labelled surrogate is present, the average percent recovery of closely eluting surrogates is used. 2-Methylfluorene uses the average recovery of fluorene-d10, phenanthrene-d10 and anthracene-d10. Fluoranthene, retene, benzo(a)fluorene, benzo(b)fluorene, 1-methylpyrene, benzo(ghi)fluoranthene and 7-methylbenzo(a)anthracene use the average recovery of pyrene-d10, benzo(a)anthracene-d12, triphenylene-d12 and chrysene-d12. Benzo(k)fluoranthene and 3-methylcholanthrene use the average recovery of benzo(b)fluoranthene-d12, benzo(e)pyrene-d12, benzo(a)pyrene-d12 and perylene-d12. Indeno(123-cd)fluoranthene, benzo(b)chrysene and anthanthrene use the average recovery of indeno(123-cd)pyrene-d12, dibenzo(ah)anthracene-d14 and Benzo(ghi)perylene-d12.

8.4 Surrogate Percent Recovery

Calculate the percent recovery of the surrogate standards, %R(X), measured in the sample extract as follows:

$$\% R(X) = [(A_s / A_i) (1 / RRF_s) \times C_i] \times (V_{ext} / M_s) \times 100$$

where:

C_i = concentration of recovery standard
 A_i = peak area of the quantitation ion for the recovery standard

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

A_s = peak area of the quantitation ion for the appropriate surrogate analyte (s).
 M_s = amount of surrogate spiked into the sample (ng)
 V_{ext} = volume of sample extract (uL)

9. SAFETY

Individual PAC compounds exhibit varying levels of toxicity and carcinogenic potential. It is the analysts' responsibility to consult the appropriate MSDS sheets to familiarize themselves with the potential hazards and the necessary precautions prior to the handling and processing of samples. Special care must be exercised in the handling of pure standards and standard solutions. Gloves, labcoats and protective eyewear must be worn. Spills of standard solutions are cleaned up immediately followed by a thorough rinsing of the spill area with solvent.

10. QUALITY ASSURANCE

The major elements of the analytical procedure used to assure acceptable method performance are as follows:

- 10.1 The calibration standards containing 30 PAH compounds or at least 2 congeners (where available) from each of the C1 to C4 substituted PAHs are periodically checked against commercially available PAH mixtures.
- 10.2 The calibration standards are run before and after each set of up to 10 samples that are injected on the GC/MS.
- 10.3 All samples are spiked with a mixture of 18 isotopically-labelled surrogate standards representing compounds containing between 2-6 aromatic rings. In addition, d₁₀-fluoranthene is added to the purified sample extract prior to GC/MS analysis as a recovery standard.
- 10.4 The percentage recovery of the labelled surrogates is calculated and reported. This serves to indicate the effectiveness of the sample workup and analytical procedures. The native PAC concentrations in the sample are not corrected for surrogate recovery unless the client specifically requests otherwise.
- 10.5 To ensure good analytical accuracy, NIST reference standard material of Urban dust (i.e. 1649b) and PAH solution (i.e. 1647e, 1491a, or 2260a) are periodically analyzed as a sample.
- 10.6 A blank filter (and/or PUF) spiked with surrogates is processed along with each batch of up to 15 field samples to demonstrate freedom from cross-contamination and the absence of other compounds which could interfere with the analysis of target analytes. Method Blanks should not contain any individual PAH at a concentration greater than 3x their MDL with the exception of naphthalene, acenaphthene, fluorene, 2-methylfluorene, phenanthrene, fluoranthene and pyrene which are ubiquitous in the environment and may contain up to 10x their MDL. Total C1 to C4 PAHs in Method Blanks should not be more than 0.25 ng/m³ except for C1 to C4 Naphthalenes which are also ubiquitous. This value was

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

established by adding 2 s to the average concentrations for 14 method blanks generated over a 6 month period. Method blanks exceeding these limits indicate potential interference or cross-contamination. Each case is investigated individually to ascertain the potential source of contamination. Records of the investigation and corrective actions are maintained.

- 10.7 A control sample consisting of either a blank filter (and/or PUF) spiked with known amounts of native and surrogate compounds, or of certified reference material spiked with surrogate compounds, is processed along with each batch of up to 15 field samples. On-going precision and accuracy can then be assessed. Control charts are used to monitor on-going performance. Target analyte concentrations should not vary by more than $\pm 40\%$ of reference values with no more than three target analytes outside of this range. The concentrations of analytes outside of this range must not vary by more than 75% of reference values.
- 10.8 Surrogates are added to each sample, method blank and control prior to extraction to produce individual concentrations of 1 ng/ μ L in the final extract. The acceptable level of surrogate recovery is from 50-120 % with no more than two surrogate recoveries outside of this range with an acceptable level of surrogate recovery ranging from 20 to 200%. Samples that fail to meet this criterion are reanalyzed and reported as a non-conformance sample if reanalysis confirms the original result.
- 10.9 The pipette ID's for all electronic pipettes used during sample preparation are recorded.

11. DETECTION LIMIT AND METHOD VALIDATION

- 11.1 Under optimum conditions an instrumental detection limit of 0.0001 to 0.01 ng/ μ L per target analyte can be achieved using the Agilent 5973N, 5975 or 5975C MSD.
- 11.2 In a single laboratory (Chemical Analysis and Methods Unit, AAQS), for 8 replicate analysis of PAH in reference material (NIST SRM 2260a) with target analyte concentrations ranging from 0.1907 to 1.001 μ g/g, the difference between results obtained and reference values varied between 0.03 % to 21.0 % (recovery corrected) and 0.2 % to 26.2 % (not recovery corrected) for individual target analytes. The mean recovery of individual surrogates ranged from 72 to 110%. 8 replicate analyses of NIST 1491a spiked onto PUFs with concentrations of C1 to C4 PAHs ranging from 0.2 to 0.5 μ g/g had an accuracies between 4 % to 38 %.
- 11.3 The limit of detection will vary depending upon the sampling site, sampling conditions, interferences, contaminants present and instrument sensitivity. The method detection limit (MDL) for PAH was obtained by 7 replicate analysis of filter/PUF samples spiked at amounts of 0.02 μ g. Based on a 1000 m^3 sample of air and a final volume of 1.0 ml, the MDLs for PAH range from 0.8 to 4 pg/m^3 per analyte (recovery corrected) and 0.8 to 5 pg/m^3 per analyte (not recovery

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

corrected) using a confidence interval of 95%. 8 replicates of PUFs spiked with 0.0125 ug of individual congeners of C1 to C4 PAHs produced method detection limits between 0.001 to 0.006 ng/m³ for individual congeners. The method detection limit for total C1 to C4 PAHs were derived by combining the average concentration of each homologue group in 14 method blanks and adding 2 times the standard deviation. The MDLs produced were between 0.03 ng/m³ and 0.7 ng/m³ for the individual homologue totals.

11.4 This method is fit for its intended use.

12. ESTIMATION OF UNCERTAINTY OF MEASUREMENT

12.1 Refer to SOP 2.10/*./S for the detailed estimation approach.

12.2 The uncertainty sources of the method and the QC data used for uncertainty estimation are listed in Appendix A,B and C

13. APPLICABLE SOPS

3.09/*./S	"Storage, Use and Preparation of Standard Solutions"
4.04/*./S	"Glassware"
4.21/*./S	"Preparation of Polyurethane Foam Plugs for Ambient Air Monitoring"
5.01/*./S	"High Resolution GC/Low Resolution MS Analysis"
5.07/*./S	"Preparation and Analysis of Sample Extract Dilutions by GC/MS-Instrumental Laboratory"
5.08/*./S	"Determination of Analyte Specific Instrument Detection Limit"
1.02/*./S	"Non-conformance"
1.10/*./S	"Recording Test Data"
2.04/*./S	"Fumehoods"
2.5/*./S	"Method Validation"
2.10/*./S	"Estimation of Uncertainty in Chemical Analysis"
3.01/*./S	"Sample Reception and Processing"
3.13/*./S	"Reagents"
16.02/*./S	"LIMS Data Entry"
16.03/*./S	"LIMS Sample Login"
16.04/*./S	"LimsLink and Laboratory Instrument Reports Using a *.csv File"
19.03/*./S	"Control Charts"

14. REVISIONS

May 2008: Lead Reviewers: Jennifer Verner, Gary Poole, David Harnish
 Section 14, added October 1997, deleted author from August 1999.
 Section 10.6, removed "blanks should not exceed 10xMDL" and replaced with "Method Blanks should not contain...up to 10x their MDL."
 Section 11.2, changed data from UD1649a to SRM 2260a

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Page:
14 of 27

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

- Sept. 2009: Lead Reviewer: David Harnish
 5.2.1 Updated List of Instrumentation
 7.4.1.1 Updated List of Instrumentation
 7.5.5 Removed reference to IDLs for 5972MSD
 8.3 Added “corrected for surrogate recovery” and modified formula
 Added section 8.3.1 re which surr recoveries used to correct which natives
 Added section 8.3.2 re client request for non recovery corrected results
 10.4 Removed “not” and added “unless the client specifically requests otherwise”
 11.1 Removed reference to IDLs for 5972MSD
 11.2 Added recovery corrected precision values
 11.3 Added recovery corrected MDLs
 15 Updated list of applicable manufacturer’s manuals
 Appendix B Updated Uncertainties
- July 2011: Lead Reviewer: Mylaine Tardif, David Harnish and Gary Poole
 Section 2: Added statement regarding in-house method and fit for purpose.
 Section 7.5.5: Added analyzed “regularly”
 All sections updated to include procedures for the analysis of C1 to C4 alkylated PAHs
 Deleted revisions history from Oct. 1997 to Mar. 2006
- October 2011 Lead Reviewer: Mylaine Tardif
 7.5.4 Added acceptance criteria for the standard accuracy of all analytes
 10.7 Added acceptance criteria for the recovery of all analytes in control samples.
 10.8 Added acceptance criteria for all surrogate recoveries.
 11.2 Rewording of sentence for reference values
- Nov. 2011 Lead Reviewer: Alison Walkey
 Section 5.1.6 Added “approximately” to temperature
 Section 6.13 Changed “surrogate recovery stds” to “surrogate stds”
 Section 7.1.4 Removed column dimensions
 Added Sections 6.15 and 10.9
 Added reference SOP 3.13 to Section 13
 Deleted reference SOPs 4.16, 4.17, 4.18 from Section 13
 Changed internal std to recovery std in Sections 2, 6.7, 7.5.3, 8.1, 8.2, 8.3, 8.4, 10.3
- Dec. 2012: Lead Reviewer: May Siu,
 Section 6.2: Added Dichloromethane
 Section 7.2: Removed “at a rate of 3 to 5 cycles/hr”
 Section 7.2: Added “or DCM” as alternative solvent for extraction and the statement: “If extraction was carried out in DCM, the solvent is exchanged to cyclohexane by adding 100 mL of cyclohexane and concentrating to 3-5

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

- mL.”
- Jan. 2013 Section 7.2: Added “or lower” to 45°C rotary evaporation temperature
Lead Reviewer: Alison Walkey
Section 7.2.1, 7.2.2, and 7.2.3: Deleted “cyclohexane” and “45°C for cyclohexane”. Added “and approx. 30°C for dichloromethane (refer to SOP4.22/*.*S). Deleted “if the extraction was carried out in DCM”.
- Sept. 2013 Section 7.2.1, 7.2.2, and 7.2.3: Added “plus approx. 10% acetone”
Lead Reviewer: David Harnish
Section 7.2.4 deleted cyclohexane added DCM
Updated Table 2 to reflect the new standards prepared using Chiron stock solutions

15. LITERATURE REFERENCES

Sampling of Polycyclic Aromatic Hydrocarbons in Ambient Air, Environment Canada, Pollution Measurement Division, September 1987.

Applicable Manufacturer’s Manuals:

Agilent 6890N Series Gas Chromatograph	
Operating Manual Volume 1. General Information	Part No. G1530-90440
Operating Manual Volume 2. Inlets	Part No. G1530-90450
Maintaining Your GC (CD)	Part No. G1530-90010
Troubleshooting (CD)	Part No. G1530-90011
Agilent 7890A Gas Chromatograph	
Maintaining Your GC (CD)	Part No. G3430-90010
Operating Guide (CD)	Part No. G3430-90011
Safety Manual (CD)	Part No. G3430-90013
Troubleshooting (CD)	Part No. G3430-90014
Advanced User Guide (CD)	Part No. G3430-90015
Agilent 5973N Mass Selective Detector	
Hardware Manual	Part No. G2589-90001
Reference Collection (3 CDs) Rev. C.00.00	
Agilent 5975 Series Mass Selective Detector	
Hydrogen Safety	Part No. G3170-90010
Operation Manual	Part No. G3170-90030
Troubleshooting and Maintenance Manual (CD)	Part No. G3170-90031
Agilent 7683B Automatic Liquid Sampler	
Installation, Operation and Maintenance (CD)	Part No. G2912-90230
Agilent 7693A Automatic Liquid Sampler	
Installation, Operation and Maintenance (CD)	Part No. G4513-90010
Agilent G1701DA GC/MSD ChemStation	
Getting Started	Part No. G1701-90061

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Page:
16 of 27

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

Agilent G1701EA GC/MSD ChemStation
Getting Started

Part No. G1701-90062

Lead Reviewer: Alison Walkey
Title: Technologist, Analysis and Air Quality Section

Lead Reviewer: David Harnish
Title: Chemist, Analysis and Air Quality Section

Approved by: May Siu
Title: Supervisor, Organic Labs, Analysis and Air Quality Section

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

Table 1 Quantitation Standard and Monitored Ions for PAH Analysis

Compounds	Abbrev.	Quantitation Ion	Confirmation Ions	Relative Intensity
Naphthalene	NAP	128	127, 102	100, 12, 7
Acenaphthylene	AL	152	151, 150	100, 20, 13
Acenaphthene	AE	153	154, 152	100, 96, 48
Fluorene	FL	166	165, 163	100, 91, 15
2-Methylfluorene	MFL	165	180, 178	100, 90, 27
Phenanthrene	PHE	178	176, 179	100, 19, 16
Anthracene	AN	178	176, 179	100, 18, 16
Fluoranthene	FLT	202	200, 101	100, 21, 13
Pyrene	PY	202	200, 101	100, 21, 13
Retene	RE	219	234, 204	100, 70, 28
Benzo(a)fluorene	B(a)FL	216	215, 108	100, 72, 12
Benzo(b)fluorene	B(b)FL	216	215, 108	100, 89, 13
1-Methylpyrene	MPY	216	215, 108	100, 68, 10
Benzo(ghi)fluoranthene	B(ghi)F	226	224, 113	100, 22, 15
Benzo(a)anthracene	B(a)A	228	226, 114	100, 27, 11
Triphenylene	T	228	226, 114	100, 28, 10
Chrysene	C	228	226, 114	100, 29, 9
7-Methylbenz(a)anthracene	MB(a)A	242	241, 239	100, 40, 28
Benzo(b)fluoranthene	B(b)F	252	250, 126	100, 22, 13
Benzo(k)fluoranthene	B(k)F	252	250, 126	100, 22, 13
Benzo(e)pyrene	B(e)P	252	250, 126	100, 28, 12
Benzo(a)pyrene	B(a)P	252	250, 126	100, 23, 14
Perylene	PER	252	250, 126	100, 27, 14
3-Methylcholanthrene	MCH	268	252, 126	100, 39, 16
Indeno(1,2,3-cd)fluoranthene	IF	276	274, 138	100, 20, 17
Indeno(1,2,3-cd)pyrene	IP	276	274, 138	100, 20, 18
Dibenzo(ah)anthracene	D(ah)A	278	276, 139	100, 28, 15
Benzo(b)chrysene	B(b)C	278	276, 139	100, 25, 15
Benzo(ghi)perylene	B(ghi)P	276	274, 138	100, 22, 20
Anthanthrene	ANT	276	274, 138	100, 20, 22
Isotopically-labelled surrogates				
Naphthalene-d ₈	*NAP	136	134	9
Acenaphthylene-d ₈	*AL	160	158	15
Acenaphthene-d ₁₀	*AE	164	162	94
Fluorene-d ₁₀	*FL	176	174	90
Phenanthrene-d ₁₀	*PH	188	184	14
Anthracene-d ₁₀	*AN	188	184	12
Pyrene-d ₁₀	*PY	212	208	17
Benzo(a)anthracene-d ₁₂	*B(a)A	240	236	22
Triphenylene-d ₁₂	*TRI	240	236	28
Chrysene-d ₁₂	*CHRY	240	236	26
Benzo(b)fluoranthene-d ₁₂	*B(b)F	264	260	20
Benzo(e)pyrene-d ₁₂	*B(e)P	264	260	24
Benzo(a)pyrene-d ₁₂	*B(a)P	264	260	18
Perylene-d ₁₂	*PER	264	260	24
Indeno(123-cd)pyrene-d ₁₂	*IP	288	284	19
Dibenzo(ah)anthracene-d ₁₄	*B(ah)A	292	288	26
Benzo(ghi)perylene-d ₁₂	*B(ghi)P	288	284	18
Internal Standard				
Fluoranthene-d ₁₀	IS	212	NA	

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

TABLE 2: Quantitation Standard and Monitored Ions for C1 to C4 PAH Analysis

COMPOUNDS	Quantitation (Ion)	Confirmation Ion	Relative Intensity
Naphthalene	128	127	13
Naphthalene, 2-methyl-	142	141	88
Naphthalene, 1-methyl-	142	141	91
Total C1-Naphthalenes			
Naphthalene, 2-ethyl-	156	141	220
Naphthalene, 1-ethyl-	156	141	227
Naphthalene, 2,6/2,7-dimethyl-	156	141	67
Naphthalene, 1,7-dimethyl-	156	141	72
Naphthalene, 1,3-dimethyl-	156	141	93
Naphthalene, 1,6-dimethyl-	156	141	72
Naphthalene, 1,4-dimethyl-	156	141	109
Naphthalene, 1,5/2,3-dimethyl-	156	141	87
Naphthalene, 1,2-dimethyl-	156	141	121
Naphthalene, 1,8-dimethyl-	156	141	80
Total C2-Naphthalenes			
Naphthalene, 2-ethyl-6-methyl-	170	155	210
Naphthalene, 1,2,6-trimethyl-	170	155	127
C3-Naphthalenes	170	155	130
Naphthalene, 7-isopropyl-1-methyl-	184	169	219
Naphthalene, 1,2,5,6-tetramethyl-	184	169	105
C4-Naphthalenes	184	169	160
Fluorene	166	165	93
Fluorene, 9-methyl-	180	165	186
Fluorene, 3-methyl-	180	165	135
Fluorene, 2-methyl-	180	165	122
Fluorene, 1-methyl-	180	165	125
Fluorene, 4-methyl-	180	165	132
Total C1-Fluorenes			
Fluorene, 9-ethyl-	194	165	357
Fluorene, 1,7-dimethyl-	194	179	124
C2-Fluorenes	194	179	180
Fluorene, 9-n-propyl-	208	179	50
C3-Fluorenes	208	193	150
Fluorene, 9-n-butyl-	222	179	48
C4-Fluorenes	222	207	240
Dibenzothiophene	184	152	8
Dibenzothiophene, 4-methyl-	198	197	65
Dibenzothiophene, 2-methyl-	198	197	67
Dibenzothiophene, 3-methyl-	198	197	66
Dibenzothiophene, 1-methyl-	198	197	66
Total C1-Dibenzothiophenes			
Dibenzothiophene, 4,6-dimethyl-	212	211	49

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

Table 2 (cont'd)

Compound	Quantitation Ion	Confirmation Ion	Relative Intensity
Dibenzothiophene, 2,6-dimethyl-	212	211	53
Dibenzothiophene, 2,8-dimethyl-	212	211	54
Dibenzothiophene, 1,8-dimethyl-	212	211	46
Dibenzothiophene, 2,3-dimethyl-	212	211	31
C2-Dibenzothiophenes	212	211	50
Dibenzothiophene, 2,4,7-trimethyl-	226	211	42
Dibenzothiophene, 2,3,7-trimethyl-	226	211	50
Dibenzothiophene, 2,3,8-trimethyl-	226	211	49
C3-Dibenzothiophenes	226	211	50
Dibenzothiophene, 4,6-diethyl-	240	225	125
Dibenzothiophene, 2-n-butyl-	240	197	315
C4-Dibenzothiophenes	240	225	120
Phenanthrene	178	176	19
Anthracene	178	176	19
Phenanthrene, 3-methyl-	192	191	58
Phenanthrene, 2-methyl-	192	191	56
Anthracene, 2-methyl-	192	191	51
Phenanthrene, 4-methyl-	192	191	76
Phenanthrene, 9-methyl/Anthracene, 1-me	192	191	53
Phenanthrene, 1-methyl-	192	191	56
Anthracene, 9-methyl-	192	191	64
Total C1-Phenanthrenes/Anthracenes			
Phenanthrene, 2,7-dimethyl-	206	191	32
Phenanthrene, 1,6-dimethyl-	206	191	36
Phenanthrene, 1,7-dimethyl-	206	191	33
Phenanthrene, 1,2-dimethyl-	206	191	76
Anthracene, 9,10-dimethyl-	206	191	56
C2-Phenanthrenes/Anthracenes	206	191	50
Phenanthrene, 9-n-propyl-	220	191	259
Phenanthrene, 1,2,6-trimethyl-	220	205	59
C3-Phenanthrenes/Anthracenes	220	205	80
Phenanthrene, 1,9-dimethyl-7-ethyl-	234	219	89
Phenanthrene, 1,9-dimethyl-5-ethyl-	234	219	89
Phenanthrene, 1,2,6,9-tetramethyl-	234	219	53
C4-Phenanthrenes/Anthracenes	234	219	90
Fluoranthene	202	200	20
Pyrene	202	200	21
Fluoranthene, 2-methyl-/8-methyl-	216	215	84
Fluoranthene, 7-methyl-	216	215	100
Fluoranthene, 1-methyl-	216	215	92
Fluoranthene, 3-methyl-	216	215	98
Pyrene, 2-methyl-	216	215	58
Pyrene, 4-methyl-	216	215	49
Pyrene, 1-methyl-	216	215	68

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

Table 2 (cont'd)

Compound	Quantitation Ion	Confirmation Ion	Relative Intensity
Total C1-Fluoranthenes/Pyrenes			
Fluoranthene, 3-ethyl-	230	215	233
Pyrene, 4,5-dimethyl-	230	215	76
C2-Fluoranthenes/Pyrenes	230	215	60
Pyrene, 1-n-propyl-	244	215	336
C3-Fluoranthenes/Pyrenes	244	229	100
Pyrene, 1-n-butyl-	258	215	337
C4-Fluoranthenes/Pyrenes	258	243	120
Benzo(a)anthracene	228	226	26
Triphenylene	228	226	38
Chrysene	228	226	28
Chrysene, 2-methyl-	242	241	26
Chrysene, 4-methyl-	242	241	55
Chrysene, 1-methyl-	242	241	27
C1-Benzo(a)anthracenes/Triphenylenes/Ch	242	241	30
Benzo(a)anthracene, 6,8-dimethyl-	256	239	24
Benzo(a)anthracene, 3,9-dimethyl-	256	239	20
Benzo(a)anthracene, 7,12-dimethyl-	256	239	42
C2-Benzo(a)anthracenes/Triphenylenes/Ch	256	239	40
Chrysene, 6-n-propyl-	270	239	89
Chrysene, 1,3,6-trimethyl-	270	239	24
C3-Benzo(a)anthracenes/Triphenylenes/Ch	270	239	50
Chrysene, 6-n-butyl-	284	239	83
C4-Benzo(a)anthracenes/Triphenylenes/Ch	284	269	160
*Naphthalene	136	134	9
*Fluorene	176	174	93
*Dibenzothiophene	192	160	9
*Phenanthrene	188	184	15
*Anthracene	188	184	14
*Pyrene	212	208	17
*Benzo(a)anthracene	240	236	23
*Triphenylene	240	236	26
*Chrysene	240	236	25
*Benzo(b)fluoranthene	264	260	19
*Benzo(e)pyrene	264	260	24
*Benzo(a)pyrene	264	260	19
*Perylene	264	260	23
*Fluoranthene	212		

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

*** Appendices follow starting on the next page *** **APPENDIX A**

PAC in Ambient Air (Method : 3.03/5.0/M)

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

Uncertainty Estimation – Major Sources

Measurement Steps	Uncertainty Sources	QC Data Used
Matrix Sample	Sample preparation Spike preparation Instrument response Preparation method Matrix interference Purity	QC - SRM 1649a/b
Standard Preparation	Bias	QC-SRM 1491
Sample size	Mass, Volume	QC-SRM 1649a/b

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Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

APPENDIX B

Reported Uncertainty (Recovery Corrected) – Summary

<i>Compound</i>	<i>Abbreviation</i>	<i>Mean</i>	<i>SD</i>	<i>RSD%</i>	<i>U% (95% CL)*</i>
Naphthalene	NAP	0.30763	0.153485	49.9	99.8
Acenaphthalene	AL	0.04004	0.020013	50.0	100.0
Acenaphthene	AE	0.15118	0.026596	17.6	35.2
Fluorene	FL	0.16143	0.041152	25.5	51.0
Methyl-fluorene	MFL	0.04561	0.010410	22.8	45.7
Phenanthrene	PHE	3.28214	0.303505	9.2	18.5
Anthracene	AN	0.32614	0.085293	26.2	52.3
Fluoranthene	FLT	5.10843	0.338882	6.6	13.3
Pyrene	PY	4.42503	0.283129	6.4	12.8
Retene	RET	0.13015	0.043472	33.4	66.8
Benzo(a)fluorene	B(a)FL	0.27045	0.037259	13.8	27.6
Benzo(b)fluorene	B(b)FL	0.08724	0.019259	22.1	44.2
Methyl-pyrene	MPY	0.22471	0.029253	13.0	26.0
Benzo(ghi)fluoranthene	B(ghi)F	0.69966	0.088084	12.6	25.2
Benzo(a)anthracene	B(a)A	1.83260	0.197697	10.8	21.6
Triphenylene	Tri	1.06249	0.113923	10.7	21.4
Chrysene	Chrysene	2.47949	0.257029	10.4	20.7
Methylbenzo(a)anthracene	MB(a)A	0.01229	0.000908	7.4	16.7
Benzo(b)fluoranthene	B(b)FLT	6.14018	1.650974	10.6	21.2
Benzo(k)fluoranthene	B(k)FLT	1.61677	0.210407	13.0	26.0
Benzo(e)pyrene	B(e)P	2.64101	0.233789	8.9	17.7
Benzo(a)pyrene	B(a)P	1.98217	0.225624	11.4	22.8
Perylene	PER	0.50847	0.053123	10.4	20.9
Methylcholanthrene	MCH				
Indeno(123-cd)fluoranthene	IF	0.19989	0.031278	15.6	31.3
Indeno(c,d)pyrene	IP	2.42336	0.334261	13.8	27.6
Dibenzo(ah)anthracene	D(ah)A	0.35463	0.047251	13.3	26.6
Benzo(b)chrysene	B(b)C	0.22329	0.040511	18.1	36.3
Benzo(ghi)perylene	B(ghi)P	2.91977	0.368957	12.6	25.3
Anthanthrene	ANT	0.30755	0.053091	17.3	34.5

Note: 1) Compounds highlighted have certified reference values.
 2)* $k=2.0$ ($n>30$) except for Methylbenzo(a)anthracene, $k=2.262$ ($n=9$)

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

APPENDIX B

Reported Uncertainty (Not Recovery Corrected) – Summary

Compound	Abbreviation	Mean	SD	RSD%	U% (95% CL)*
Naphthalene	NAP	0.19612	0.081662	41.6	83.3
Acenaphthalene	AL	0.03161	0.015392	48.7	97.4
Acenaphthene	AE	0.10924	0.021579	19.8	39.5
Fluorene	FL	0.12041	0.030904	25.7	51.3
Methyl-fluorene	MFL	0.03735	0.010284	27.5	55.1
Phenanthrene	PHE	2.66745	0.290388	10.9	21.8
Anthracene	AN	0.26255	0.071193	27.1	54.2
Fluoranthene	FLT	4.91195	0.439395	8.9	17.9
Pyrene	PY	4.09645	0.375404	9.2	18.3
Retene	RET	0.11714	0.042970	36.7	73.4
Benzo(a)fluorene	B(a)FL	0.26329	0.044995	17.1	34.2
Benzo(b)fluorene	B(b)FL	0.08532	0.020475	24.0	48.0
Methyl-pyrene	MPY	0.21690	0.032829	15.1	30.3
Benzo(ghi)fluoranthene	B(ghi)F	0.68229	0.095880	14.1	28.1
Benzo(a)anthracene	B(a)A	1.86541	0.218017	11.7	23.4
Triphenylene	Tri	1.00274	0.132869	13.3	26.5
Chrysene	Chrysene	2.34607	0.245079	10.4	20.9
Methylbenzo(a)anthracene	MB(a)A	0.01149	0.001359	11.8	25.1
Benzo(b)fluoranthene	B(b)FLT	6.42603	0.725650	11.3	22.6
Benzo(k)fluoranthene	B(k)FLT	1.68309	0.254987	15.1	30.3
Benzo(e)pyrene	B(e)P	2.68570	0.277464	10.3	20.7
Benzo(a)pyrene	B(a)P	2.03640	0.254404	12.5	25.0
Perylene	PER	0.49698	0.054374	10.9	21.9
Methylcholanthrene	MCH				
Indeno(123-cd)fluoranthene	IF	0.21589	0.040729	18.9	37.7
Indeno(c,d)pyrene	IP	2.72893	0.449414	16.5	32.9
Dibenzo(ah)anthracene	D(ah)A	0.38114	0.050051	13.1	26.3
Benzo(b)chrysene	B(b)C	0.23654	0.043027	18.2	36.4
Benzo(ghi)perylene	B(ghi)P	3.10915	0.448107	14.4	28.8
Anthanthrene	ANT	0.32581	0.072106	22.1	44.3

Note: 1) Compounds highlighted have certified reference values.
 2)* k=2.0 (n>30) except for Methylbenzo(a)anthracene, k=2.12 (n=16)

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

APPENDIX C

C1-C4 PAH in Ambient Air - Uncertainty

COMPOUND	Abbreviation	Mean	SD	RSD%	U% (95 % CL)
Naphthalene	NAP	0.43089	0.068467	15.9	35.4
	C1-NAP	0.91374	0.151459	16.6	36.9
	C2-NAP	1.22104	0.145616	11.9	26.6
	C3-NAP	1.33877	0.140327	10.5	23.4
	C4-NAP	0.66800	0.052975	7.9	17.7
Fluorene	FL	0.08108	0.006364	7.8	17.5
	C1-FL	0.10682	0.014313	13.4	29.9
	C2-FL	0.24268	0.032144	13.2	30.5
	C3-FL	0.53267	0.049311	9.3	20.6
	C4-FL	0.34609	0.056563	16.3	36.4
Dibenzothiophene	DBT	0.06885	0.009707	14.1	31.4
	C1-DBT	0.11563	0.016352	14.1	31.5
	C2-DBT	0.25187	0.026090	10.4	23.1
	C3-DBT	0.25364	0.017022	6.7	15.0
	C4-DBT	0.23595	0.027904	11.8	26.3
Phenanthrene	PH	2.91889	0.130746	4.5	10.0
Anthracene	AN	0.21949	0.012429	5.7	12.6
	C1-PH/AN	1.45985	0.066327	4.5	10.1
	C2-PH/AN	2.01428	0.133195	6.6	14.7
	C3-PH/AN	1.60005	0.133866	8.4	18.6
	C4-PH/AN	0.63849	0.045329	7.1	15.8
Fluoranthene	FLT	5.16803	0.127071	2.5	5.5
Pyrene	PY	4.23067	0.113877	2.7	6.0
	C1-FLT/PY	1.41763	0.044932	3.2	7.1
	C2-FLT/PY	1.51960	0.074906	4.9	11.0
	C3-FLT/PY	1.23723	0.081941	6.6	14.8
	C4-FLT/PY	0.53366	0.069002	12.9	28.8
Benzo(a)Anthracene	B(a)AN	1.85007	0.055078	3.0	6.6
Triphenylene	TRI	1.21270	0.040667	3.4	7.5
Chrysene	CHRY	2.56175	0.083794	3.3	7.3
	C1-BTC	2.24116	0.090477	4.0	9.0
	C2-BTC	1.10700	0.086482	7.8	17.4
	C3-BTC	1.01989	0.072590	7.1	15.9
	C4-BTC	0.78928	0.141196	17.9	39.9
# of compounds, n					34
Average					19.4

Uncertainty based on SRM1649b (Urban Dust) Control samples (n=10)
 Analysed between July 6, 2011 and August 22, 2011

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Page:
26 of 27

Title: Analytical Method for the Determination of Selected PACs in Ambient Air Samples		Copy No: ##
Method No.: 3.03/5.2/M	Effective Date: September 25, 2013	Location: ###

APPENDIX D
 Form 3.03M/F1-ver*.*

Tracking Sheet #:

SPLIT?

ORGANIC LAB CLEANUP DATA SHEET

Reference Method 3.03/x.x/M

Project Name:

Batch #:

Target Compounds:

SAMPLE CODE #'s:

SPIKE:

DATE

Pipette ID:

Sequence	Complete	EXTRACTION:	DATE:	SOLVENT:
		Pass through Na ₂ SO ₄ (if needed)		
		RV Exchange to Cyclohexane		
		SPLIT - NPAH archive to HPLC Lab		
		Silica Cleanup		
		F1 - Archive		
		F2 - Concentrate to 1.0mL		
		F2 - Concentrate to 0.5mL		
		Add Recovery Standard		
		Pipette ID:		
		Make SRS #		
		Pipette IDs:		
		Deliver to Instrumentation Lab - DATE:		

Notes: