California Environmental Protection Agency

Air Resources Board

Method 429

Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources

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1 INTRODUCTION

1.1 APPLICABILITY

This method applies to the determination of nineteen polycyclic aromatic hydrocarbons (PAH) in emissions from stationary sources. These are listed in Table 1. The sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample as well as the original sample size and instrument sensitivity.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to approval by the Executive Officer of the California Air Resources Board or his or her authorized representative.

1.2 PRINCIPLE

Particulate and gaseous phase PAH are extracted isokinetically from the stack and collected on XAD-2 resin, in impingers, or in upstream sampling train components (filter, probe, nozzle). Only the total amounts of each PAH in the stack emissions can be determined with this method. It has not been demonstrated that the partitioning in the different parts of the sampling train is representative of the partitioning in the stack gas sample for particulate and gaseous PAH.

The required analytical method is isotope dilution mass spectrometry combined with high resolution gas chromatography. This entails the addition of internal standards to all samples in known quantities, matrix-specific extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of extracts and analysis of the processed extract for PAH using high-resolution capillary column gas chromatography coupled with either low resolution mass spectrometry (HRGC/LRMS), or high resolution mass spectrometry (HRGC/HRMS). To ensure comparable results, the same MS method must be used for samples collected at all tested locations at those sources where more than one location is tested.

Minimum performance criteria are specified herein which must be satisfied to ensure the quality of the sampling and analytical data.

1.3 DEFINITIONS AND ABBREVIATIONS

1.3.1 Internal Standard

An internal standard is a ^{2}H-labelled PAH which is added to all field samples, blanks and other quality control samples before extraction. It is also present in the calibration solutions. Internal standards are used to measure the concentration of the analyte and surrogate compounds. There is one internal standard assigned to each of the target analytes and surrogates.

1.3.2 Surrogate Standard

A surrogate standard is a labelled compound added in a known amount to the XAD-2 resin of the sampling train, and allowed to equilibrate with the matrix before the gaseous emissions are sampled. The surrogate standard has to be a component that can be completely resolved, is not present in the sample, and does not have any interference effects. Its measured concentration in the extract is an indication of the how effectively the sampling train retains PAH collected on the XAD-2 resin. The recovery of the surrogate standards in the field blanks can be used to determine whether there are any matrix effects caused by time or conditions under which the sample is transported and stored prior to analysis.

1.3.3 Alternate Standard

An alternate standard is a ^{2}H-labelled PAH compound which is added to the impinger contents prior to extraction to estimate the extraction efficiency for PAHs in the impinger sample.

1.3.4 Recovery Standard

A recovery standard is a ^{2}H-labelled PAH compound which is added to the extracts of all field samples, blanks, and quality control samples before HRGC/MS analysis. It is also present in the calibration solution. The response of the internal standards relative to the recovery standard is used to estimate the recovery of the internal standards. The internal standard recovery is an indicator of the overall performance of the analysis.

1.3.5 Relative Response Factor

The relative response factor is the response of the mass spectrometer to a known amount of an analyte or labelled compound (internal standard or surrogate standard) relative to a known amount of an internal standard or another labelled compound (recovery standard or internal standard).

1.3.6 Performance Standard

A performance standard is a mixture of known amounts of selected standard compounds. It is used to demonstrate continued acceptable performance of the GC/MS system. These checks include system performance checks, calibration checks, quality checks, matrix recovery, and surrogate recoveries.

1.3.7 Performance Evaluation Sample

A performance evaluation sample is one prepared by EPA or other laboratories that contains known concentrations of method analytes, and has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Concentrations must be in the same range as typical field samples. Analyte concentrations are not known by the analyst.

1.3.8 Laboratory Control Sample

A laboratory control sample is one that contains known concentrations of method analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze field samples containing the same analytes. Analyte concentrations are known by the analyst. The laboratory must prepare the control sample from stock standards prepared independently from those used for calibration.

1.3.9 End User

The regulating agency shall be considered the end user if this test method is conducted for regulatory purposes, or the regulating agency shall designate the end user for the purposes of this method. Otherwise the end user shall be the party who defrays the cost of performing this test method. In any case, the pre-test protocol (Section 2) must identify the end user.

1.3.10 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). In some cases, the tester may be part of the regulating agency. The tester shall be the party ultimately responsible for the performance of this test method whether directly or indirectly through the co-ordination of the efforts of the analytical group and the efforts of the sampling group.

1.3.11 Analyst

This term refers to the analytical group that performs the analytical procedures to generate the required analytical data.

1.3.12 Source Target Concentration

This is the target concentration for each emitted PAH of interest specified by the end user of the test results. The target concentration shall be expressed in units of mass of target substance per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/dscm or µg/dscm)

1.3.13 The Method Detection Limit

The method detection limit (MDL) is based on the precision of detection of the analyte concentration near the detection limit. It is the product of the standard deviation of seven replicate analyses of resin samples spiked with low concentrations of the analyte and Student's t value for 6 degrees of freedom at a confidence level of 99%.

1.3.14 The Practical Quantitation Limit

The practical quantitation limit (PQL) is a limit for each compound at or below which data must not be reported. It is the minimum sample mass that must be collected in the sampling train to allow detection during routine laboratory operation within the precision limits established by the

MDL determination. The PQLs will be estimated at 5 times the MDL for those PAH that are not contaminants of the resin. The PQL for the remainder will be estimated at 5 times the blank XAD-2 resin level.

2 THE SOURCE TEST PROTOCOL

Every performance of this test method shall have an identified operator of the source to be tested, an identified end user of the test method results, and an identified tester who performs this test method. Figure 1 is a summary of the responsibilities of the parties involved in the coordination and performance of the source test. The protocol for the entire test procedure should be understood and agreed upon by the responsible parties prior to the start of the test.

2.1 RESPONSIBILITIES OF THE END USER AND THE TESTER

2.1.1 The End User

Before testing may begin, the end user of the test results (1.3.9) shall specify a source target concentration for each of the PAH to be determined by this method using the guidelines of Section 2.2.1.

The end user shall approve the source test protocol only after reviewing the document and determining that the minimum pre-test requirements (Sections 2.2 to 2.5) have been met.

2.1.2 The Tester

The tester (1.3.10) shall have the primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the analytical group and the efforts of the sampling group.

The tester shall be responsible for the selection of an analyst with documented experience in the satisfactory performance of the method. The tester shall obtain from the analyst all of the analytical data (Section 2.3) that are required for pre-test calculations of sampling parameters.

Before performing the rest of this method, the tester shall develop and write a source test protocol (Section 2.2) to help ensure that useful test method results are obtained. The tester shall plan the test based on the information provided by the end user, the results of pre-test surveys of the source, and the tester's calculations of target source testing parameters (Section 2,2).

The tester shall be responsible for ensuring that all of the sampling and analytical reporting requirements (Section 10) are met.

2.1.3 The Analyst

The analyst shall be responsible for performing all of the required analytical procedures described in this test method and reporting the results as required by Sections 2.3, 4.2.1, 4.2.2, 10.1.1, 10.1.2, 10.1.3, and 10.2).

2.2 PRE-TEST REQUIREMENTS

The source test protocol shall specify the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

(1) source target concentration of each emitted PAH of interest (2.2.1),

(2) preliminary analytical data (2.3) for each target PAH, and

(3) planned sampling parameters (2.5.4, 2.5.5, and 2.5.6).

The protocol must demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. The source test protocol shall describe the procedures for all aspects of the source test including information on supplies, logistics, personnel and other resources necessary for an efficient and coordinated test.

The source test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be signed by the end user of the results and the tester.

The tester shall not proceed with the performance of the remainder of this method unless the source test protocol is signed by the tester and the end user.

2.2.1 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. This will be the primary reporting objective of the emissions test. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

2.2.1.1 Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

2.2.1.2 Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

Note that some risk assessment methodologies will assume that a PAH is present at the detection limit or one half of the detection limit even when the compound is not detected. This is inappropriate for planning for the performance of the test method because by definition a substance cannot be detected at one half of its detection limit. In such cases, the target sampling parameter must be the maximum practical sample volume.

2.2.1.3 Interests of the End User, the Tester and the Stationary Source

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user may use emissions results from previous tests of the facility or from similar facilities.

If estimates of the emissions are not available, the tester must conduct a preliminary test at each emissions point of interest. This target concentration is necessary for the calculation of the target sampling parameters required by Section 2.5. Therefore, the emissions measured during the preliminary test must be representative of source operation. The tester must document operating conditions, and know from historical data, the extent to which the results of this preliminary run are representative of emissions from the source. This will require documentation of operating conditions during the preliminary test, and a knowledge of the potential variability in emissions with differences in source operation.

As an alternative to conducting a preliminary test, the end user may specify, as a sampling target, the longest practical sampling time so as to obtain the lowest practically achievable source reporting limit (Section 2.5.6).

2.3 REQUIRED PRELIMINARY ANALYTICAL DATA

2.3.1 Results of Blank Contamination Checks

The tester must obtain from the analyst the results of the PAH contamination checks. The analytical report must satisfy the reporting requirements of Sections 10 and 10.1.

The analyst shall use the procedures described in Sections 4.2.1 and 4.2.2 to clean the sampling media (filters and XAD-2 resin) and check for PAH contamination.

Table 3 shows the results of analyses of different lots of re-cleaned XAD-2 resin. The purpose of this table is to show typical variability. Actual results may vary from one test to another.

2.3.2 The Method Detection Limit

The method detection limit (MDL) must be determined by the same analyst (1.3.11) that will perform the analyses subsequent to sampling. Before estimating the method detection limit (MDL), the analyst shall identify those PAH that are contaminants of the XAD-2 resin using the procedures described in Sections 4.2.2.1 to 4.2.2.4. The analyst shall determine the MDL as described in Section 8.3 and Appendix A.

2.3.3 The Practical Quantitation Limit

The analyst shall calculate the practical quantitation limits (PQLs) for the target PAH. This value will be 5 times the MDL or 5 times the XAD-2 background level for those compounds that have been identified by the analyst as contaminants.

Table 2 lists practical quantitation limits obtained during ARB's development of this method. The values for the PQLs will vary with the performance of individual laboratories. Therefore, the tester must obtain PQL values for all of the target analytes from the analyst .

2.4 EXPECTED RANGE IN TARGET CONCENTRATIONS OF INDIVIDUAL PAHs

The PAH compounds in a source test sample can show large differences in concentrations. A sample that might provide sufficient analyte for the detection and quantitation of the lowest concentration PAH could contain levels of other PAHs that exceed the upper limit of the method.

In some cases the solution is two GC/MS injections - first with the undiluted extract, and then again after appropriate dilution of the extract. At other times the required minimum dilution might be so large as to result in the reduction of the internal standard response below the minimum required by the method. With prior notification of expected levels of the target analytes, the analyst can modify the preparation of the samples so that useful results might be obtained. All major modifications must be approved by the Executive Officer.

2.5 SAMPLING RUNS, TIME, AND VOLUME

2.5.1 Sampling Runs

A test shall include at least three sampling runs in series and a blank sampling train.

2.5.2 Minimum Sample Volume (MSV)

This is the minimum sample volume that must be collected in the sampling train to provide the minimum reportable mass of PAH for quantitation. It must be based on a) the practical quantitation limit (2.3.3), b) the source target concentration (2.2.1), and c) sampling limitations. Use Equation 429-1 to calculate the target MSV for each PAH analyte.

$$\mathrm{MSV\,(dscm)} = \mathrm{PQL} \times \frac{1}{\mathrm{STC}} \qquad \text{429-1}$$

Where:

PQL = The practical quantitation limit, ng/sample (Section 2.3.3)
STC = The source target concentration, ng/dscm (Section 2.2.1)

2.5.3 Minimum Sampling Time (MST)

This is the minimum time required to collect the minimum sample volume at the expected average volumetric sampling rate (VSR). Use Equation 429-2 to calculate the minimum sampling time (MST) required to collect the minimum sample volume calculated in Section 2.5.2. The tester must use an average volumetric sampling rate (VSR) appropriate for the source to be tested.

$$\text{MST (hours)} = \frac{\text{MSV}}{\text{VSR}} \times \frac{1}{0.028317} \times \frac{1}{60} \qquad \text{429-2}$$

Where:

VSR	=	Expected average volumetric sampling rate, dscfm
60	=	Factor to convert minutes to hours
0.028317	=	Factor to convert dscf to dscm

The end user must decide whether the MSTs are all practically feasible and whether they can be increased to allow for any deviation from the sampling and analytical conditions assumed by the test plan. Based on this decision, the tester must use either Section 2.5.4 (a) or 2.5.4 (b) to calculate a planned sample volume (PSV).

2.5.4 Planned Sample Volume (PSV)

This is the volume of emissions that must be sampled to provide the target analytes at levels between the PQL and the limit of linearity. The planned sample volume is the primary sampling target whenever practically feasible. The PSV is calculated according to either 2.5.4 (a) or 2.5.4 (b).

(a) If the end user has decided that the MSTs can be increased, the tester must use Equation 429-3 to calculate the PSV using the largest of the 19 MSV values calculated in Section 2.5.2. and the largest value for F that will give a practically achievable sample volume that provides the target analytes at levels between the PQL and the limit of linearity. Use this PSV to calculate the planned sampling time (Section 2.5.5 a) and Equation 429-6.

(b) If the MSTs are not all practically achievable, the tester and the end user must agree on a maximum practical sampling time (Section 2.5.5b). This value must then be used for the PST in Equation 429-4 to calculate the PSV. The tester must identify in the source test protocol the target analytes for which the PSV is lower than the MSV. The primary reporting objective of the test cannot be achieved for those analytes. If the primary reporting objective cannot be achieved for all of the target analytes, it must be discussed in the protocol and the alternative reporting objective (Section 2.5.6) must be approved by the end user of the results.

The volume of sample that is actually collected will be determined by practical sampling limitations, the intended use of the data and the level of uncertainty that the end user can

tolerate in the measurement of the target concentrations. This uncertainty will decrease as the value of F (Equation 429-5) increases.

$$PSV\,(dscm) = MSV \times F \qquad 429\text{-}3$$

$$PSV\,(dscm) = PST \times VSR \qquad 429\text{-}4$$

$$F = \frac{PSV}{MSV} \qquad 429\text{-}5$$

Where:

PST = Planned sampling time from Section 2.5.5
F = A safety factor (>1) that allows for deviation from ideal sampling and analytical conditions

2.5.5 Planned Sampling Time (PST)

Two options are available for calculating the planned sampling time depending on whether the primary objective can be achieved for all of the target analytes.

(a) The planned sampling time (PST) shall be long enough to 1) collect the planned sample volume with reportable levels of the target analytes and 2) sample representative operating conditions of the source. If the average sampling rate (VSR) used to estimate the planned sampling time cannot be achieved in the field (Section 4.4.4.1), the sampling time must be recalculated using the actual VSR and the target PSV in equation 429-6.

(b) The planned sampling time shall be a practical maximum approved by the end user and it shall be long enough to sample representative operating conditions of the source.

$$PST\,(hours) = \frac{PSV}{VSR} \times \frac{1}{0.028317} \times \frac{1}{60} \qquad 429\text{-}6$$

2.5.6 Preliminary Estimate of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the source reporting limit for each target PAH. The SRL shall be calculated using Equation 429-7. The planned sample volume will contain reportable levels of a given analyte if that analyte is present in the emissions at a concentration that is equal to or greater than the calculated SRL.

$$\text{SRL (ng/dscm)} = \frac{\text{PQL}}{\text{PSV}} \qquad \text{429-7}$$

Where:

SRL	=	Preliminary estimate of source reporting limit, ng/dscm
PQL	=	Practical quantitation limit, ng
PSV	=	Planned sample volume, dscm

2.5.7 Example Calculations

Figure 9 B is an example of the minimum required calculations of sampling parameters for the source test protocol.

3 INTERFERENCES

Interferences may be caused by contaminants in solvents, reagents, sorbents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 6.1.1.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Transformation of PAH and the formation of artifacts can occur in the sampling train. PAH degradation and transformation on sampling train filters have been demonstrated. Certain reactive PAH such as benzo[a]pyrene, benzo[a]anthracene, and fluoranthene when trapped on filters can readily react with stack gases. These PAH are transformed by reaction with low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides.

PAH degradation may be of even greater concern when they are trapped in the impingers. When stack gases such as sulfur oxides and nitrogen oxides come in contact with the impinger water they are converted into sulfuric acid and nitric acid respectively. There is evidence that under such conditions certain PAH will be degraded. It is recommended that the PAH levels in the impingers be used as a qualitative tool to determine if breakthrough has occurred in the resin.

4 SAMPLING APPARATUS, MATERIALS AND REAGENTS

4.1 SAMPLING APPARATUS

The sampling train components listed below are required. All surfaces which may come in contact with the sample or recovery solvents shall be of quartz, borosilcate glass or Teflon. The tester may use an alternative to the required sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

A schematic of the sampling train is shown in Figure 2. The train consists of nozzle, probe, heated particulate filter, condenser, and sorbent module followed by three impingers and a silica gel drying cartridge. An in-stack filter may not be used because at the in-stack temperatures the filter material must be of a material other than the Teflon required by the method. A cyclone or similar device in the heated filter box may be used for sources emitting a large amount of particulate matter.

For sources with a high moisture content, a water trap may be placed between the heated filter and the sorbent module. Additional impingers may also be placed after the sorbent module. If any of these options are used, details must be provided in the test report. The train may be constructed by adaptation of an ARB Method 5 train. Descriptions of the train components are contained in the following sections.

4.1.1 Probe Nozzle

Quartz, or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30^{o} and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1 of ARB method 5.

4.1.2 Probe

The probe must be lined or made of Teflon, quartz, or borosilicate glass. Other inert materials may be used only if they have been approved by the Executive Officer. The liner or probe extends past the retaining nut into the stack. A temperature-controlled jacket provides protection of the liner or probe. The liner shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without the use of sealing greases.

4.1.3 Preseparator

A cyclone, a high capacity impactor or other device may be used if necessary to remove the majority of the particles before the gas stream is filtered. This catch must be used for any

subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other inert materials may be used subject to approval by the Executive Officer.

4.1.4 Filter Holder

The filter holder shall be constructed of borosilicate glass, with a Teflon frit or Teflon coated wire support and glass-to-glass seal or Teflon gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe, cyclone, or nozzle depending on the configuration used. Whenever "O" ring seals are used, they shall be of Teflon or Teflon coated material. Other inert holder and gasket materials may be used subject to approval by the Executive Officer.

4.1.5 Sample Transfer Line

The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings that are capable of forming leak-free, vacuum tight connections without using sealing greases. The line should be as short as possible.

4.1.6 Condenser

The condenser shall be constructed of borosilicate glass and shall be designed to allow the cooling of the gas stream to at least 20^{o}C before it enters the sorbent module. Design for the normal range of stack gas conditions is shown in Figure 3.

4.1.7 Sorbent Module

The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum tight seals without the use of sealant greases (Figure 3). The vertical resin trap is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must have been cooled to 20^{o}C (68^{o}F) or less. The gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

4.1.8 Impinger Train

Connect three or more impingers in series with ground glass fittings able to form leak-free, vacuum tight seals without sealant greases. Whenever "O" ring seals are used, they shall be of Teflon or Teflon coated material. All impingers shall be of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) I.D. glass tube extending to 1.3 cm (1/2 in.)from the bottom of the flask.

The first impinger may be oversized for sampling high moisture streams. The first and second impingers shall contain 100 mL of 3 mM sodium bicarbonate ($NaHCO_3$) and 2.4 mM sodium carbonate (Na_2CO_3) (Section 4.2.5). This is intended to neutralize any acids that might form in

the impingers. The third impinger shall be empty. Silica gel shall be added to the fourth impinger.

A thermometer which measures temperatures to within 1°C (2°F), shall be placed at the outlet of the third impinger.

4.1.9 Silica Gel Cartridge

This may be used instead of a fourth impinger. It shall be sized to hold 200 to 300 gm of silica gel.

4.1.10 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube occurs with other sampling components as part of an assembly, the arrangements must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free arrangements are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

Source-sampling assemblies that do not meet these minimum spacing requirements (or the equivalent of these requirements) may be used only if the pitot tube coefficients of such assemblies have been determined by calibration procedures approved by the Executive Officer.

4.1.11 Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head (ΔP) readings and the other for orifice differential pressure readings.

4.1.12 Metering System

Vacuum gauge, leak-free pump, thermometers accurate to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 2. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

4.1.13 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

4.1.14 Gas Density Determination Equipment

Temperature sensor and pressure gauge, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred configuration and alternative arrangements of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

4.1.15 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder during sampling of (120±14^{o}C) (248±25^{o}F). A temperature gauge capable of measuring temperature to within 3^{o}C (5.4^{o}F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

4.1.16 Balance

To weigh the impingers and silica gel cartridge to within 0.5 g.

4.2 SAMPLING MATERIALS AND REAGENTS

4.2.1 Filters

The filters shall be Teflon coated glass fiber filters without organic binders, or Teflon membrane filters, and shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard Method D 2986-71 (Reapproved 1978). Test data from the supplier's quality control program are sufficient for this purpose. Record the manufacturer's lot number.

4.2.1.1 Contamination Check of Filter

The tester must have the filters cleaned by the analyst and checked for contamination prior to use in the field. The contamination check must confirm that there are no PAH contaminants present that will interfere with the analysis of the sample PAHs of interest at the target reporting limits. The analyst must record the date the filter was cleaned.

The filters shall be cleaned in batches not to exceed 50 filters. To clean the filters, shake for one hour in methylene chloride in a glass dish that has been cleaned according to Section 6.2. After extraction, remove the filters and dry them under a clean N_2 stream. Analyze one filter using the same extraction, clean-up and analysis procedures to be used for the field samples (Sections 6.5.1.2, 6.6, and 7.5).

$$\text{Blank value per filter} = \frac{\text{Total mass (ng) of analyte}}{\text{No. filters extracted}} \qquad \text{429-8}$$

The acceptance criteria for filter cleanliness depends on 1) the method reporting limit, 2) the expected field sample volume and 3) the desired reporting limit for the sampled emissions stream. Filters with PAH levels equal to or greater than the target reporting limit for the analyte(s) of concern shall be rejected for field use.

If the filter does not pass the contamination check, re-extract the batch and analyze a clean filter from the re-extracted batch. Repeat the re-extraction and analysis until an acceptably low background level is achieved. Store the remainder tightly wrapped in clean hexane-rinsed aluminum foil as described in Section 4.3.3.

Record the date of the last cleaning of the filters and the date of the PAH analysis, and prepare a laboratory report of the analytical results that includes all of the information required by Section 10.2.

The tester shall obtain this laboratory report with the date of cleaning of the filters, and the date of the filter contamination check from the analyst, and report them in the source test protocol and the test report as required by Sections 10.1 and 10.3.

4.2.2 Amberlite XAD-2 Resin

The XAD-2 resin must be purchased precleaned and then cleaned again as described below before use in the sampling train.

4.2.2.1 Cleaning XAD-2 Resin

This procedure must be carried out in a Soxhlet extractor which will hold enough XAD-2 for several sorbent traps, method blanks and QC samples. Use an all glass thimble containing an extra coarse frit for extraction of the XAD-2. The frit is recessed 10 to 15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen to prevent floating on the methylene chloride.

Clean the resin by two sequential 24 hour Soxhlet extractions with methylene chloride. Replace with fresh methylene chloride after the first 24 hour period.

4.2.2.2 Drying Cleaned XAD-2 Resin

The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. A 10.2 cm ID Pyrex pipe 0.6 m long with suitable retainers as shown in Figure 4 will serve as a satisfactory column. Connect the liquid nitrogen cylinder to the column by a length of cleaned 0.95 cm ID copper tubing, coiled to pass through a heat source. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40^{o}C.

Continue the flow of nitrogen through the adsorbent until all the residual solvent is removed. The rate of flow should be high enough that the particles are gently agitated but not so high as to cause the particles to break up.

4.2.2.3 Residual Methylene Chloride Check.

Extraction: Weigh a 1.0 g sample of dried resin into a small vial, add 3 mL of hexane, cap the vial and shake it well.

Analysis: Inject a 2 µL sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft x 1/8 in stainless steel containing 10% OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 mL/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250°C.

Detector Temperature: 305°C.

Oven Temperature: 30°C for 4 min; programmed to rise at 40°C per min until it reaches 250°C; return to 30°C after 1000 seconds.

Compare the results of the analysis to the results from a reference solution prepared by adding 2.5 µL of methylene chloride into 100 mL of hexane. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the methylene chloride in the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

4.2.2.4 Contamination Check of XAD-2 Resin

The cleaned, dried XAD-2 resin must be checked for PAH contamination. Analyze a sample of the resin equivalent in size to the amount required to charge one sorbent cartridge for a sampling train. The extraction, concentration, cleanup and GC/MS analytical procedures shall be the same for this sample as for the field samples (Sections 6.5.1.2, 6.6, and 7.5).

The acceptance limit will depend on the PQL, the expected concentration in the sampled gas stream, and the planned sample volume. The contamination level must be less than the PQL or no more than 20 percent of the expected sample level.

If the cleaned resin yields a value for a target analyte which is not acceptable for the end user's intended application of the test results, repeat the extraction unless the analyst has historical data that demonstrate that re-extraction cannot reasonably be expected to further reduce the contamination levels. The tester must obtain these data from the analyst and include them in both the source test protocol and the emissions test report.

The contamination check shall be repeated if the analyst does not have such historical data. The analyst shall reclean and dry the resin (4.2.2.1, 4.2.2.2, and 4.2.2.3) and repeat the PAH analysis of the re-cleaned resin. If the repeat analysis yields a similar result to the first, record the contamination level for both the initial cleaning and the re-cleaning.

The analyst shall record the dates of the cleaning and extraction of the resin, and prepare a laboratory report of the analytical results that includes all of the information required by Section 10.2.

The tester shall obtain the dates of cleaning and the laboratory report of the results of the contamination check from the analyst, and report them in both the source test protocol and the emissions test report as required by Sections 10.1 and 10.3.

The tester shall identify the analytes for which the PQLs will be based on a blank contamination value, and calculate the PQLs as required by Section 2.3.3.

4.2.2.5 Storage of XAD-2 Resin

After cleaning, the resin may be stored in a wide mouth amber glass container with a Teflon-lined cap, or placed in one of the glass adsorbent modules wrapped in aluminum foil and capped or tightly sealed with Teflon film at each end. The containers and modules shall then be stored away from light at temperatures 4^{o}C or lower until the resin is used in the sampling train.

The adsorbent must be used within twenty one (21) days of cleaning. If the adsorbent is not used within 21 days, it must be re-checked for contamination before use.

4.2.3 Silica Gel

Indicating type, 6 to 16 mesh. If previously used, dry at 175^{o}C (350^{o}F) for 2 hours. New silica gel may be used as received. Alternatively, other desiccants (equivalent or better) may be used, subject to approval by the Executive Officer.

4.2.4 Reagent Water

Deionized, then glass-distilled, and stored in hexane- and methylene chloride-rinsed glass containers with TFE-lined screw caps.

4.2.5 Impinger Solution

Sodium bicarbonate 3 mM, and sodium carbonate 2.4 mM. Dissolve 1.0081 g sodium bicarbonate ($NaHCO_3$) and 1.0176 g of sodium carbonate (Na_2CO_3) in reagent water (4.2.4), and dilute to 4 liters.

4.2.6 Crushed Ice

Place crushed ice in the water bath around the impingers.

4.2.7 Glass Wool

Clean by methylene chloride soxhlet extraction for 16 hours. Air dry in a clean container in a clean hood. Store in methylene chloride washed glass jar with TFE-lined screw cap.

4.2.8 Chromic Acid Cleaning Solution

Dissolve 200 g of sodium dichromate in 15 mL of reagent water, and then carefully add 400 mL of concentrated sulfuric acid.

4.3 PRE-TEST PREPARATION

The positive identification and quantitation of PAH in an emissions test of stationary sources are strongly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in Sections 4.3.7 and 8 are to be used to monitor the performance of the sampling methods, identify problems, and take corrective action.

4.3.1 Calibration

All sampling train components shall be maintained and calibrated according to the procedure described in APTD-0576 (Section 11.7), unless otherwise specified herein. The tester shall maintain a record of all calibration data.

4.3.1.1 Probe Nozzle

Probe nozzles shall be calibrated according to the procedure described in ARB Method 5.

4.3.1.2 Pitot Tube

Calibrate the Type S pitot tube assembly according to the procedure described in Section 4 of ARB Method 2.

4.3.1.3 Metering System

Calibrate the metering system before and after use according to the requirements of Section 5.3 of ARB Method 5.

4.3.1.4 Temperature Gauges

Use the procedure in Section 4.3 of ARB Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as those used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

4.3.1.5 Leak-Check of Metering System Shown in Figure 1

The tester shall use the procedure described in Section 5.6 of ARB Method 5

4.3.1.6 Barometer

Calibrate against a mercury barometer.

4.3.2 Cleaning Glassware for Sampling and Recovery

All glass parts of the train upstream of and including the sorbent module and the first impingers shall be cleaned as described in Section 3A of the 1974 issue of Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples (Reference 11.4). Take special care to remove residual silicone grease sealants on ground glass connections of used glassware. These greasy residues shall be removed by soaking several hours in a chromic acid cleaning solution (4.2.8) prior to routine cleaning as described above. Other cleaning procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are stated in Section 8.2.

Rinse all glassware with acetone, hexane, and methylene chloride prior to use in the PAH sampling train.

Glassware used in sample recovery procedures must be rinsed as soon as possible after use with the last solvent used in it. This must be followed by detergent washing with hot water, and rinses with tap water, deionized water, acetone, hexane, and methylene chloride. Other cleaning procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are stated in Section 8.2.

4.3.3 Preparation of Filter

The clean dry filter (4.2.1) must be kept tightly wrapped in hexane-rinsed aluminum foil and stored at 0 to 4^{o}C in a container away from light until sampling. Before inserting the filter in the sampling train, check visually against light for irregularities and flaws or pinhole leaks.

4.3.4 Preparation of Sorbent Cartridge, Method Blank, and Laboratory Control Samples

Sorbent Cartridge

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned resin to completely fill the glass sorbent cartridge which has been thoroughly cleaned as prescribed (4.2.2).

Add the required surrogate standards (Table 7) to the sorbent cartridges for all of the sampling and blank trains for each series of test runs. Follow the resin with hexane-rinsed glass wool, cap both ends, and wrap the cartridge in aluminum foil. Store the prepared cartridges as required by Section 4.3.5.

The sorbent cartridges must be loaded, and the surrogate standards must be added to the resin in a clean area in the laboratory. There must be no turnaround of a used cartridge in the field.

The analyst shall record the date that the surrogate standards were added to the resin and the amount of each compound. The tester shall obtain these data from the analyst and report them in the source test protocol and the test report.

The appropriate levels for the surrogate standards are given in Table 7 which shows the spiking plan for surrogate standards, internal standards, alternate standards, and recovery standards. All of these required compounds are generally available. Additional labelled PAH may also be used if available. The labelled compounds used as surrogate standards must be different from the internal standards used for quantitation, and from the alternate and recovery standards. If the spiking scheme (Table 7) is modified, the tester must demonstrate that the proposed modification will generate data of satisfactory quality. Table 7A shows an approved modification that has been used in ARB's method development. All modifications must be approved by the Executive Officer before the emissions test is performed.

Laboratory Method Blank

Take a sample of XAD-2 resin from the same batch used to prepare the sampling cartridge. This will serve as the laboratory method blank (Section 8.1.1). The mass of this sample must be the same as that used in the sampling train. Spike with the same surrogate standards at the same levels used in the sampling cartridges.

Laboratory Control Sample

Set aside two samples of XAD-2 resin from the same batch used to prepare the sampling cartridge. These will serve as the laboratory control samples. (Section 8.1.3). The mass of each sample must be the same as that used in the sampling train.

4.3.5 Storage of Prepared Cartridges, Method Blank and Laboratory Control Sample

Store the aluminum foil wrapped sorbent cartridges away from light at 4^{o}C or lower until they are fitted into the sampling trains. Do not remove the caps before the setup of the sampling train.

The maximum storage time from cleaning of the resin to sampling with the spiked resin cartridge must not exceed 21 days (4.2.2.5).

Store the laboratory method blank and laboratory control samples in amber glass jars with Teflon-lined lids at temperatures no higher than 4^{o}C.

4.4 SAMPLE COLLECTION

Because of the complexity of this method, testers must be experienced with the test procedures in order to ensure reliable results.

4.4.1 Preliminary Field Determinations

Select the sampling site and the minimum number of sampling points according to ARB Method 1 or as specified by the Executive Officer.

Determine the stack pressure, temperature, and the range of velocity heads using ARB Method 2. Conduct a leak-check of the pitot lines according to ARB Method 2, Section 3.1.

Determine the moisture content using ARB Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings.

Determine the stack gas dry molecular weight, as described in ARB Method 2, Section 3.6. If integrated sampling (ARB Method 3) is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. Do not change the nozzle size during the run. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of ARB Method 2).

Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

The target sample volume and sampling time must already have been calculated for the source test protocol and approved by the end user as required by Sections 2.2 and 2.5. The total sampling time must be such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Executive Officer), and (2) the total gas sample volume collected (corrected to standard conditions) will not be less than the target value calculated for the source test protocol (Section 2.5.5).

To avoid timekeeping errors, the number of minutes sampled at each point should be an integer or an integer plus one-half minute.

4.4.2 Preparation of Collection Train

Keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Caution: Do not use sealant greases in assembling the sampling train.

Record the performance of the setup procedures for the sampling train. Figure 10 is an example of a form for recording the sampling train setup data. The tester must record all of the routine information indicated on this form as well as any additional data which are necessary for documenting the quality of any reported results.

Place 100 ml of the impinger solution (4.2.5) in the first impinger and weigh. Record the total weight. Repeat the procedure for the second impinger. Leave the third impinger empty. Weigh the empty third impinger and record the weight.

Weigh 200 to 300 g of silica gel to the nearest 0.5 g directly into a tared impinger or silica gel cartridge just prior to assembly of the sampling train. The tester may optionally measure and record in advance of test time the weights of several portions of silica gel in air-tight containers.

One portion of the preweighed silica gel must then be transferred from its container to the silica gel cartridge or fourth impinger. Place the container in a clean place for later use in the sample recovery.

Using tweezers or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly of the filter holder is completed.

Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Assemble the train as in Figure 2. Place crushed ice around the impingers.

4.4.3 Leak-Check Procedures

4.4.3.1 Pretest Leak-Check

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperature to stabilize. Leak-check the train at the sampling site by plugging the nozzle with a TFE plug and pulling a vacuum of at least 380 mm Hg (15 in. Hg).

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

The following leak-check instructions for the sampling train are described in Section 4.1.4.1 of ARB Method 5. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse the direction of the by-pass valve. This will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as described below and start over.

Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3 per min. (0.02 cfm), whichever is less, is unacceptable. Repeat the leak-check procedure until an acceptable leakage rate is obtained. Record the leakage rate on the field data sheet (Figure 5).

When the leak-check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

4.4.3.2 Leak-Checks During Sample Run

If, during the sampling run, it becomes necessary to change a component (e.g., filter assembly or impinger), a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure described in Section 4.4.3.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than

0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either (1) record the leakage rate and correct the volume of gas sampled since the last leak-check as shown in Section 4.4.3.4 below, or (2) void the sampling run. Record the leakage rate.

Immediately after component changes, leak-checks must be conducted according to the procedure outlined in Section 4.4.3.1 above. Record the leakage rate on the field data sheet (Figure 5).

4.4.3.3 Post Test Leak-Check

A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.4.3.1 except that it shall be conducted at a vacuum equal to or greater than the maximum value recorded during the sampling run. Record the leakage rate on the field data sheet (Figure 5). If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either, (1) record the leakage rate and correct the sample volume as shown in Section 4.4.3.4 below, or (2) void the sampling run.

4.4.3.4 Correcting for Excessive Leakage Rates

If the leakage rate observed during any leak-check after the start of a test exceeds the maximum leakage rate L_a (see definition below), replace V_m in Equation 429-9 with the following expression.

$$V_m - \sum_{i=1}^{n} (L_i - L_a)\theta_i - (L_p - L_a)\theta_p \qquad 429\text{-}9$$

Where:

V_m = Volume of gas sampled as measured by the dry gas meter (dscf).

L_a = Maximum acceptable leakage rate equal to 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.

L_p = Leakage rate observed during the post-test leak-check, m^3/min (ft^3/min).

L_i = Leakage rate observed during the leak-check performed prior to the "ith" leakcheck (i = 1,2,3...n), m^3/min (ft^3/min).

θ_i = Sampling time interval between two successive leak-checks beginning with the interval between the first and second leak-checks, min.

θ_p = Sampling time interval between the last (n^{th}) leak-check and the end of the test, min.

Substitute only for those leakage rates (L_i or L_p) which exceed L_a.

4.4.4 Train Operation

No smoking is allowed.

4.4.4.1 Sampling Train

During the sampling run maintain a sampling rate within 10 percent of true isokinetic, unless otherwise specified or approved by the Executive Officer. The actual sampling rate must be at or above the VSR (Equation 429-4) to collect the target sample mass in the estimated sampling time. If the target sampling rate cannot be achieved, adjust the planned sampling time to achieve the target sample volume (PSV).

For each run, record the data required on the sample data sheet shown in Figure 5. The operator must record the dry gas meter reading at the beginning of the test, at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted.

Record other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate.

Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream.

Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85±0.02, and the stack gas equivalent density (dry molecular weight) (M_d) is equal to 29±4. APTD-0576 (Reference 11.7) details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 11.8) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Turn on the recirculating pump for the adsorbent module and the condenser, and begin monitoring the temperature of the gas entering the adsorbent trap. Ensure that the temperature of the gas is 20^{o}C or lower before sampling is started.

Traverse the stack cross section, as required by ARB Method 1 or as specified by the Executive Officer, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes. This minimizes the chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain the temperature at the condenser outlet below 20^{o}C (68^{o}F). Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced during a sample run. Another complete filter assembly must be used rather than changing the filter itself. Before a new filter assembly is installed, conduct a leak-check as outlined in Section 4.4.3.2. The total PAH analysis shall include the combined catches of all filter assemblies.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to approval by the Executive Officer.

Note that when two or more trains are used, a separate analysis of each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 4.4.3.3. Also, leak-check the pitot lines as described in ARB Method 2; the lines must pass this leak-check, in order to validate the velocity head data. Record leakage rates.

Record any unusual events during the sampling period.

4.4.4.2 Blank Train

There shall be at least one blank train for each series of three or fewer test runs. For those sources at which emissions are sampled at more than one sampling location, there shall be at least one blank train assembled at each location for each set of three or fewer runs. Prepare and set up the blank train in a manner identical to that described above for the sampling trains. The blank train shall be taken through all of the sampling train preparation steps including the leak-check without actual sampling of the gas stream. Recover the blank

train as described in Section 5.3. Follow all subsequent steps specified for the sampling train including extraction, analysis, and data reporting.

4.4.5 Calculation of Percent Isokinetic

Calculate percent isokinetic (Section 4.5.7) to determine whether the run should be repeated. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Executive Officer for possible variance on the isokinetic rates.

4.5 CALCULATIONS

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

4.5.1 Nomenclature

A = Cross-sectional area of stack, ft^2.

A_n = Cross-sectional area of nozzle, ft^2.

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_s = Concentration of PAH in stack gas, ng/dscm, corrected to standard conditions of 20^oC, 760 mm Hg (68^oF, 29.92 in. Hg) on dry basis.

G_s = Total mass of PAH in stack gas sample, ng.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

I = Percent isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "ith" component change (i = 1, 2, 3, ...n), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).

M_d = Molecular weight of stack gas, dry basis, lb/lb-mole (g/g-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

M_s = Molecular weight of stack gas, wet basis, lb/lb-mole (g/g-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{std} = Dry volumetric stack gas flow rate corrected to standard conditions, dscf/min (dscm/min).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

R = Ideal gas constant 0.06236 mm Hg-$m^3/^oK$-g-mole (21.85 in Hg-ft^3/R-lb-mole).

T_m = Absolute average dry gas meter temperature, ^oK (^oR).

T_s = Absolute average stack gas temperature ^oK (^oR).

T_{std} = Standard absolute temperature, 293^oK (528^oR).

V_{1c} = Total volume of liquid collected in impingers and silica gel, mL.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf).

v_s = Stack gas velocity, calculated by ARB Method 2, Equation 2-9, ft/sec (m/sec).

Y = Dry gas meter calibration factor.

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

φ_w = Sampling time interval, from the final (n^{th}) component change until

13.6 = Specific gravity of mercury.

60 = Conversion factor, sec/min.

100 = Conversion to percent.

4.5.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See sampling run record (Figure 5).

4.5.3 Dry Gas Volume

Use Equation 429-10 to correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in Hg).

$$V_{m(std)} = V_m \, Y \, \frac{T_{std}}{T_m} \, \frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{P_{std}} = K_1 \, V_m \, Y \, \frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m} \qquad \text{429-10}$$

Where:

$$K_1 = \frac{T_{std}}{P_{std}} = 0.3858 \ ^oK/\text{mm Hg for metric units}$$

$$= 17.65 \ ^oR/\text{in Hg for English units}$$

NOTE: Equation 429-10 may be used as written unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, V_m in Equation 429-10 must be modified as described in Section 4.4.3.4.

4.5.4 Average Stack Gas Velocity

Calculate the average stack gas velocity, v_s, as specified in ARB Method 2, Section 5.2.

4.5.5 Volume of Water Vapor

Calculate the volume of water vapor using Equation 429-11 and the weight of the liquid collected during sampling (Sections 5.3.6 and 5.3.8).

$$V_{w(std)} = V_{1c} \, \frac{\rho_w}{M_w} \, \frac{RT_{std}}{P_{std}} = K_2 \, V_{1c} \qquad \text{429-11}$$

Where:

K_2 = 0.001333 m^3/mL for metric units, or
= 0.04707 ft^3/mL for English units.

4.5.6 Moisture Content

Calculate the moisture content of the gas, B_{ws}.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad 429\text{-}12$$

NOTE: In saturated or water-droplet laden streams, the procedure for determining the moisture content is given in the note to Section 1.2 of Method 4. For the purpose of this method, the average stack-gas temperature from Figure 5 may be used for this determination, provided that the accuracy of the in-stack temperature sensor is ±1°C (2°F)

4.5.7 Isokinetic Variation

4.5.7.1 Calculation from Raw Data

$$I = \frac{100\,T_s \left[K_3 V_{1c} + \frac{V_m Y}{T_m} \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60\ \theta\ v_s\ P_s\ A_n} \qquad 429\text{-}13$$

Where:

K_3 = 0.003454 mm Hg-m^3/mL-°K for metric units

= 0.002669 in Hg-ft^3/mL-°R for English units

4.5.7.2 Calculation from Intermediate Values

$$I = \frac{100\,T_s\ V_{m(std)}\ P_{std}}{T_{std}\ v_s\ \theta\ A_n\ P_s\ 60\ (1 - B_{ws})} \qquad 429\text{-}14$$

$$= K_4 \frac{T_s\ V_{m(std)}}{P_s\ v_s\ \theta\ A_n\ (1 - B_{ws})}$$

Where:

K_4 = 4.320 for metric units.

= 0.09450 for English units.

4.5.8 Average stack gas dry volumetric flow rate

Use Equation 429-15 to calculate the average dry volumetric flow rate of the gas.

$$Q_{std} = 60\ K_1\ (1 - B_{ws})\ v_s\ A \left(\frac{P_s}{T_s} \right) \qquad 429\text{-}15$$

Where:

$$K_1 = \frac{T_{std}}{P_{std}} = 0.3858\ ^{o}K/mm\ Hg \text{ for metric units}$$

= 17.65 ^{o}R/in Hg for English units

4.6 ISOKINETIC CRITERIA

If 90 percent < I < 110 percent, the isokinetic results are acceptable. If there is a bias to the results because I < 90 percent or I > 110 percent, then the results must be rejected and the test repeated, unless the test results are accepted by the Executive Officer.

5 SAMPLE RECOVERY

5.1 SAMPLE RECOVERY APPARATUS

5.1.1 Probe Nozzle Brush

Teflon brush with Teflon handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

5.1.2 Wash Bottles

Teflon wash bottles are required; Teflon FEP®.

5.1.3 Glass Sample Storage Containers

Precleaned narrow mouth amber glass bottles, 500 mL or 1000 mL. Screw cap liners shall be Teflon.

5.1.4 Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with Teflon-lined screw caps.

5.1.5 Balance

To measure condensed water to within 0.5 g.

5.1.6 Silica Gel Storage Containers

Air tight metal containers to store silica gel.

5.1.7 Funnel and Rubber Policeman

To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

5.1.8 Funnel

To aid in sample recovery. Glass or Teflon® must be used.

5.1.9 Ground Glass Caps or Hexane Rinsed Aluminum Foil

To cap off adsorbent tube and the other sample-exposed portions of the aluminum foil.

5.1.10 Aluminum Foil

Heavy-duty, precleaned with methylene chloride.

5.2 SAMPLE RECOVERY REAGENTS

5.2.1 Reagent Water

Deionized (DI), then glass distilled, and stored in hexane and methylene chloride-rinsed glass containers with TFE-lined screw caps.

5.2.2 Acetone

Nanograde quality. "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

5.2.3 Hexane

Nanograde quality. "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

5.2.4 Methylene Chloride

Nanograde quality or equivalent. A blank must be screened by the analytical detection method.

5.3 SAMPLE RECOVERY PROCEDURE

No smoking is allowed.

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period and a post test leak-check has been performed (4.4.3.3). Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle. Conduct the post test leak-check as described in Section 4.4.3.3. Remove the probe from the train and close off both ends of the probe with precleaned aluminum foil (5.1.10). Seal off the inlet to the train with a ground glass cup or precleaned aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area must be clean, and enclosed so that the chances of contaminating the sample will be minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions, broken filters, color of the impinger liquid, etc. Figure 6 summarizes the recovery procedure described in Sections 5.3.1 to 5.3.8.

Figure 11 is an example of a form for recording the performance of the sample recovery procedure. The tester must record all of the routine information indicated on this form as well as any additional data which are necessary for documenting the quality of any reported results.

5.3.1 Sample Container No. 1 (front half rinses)

Quantitatively recover material deposited in the nozzle, probe, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with acetone, hexane, and methylene chloride three times each. Place all these rinses in Container No.1. Mark the liquid level.

5.3.2 Cyclone Catch

If the optional cyclone is used, quantitatively recover the particulate matter by sequentially rinsing the cyclone with acetone, hexane, and methylene chloride. Store in a clean sample container and cap.

5.3.3 Sample Container No. 2 (filter)

Carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. Do not wrap the filter in aluminum foil. If it is necessary to fold the filter, make sure that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

5.3.4 Sorbent Module

Remove the sorbent module from the train and cap it.

5.3.5 Sample Container No. 3 (back half rinses)

Rinse the back half of the filter holder, the transfer line between the filter and the condenser, and the condenser (if using the separate condenser-sorbent trap) three times each with acetone, hexane and methylene chloride, and collect all rinses in Container No. 3. If using the combined condenser/sorbent trap, the rinse of the condenser shall be performed in the laboratory after removal of the XAD-2 portion. If the optional water knockout trap has been employed, the contents and rinses shall be placed in Container No. 3. Rinse it three times each with acetone, hexane, and methylene chloride. Mark the liquid level.

The back half rinses may also be combined in a single container with the front half rinses (Section 5.3.1).

5.3.6 Sample Container No. 4 (Impinger contents)

Wipe off the outside of each of the first three impingers to remove excess water and other material. Weigh the impingers and contents to the nearest ±0.5 g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the silica gel (Section 5.3.8) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6). Pour the impinger catch directly into Container No. 4. Mark the liquid level.

5.3.7 Sample Container No. 5 (Impinger rinses)

Rinse each impinger sequentially three times with acetone, hexane, and methylene chloride and pour rinses into Container No. 5. Mark the liquid level. These rinses may be combined with the previously weighed impinger contents in Container No. 4.

5.3.8 Weighing Silica Gel

Weigh the spent silica gel to the nearest 0.5 g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the impingers (Section 5.3.6) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6). .

5.4 SAMPLE PRESERVATION AND HANDLING

From the time of collection to extraction, maintain all samples (Sections 5.3.1 to 5.3.7) at 4^{o}C or lower and protect from light. All samples must be extracted as soon as practically feasible, but within 21 days of collection; and all extracts must be analyzed as soon as practically feasible, but within 40 days of extraction. Success in meeting the holding time requirement will depend on pre-test planning by the tester and the laboratory.

6 ANALYTICAL PREPARATION

This method is restricted to use only by or under the supervision of analysts experienced in the use of capillary column gas chromatography/mass spectrometry and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedures described in Sections 7.3, 8.2.6, and 8.3.1.

6.1 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Nevertheless, each chemical compound should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Reference 11.9 describes procedures for handling hazardous chemicals in laboratories.

The following method analytes have been classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene and dibenzo- (a,h,)anthracene. A guideline for the safe handling of carcinogens can be found in Section 5209 of Title 8 of the California Administrative Code.

6.2 CLEANING OF LABORATORY GLASSWARE

Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) must be cleaned as soon as possible after use by rinsing with the last solvent used in it. This must be followed by detergent washing with hot water, and rinses with tap water, deionized water, acetone, hexane, and methylene chloride. Other cleaning procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are given in Section 8.2.

Clean aluminum foil with acetone followed by hexane and methylene chloride.

6.3 APPARATUS

6.3.1 Grab Sample Bottle

Amber glass, 125-mL and 250-mL, fitted with screw caps lined with Teflon. The bottle and cap liner must be acid washed and solvent rinsed with acetone and methylene chloride, and dried before use.

6.3.2 Concentrator Tube, Kuderna-Danish

10-mL, graduated (Kontes-K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper must be used to prevent evaporation of extracts.

6.3.3 Evaporation Flask, Kuderna-Danish

500-mL (Kontes K-570001-0500 or equivalent). (Attached to concentrator tube with springs).

6.3.4 Snyder Column, Kuderna-Danish

Three-ball macro (Kontes K-569001-0121 or equivalent).

6.3.5 Snyder Column, Kuderna-Danish

Two-ball micro (Kontes K-569001-0219 or equivalent).

6.3.6 Minivials

1.0 mL vials; cone-shaped to facilitate removal of very small samples; heavy wall borosilicate glass; with Teflon-faced rubber septa and screw caps.

6.3.7 Soxhlet Apparatus

1 liter receiver, 1 heating mantle, condenser, Soxhlet extractor.

6.3.8 Rotary Evaporator

Rotovap R (or equivalent), Brinkmann Instruments, Westbury, NY.

6.3.9 Nitrogen Blowdown Apparatus

N-Evap Analytical Evaporator Model 111 (or equivalent), Organomation Associates Inc., Northborough, MA.

6.3.10 Analytical Balance

Analytical. Capable of accurately weighing to the nearest 0.0001 g.

6.3.11 Disposable Pipet

5 3/4 inch x 7.0 mm OD.,

6.4 SAMPLE PREPARATION REAGENTS

6.4.1 Reagent water

Same as 5.2.1.

6.4.2 Acetone

Same as 5.2.2.

6.4.3 Hexane

Same as 5.2.3.

6.4.4 Methylene Chloride

Same as 5.2.4.

6.4.5 Sulfuric Acid

ACS. Reagent grade. Concentrated, sp. gr. 1.84.

6.4.6 Sodium Sulfate

ACS. Reagent grade. Granular, anhydrous. Purify prior to use by extracting with methylene chloride and oven drying for 4 or more hours in a shallow tray. Place the cleaned material in a glass container with a Teflon-lined screw cap, and store in a desiccator.

6.4.7 Silica Gel

For column chromatography, type 60, EM reagent, 100-200 mesh, or equivalent. Soxhlet extract with methylene chloride, and activate by heating in a foil covered glass container for longer than 16 hours at 130 ^{o}C, then store in a desiccator. The storage period shall not exceed two days.

NOTE: The performance of silica gel in the column cleanup procedure varies with manufacturers and with the method of storage. The analyst shall establish a procedure that satisfies the performance criteria of Section 6.6.1.

6.4.8 Alumina: Acidic

Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 190 ^{o}C.

NOTE: The performance of alumina in the column cleanup procedure varies with manufacturers and with the method of storage. The analyst shall establish a procedure that meets the performance criteria of Section 6.6.1.

6.4.9 Nitrogen

Obtained from bleed from liquid nitrogen tank.

6.5 SAMPLE EXTRACTION

WARNING: Stack sampling will yield both liquid and solid samples for PAH analysis. Samples must not be split prior to extraction even when they appear homogeneous as in the case of single liquid phase samples. Solid samples such as the resin are not homogeneous and particulate matter may not be uniformly distributed on the filter. In addition, filter samples are generally so small that the desired detection limit might not be achieved if the sample were split.

The recovered samples may be combined as follows:

1) Particulate filter and particulate matter collected on the filter (Section 5.3.3), cyclone catch (Section 5.3.2) and sample container No. 1 (Section 5.3.1).

2) Sample container No. 3 (Section 5.3.5), resin (Section 5.3.4) and rinse of resin cartridge.

3) Sample container No.4 (Section 5.3.6) and sample container No.5 (Section 5.3.7)

Two schemes for sample preparation are described in Sections 6.5.1 and 6.5.2 below. One of these must be used.

Section 6.5.1 describes sample preparation procedures for separate GC/MS analyses of impingers and the remainder of the sampling train. Figure 7 is a flowchart of the extraction and cleanup procedures.

Section 6.5.2 describes sample preparation procedures for GC/MS analysis of a single composite extract from each sampling train. The recovered samples are combined as shown in Figure 8.

6.5.1 Separate Analysis of Impingers

A separate analysis of the impingers can be used to determine whether there has been breakthrough of PAHs past the resin.

6.5.1.1 Extraction of Liquid Samples

A. Sample Container No. 1 (Front half rinses)

Concentrate the contents of sample container No. 1 (Section 5.3.1) to a volume of about 1-5 mL using the nitrogen blowdown apparatus. Rinse the sample container three times with small amounts of methylene chloride and add these rinses to the concentrated solution. Concentrate further to about 1-5 mL. This residue will likely contain particulate matter which was removed in the rinses of the probe and nozzle. Transfer the residue (along with three rinses of the final sample vessel) to the Soxhlet apparatus with the filter and particulate catch and proceed as described under Section 6.5.1.2 below.

B. Sample Container No. 3 (Back half rinses)

Concentrate the contents of sample container No. 3 (Section 5.3.5) to a volume of about 1-5 mL using the nitrogen blowdown apparatus. Rinse the sample container three times with small amounts of methylene chloride and add these rinses to the concentrated solution. Concentrate further to about 1-5 mL. Combine this residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the resin sample, and proceed as described under Section 6.5.1.2 below.

C. Containers No. 4 and No. 5 (Impinger contents and rinses)

Place the contents of Sample Containers No. 4 and No. 5 (Sections 5.4.6 and 5.4.7) in a separatory funnel. Add the appropriate amount of ^{2}H-labelled alternate standard solution (Section 7 and Table 7 or 7A) to achieve the final extract concentrations indicated in Table 8 or 8A. The amounts required by Section 7.2.4 are based on a final volume of 500 µL for analysis (450 µL of sample extract and 50 µL of recovery standard solution). Extract the sample three times with 60 mL aliquots of methylene chloride. Combine the organic fractions. Divide the extract in two: one half to be archived, and the other for cleanup and GC/MS analysis. Store the archive sample at 4^{o}C away from light.

Pour the remaining extract through Na_2SO_4 into a round bottom flask. Add 60 to 100 mL hexane and evaporate to about 10 mL. Repeat three times or less if the methylene chloride can be removed with less hexane. Add the appropriate amount of alternate standard (Section 7.2.7) to achieve the final extract concentrations shown in Table 6 or 6A. This standard must be used to monitor the efficiency of the cleanup procedure.

Concentrate the remaining sample to 2 mL with a Kuderna-Danish concentrator or rotary evaporator, then transfer the extract to a 8 mL test tube with hexane. Proceed with sample cleanup procedures below (Section 6.6).

6.5.1.2 Extraction of Solid Samples

Filter, Particulate matter, and Resin

The Soxhlet apparatus must be large enough to allow extraction of the sample in a single batch. Clean the Soxhlet apparatus by a 4 to 8 hr Soxhlet with methylene chloride at a cycling rate of 3 cycles per hour. Discard the solvent. Add 20 g Na_2SO_4 to the thimble. Combine the filter, resin, glass wool, and concentrated front and back half rinses (6.5.1.1A and 6.5.1.1B) and place on top of the Na_2SO_4. Add the appropriate amount of internal standard (Section 7.2.4 and Table 7) to achieve the final extract concentrations indicated in Table 8.

Place the thimble in the Soxhlet apparatus, and add about 700 mL of methylene chloride to the receiver. Assemble the Soxhlet, turn on the heating controls and cooling water, and allow to reflux for 16 hours at a rate of 3 cycles per hour. After extraction, allow the Soxhlet to cool. Divide the sample in two: one half to be archived, and the other for cleanup and GC/MS analysis. Store the archive sample at 4^{o}C away from light.

Exchange the remaining extract to hexane. Add 60 to 100 mL hexane and evaporate to about 10 mL. Repeat three times or as necessary to remove the methylene chloride. Add the appropriate amount of alternate standard (Section 7.2.7 and Table 7 or 7A) to achieve the final extract concentrations shown in Table 8 or 8A. This alternate standard must be used to monitor the efficiency of the cleanup procedure when the impingers are analyzed separately from the remainder of the sampling train.

Concentrate the remaining sample to about 2 mL with a Kuderna-Danish concentrator or rotoevaporator, then transfer the extract to a 8-mL test tube with hexane. Proceed with sample cleanup procedures below (Section 6.6).

6.5.2 Single Composite Extract For Analysis

6.5.2.1 Extraction of Aqueous Samples

Containers No. 4 and No. 5 (Impinger contents and rinses)

Pour the contents of Sample Containers No. 4 and No. 5 (Sections 5.3.6 and 5.3.7) into an appropriate size separatory funnel. Do not add internal standards. Instead, add the appropriate amount of alternate standard spiking solution (Section 7 and Table 7 or 7A) to achieve the final extract concentrations indicated in Table 8 or 8A.

Extract the sample three times with 60 mL aliquots of methylene chloride. Combine the organic fractions with the solid samples and concentrated rinses (6.5.2.2) in a Soxhlet extractor.

6.5.2.2 Extraction of Solid Samples

Concentrate the front and back half rinses as described in Sections 6.5.1.1A and 6.5.1.1B. Clean the Soxhlet apparatus as in Section 6.5.1.2. Place the filter and resin in the Soxhlet apparatus along with the concentrated front and back half rinses and the impinger extract. Add the internal standards, extract the sample, and concentrate the extract as described in Section 6.5.1.2. Divide the extract into two equal portions. Store one of these, the archive sample, at 4 ^{o}C away from light. The remaining extract must be exchanged to hexane as described in Section 6.5.1.2. Do not add the alternate standard to this composite extract. It has already been added to the impinger sample (6.5.2.1).

Concentrate the extract to 2 mL with a Kuderna-Danish concentrator or rotary evaporator, then transfer to a 8-mL test tube with hexane or equivalent non-polar solvent such as isooctane. Proceed with sample cleanup procedures below (Section 6.6)

6.6 COLUMN CLEANUP

Several column chromatographic cleanup options are available. Either of the two described below may be sufficient. Before using a procedure for the cleanup of sample extracts, the analyst must demonstrate that the requirements of Sections 8.1.3.1 and 8.2.6 can be met using the cleanup procedure. Acceptable alternative cleanup procedures may also be used provided that the analyst can demonstrate that the performance requirements of Sections 8.1.3.1 and 8.2.6 can be met. Compliance with the requirements of Sections 8.1.1.1 and 8.2.6 must also be demonstrated whenever there is a change in the column cleanup procedure used for the initial demonstration.

The sample extract obtained as described in Sections 6.5.1C and 6.5.1.2 or 6.5.2.2 is concentrated to a volume of about 1 mL using the nitrogen blowdown apparatus, and this is transferred quantitatively with hexane rinsings to at least one of the columns described below.

6.6.1 Column Preparation

A. Silica Gel Column

Pack a glass gravity column (250 mm x 10 mm) in the following manner:

Insert a clean glass wool plug (Section 4.2.7) into the bottom of the column and add 10 grams of activated silica gel (Section 6.4.7) in methylene chloride. Tap the column to settle the silica gel, and then add a 1 cm layer of anhydrous sodium sulfate (Section 6.4.6)

Variations among batches of silica gel may affect the elution volume of the various PAH. Therefore, the volume of solvent required to completely elute all of the PAH must be verified by the analyst. The weight of the silica gel can then be adjusted accordingly. Satisfactory recovery (as defined in Section 6.6) of each native PAH in the LCS (8.1.3) must be demonstrated whenever there is a change in the method of preparing the silica gel columns.

B. Acid Alumina Column

Pack a 250 mm x 10 mm glass gravity column as follows:

Insert a clean glass wool plug (Section 4.2.7) into the bottom of the column. Add 6 g of acid alumina prepared as described in Section 6.4.8. Tap the column gently to settle the alumina, and add 1 cm of anhydrous sodium sulfate to the top.

Satisfactory recovery (as defined in Section 6.6) of each native PAH in the LCS (8.1.3) must be demonstrated whenever there is a change in the method of preparing the acid alumina columns.

6.6.2 Column Chromatography Procedure

A. Silica Gel Column

Elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 mL sample extract onto the column using two additional 2 mL rinses of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, begin elution of the column with 25 mL of hexane followed by 25 mL of methylene chloride/hexane (2:3)(v/v). Collect the entire eluate. Concentrate the collected fraction to about 5 mL using the K-D apparatus or a rotary evaporator. Do not allow the extract to go to dryness.

Transfer to a minivial using a hexane rinse and concentrate to 450 µL using a gentle stream of nitrogen. Store the extracts in a refrigerator at 4 ^{o}C or lower away from light until GC/MS analysis (Section 7).

B. Alumina Column

Elute the column with 50 mL of hexane. Let the solvent flow through the column until the head of the liquid in the column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow.

Transfer 1 mL of the sample extract onto the column. Rinse out extract vial with two 1 mL rinses of hexane and add it to the top of the column immediately. To avoid overloading the column, it is suggested that no more than 300 mg of extractable organics be placed on the column.

Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 2 mL of hexane was used as a rinse, then 12 mL of additional hexane should be used. Collect the effluent and concentrate to about 2 mL using the K-D apparatus or a rotary evaporator.

Transfer to a minivial using a hexane rinse and concentrate to 450 µL using a gentle stream of nitrogen. Store the extracts at 4^{o}C or lower away from light until GC/MS analysis.

7 GC/MS ANALYSIS

7.1 APPARATUS

7.1.1 Gas Chromatograph

An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The GC injection port must be designed for capillary columns. Splitless injection is recommended.

7.1.2 Column

Fused silica columns are required.

A. 30 M long x 0.32 mm ID fused silica capillary column coated with a crosslinked phenyl methyl silicone such as DB-5.

B. Any column equivalent to the DB-5 column may be used as long as it has the same separation capabilities as the DB-5.

7.1.3 Mass Spectrometer

7.1.3.1 Low Resolution

A low resolution mass spectrometer (LRMS) equipped with a 70 eV (nominal) ion source operated in the electron impact ionization mode, and capable of monitoring all of the ions in each Selected Ion Monitoring (SIM) group (Table 13) with a total cycle time of 1 second or less.

7.1.3.2 High Resolution

The high resolution mass spectrometer (HRMS) must be capable of operation in the SIM mode at a resolving power of 8,000. Electron impact ionization must be used. The mass spectrometer must be capable of monitoring all of the ions listed in each of the three SIM descriptors (Table 14) with a total cycle time of 1 second or less.

7.1.4 GC/MS Interface

Any gas chromatograph to mass spectrometer interface may be used as long as it gives acceptable calibration response for each analyte of interest at the desired concentration and achieves the required tuning performance criteria (Sections 7.3.5 and 7.3.6). All components of the interface must be glass or glass-lined materials. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the mass spectrometer ion source without being exposed to the ionizing electron beam.

7.1.5 Data Acquisition System

A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and plot a Selected Ion Current Profile or SICP (a plot of the abundances of the selected ions versus time or scan number). Software must also be able to integrate, in any SICP, the abundance between specified time or scan-number limits.

The data system must provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals.

The data system must also be able to provide hard copies of a summary report of the results of the GC/MS runs. Figures 14A to 14C show the minimum data that the system must be available to provide.

7.2 REAGENTS

7.2.1 Stock Standard Solution (1.00 µg/µL)

Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.2.2 Preparation of Stock Solutions

A. Calibration standards. Prepare stock calibration standard solutions of each of the PAH analytes by accurately weighing the required amount of pure material. Dissolve the material in isooctane and dilute to volume. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

B. Internal standards. Prepare stock solutions in isooctane of the fourteen internal standards listed in Table 4 or 4A at concentrations of 1000 ng/µL.

C. Recovery standards. Prepare stock solutions in isooctane of the three recovery standards listed in Table 4 or 4A at concentrations of 1000 ng/µL.

D. Alternate standard. Prepare a stock solution in isooctane of the alternate standard listed in Table 4 or 4A at a concentration of 1000 ng/µL.

E. Surrogate standards. Prepare stock solutions in isooctane of the surrogate standards listed in Table 4 or 4A at a concentration of 1000 ng/µL.

Store stock standard solutions in Teflon®-sealed screw-cap bottles at 4°C and protect from light. Stock standard solutions must be checked frequently for signs of degradation or evaporation, especially just before using them to prepare calibration standard solutions or spiking solutions.

Replace stock standard solutions every 12 months or more frequently if comparison with quality control check samples according to Section 7.4.1 indicates a problem.

7.2.3 Calibration Standards

Prepare calibration standards at a minimum of five concentration levels. One of the calibration standards should be at a concentration near, but above, the method detection limit. The others should include the range of concentrations found in real samples but should not exceed the linear range of the GC/MS system.

Prepare calibration working standard solutions by combining appropriate volumes of individual or mixed calibration standards with internal standard, recovery standards, and alternate standard spiking solution and making up to volume with hexane to obtain the solution concentrations given in Tables 5, 6, and 6A. The suggested ranges are 0.25 ng/µL to 5.0 ng/µL for LRMS and 10 pg/µL to 500 pg/µL for HRMS.

All standards must be stored at 4°C or lower and must be freshly prepared if the check according to Section 7.4.1 indicates a problem.

7.2.4 Internal Standard (IS) Spiking Solution

The concentration of internal standard in the IS spiking solution must be such that the amount of solution added to the calibration standard solution and the sample is at least 2 mL.

Prepare the internal standard spiking solution by using appropriate volumes of stock solutions of Section 7.2.2B to give the concentrations shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the internal standards that must be added to the sample (Table 7 or 7A) before extraction to achieve, in a final volume of

500 µL, the sample extract concentrations shown in Table 8 for LRMS and Table 8 or 8A for HRMS analysis. The target concentrations in Tables 8 and 8A are based on a final volume of 500 µL and 100 percent recovery of the internal standards added to the sample.

7.2.5 Recovery Standard Spiking Solution

The concentration of recovery standard in this spiking solution must be such that the amount of solution added to the concentrated sample extract is 50 µL to give a final extract volume of 500 µL.

Use an appropriate volume of stock solution of Section 7.2.2C to prepare a recovery standard spiking solution with the concentrations shown in Table 4 or 4A. Store at 4 ^{o}C or lower.

A volume of 50 µL of the recovery standard spiking solution shown in Table 4 or 4A will provide the amount of each recovery standard required by Table 7 or 7A to achieve the target sample concentration of Table 8 or 8A. Final volumes, may be adjusted depending on the target detection limit.

7.2.6 Surrogate Standard Spiking Solution

The concentration of surrogate standard in this spiking solution must be such that the amount of solution added to the calibration standard solution and the sorbent module is at least 2 mL.

Prepare the surrogate standard spiking solution by using the appropriate volume of stock solution of Section 7.2.2E to give the concentration shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the surrogate standards that must be added to the sample (Table 7 or 7A) before sampling to achieve the sample extract concentrations shown in Table 8 or 8A in a final sample volume of 500 µL.

7.2.7 Alternate Standard Spiking Solution

The concentration of alternate standard in this spiking solution must be such that the amount of solution added to the calibration standard solution and the sample extracts is at least 2 mL.

Prepare the alternate standard spiking solution by using the appropriate volume of stock solution of Section 7.2.2D to give the concentration shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the alternate standard that must be added to the sample (Table 7 or 7A) before extraction to achieve the sample extract concentrations shown in Table 8 or 8A in a final sample volume of 500 µL.

7.2.8 Calibration Check Standard

The calibration check standard shall be used for column performance checks, and for continuing calibration checks. Solution #3 from Table 5 shall be the calibration check standard for LRMS, while Solution #3 from Table 6 or 6A shall be the calibration check standard for HRMS.

7.3 INITIAL CALIBRATION

An acceptable initial calibration (7.3.8) is required before any samples are analyzed, and then intermittently throughout sample analyses as dictated by results of the continuing calibration procedures described in Section 7.4. The GC/MS system must be properly calibrated and the performance documented during the initial calibration.

7.3.1 Retention Time Windows

Before sample analysis, determine the retention time windows during which the selected ions will be monitored. Determine Relative Retention Time (RRTs) for each analyte by using the corresponding ^{2}H - labelled standard.

7.3.2 GC Operating Conditions

The GC column performance (Section 7.3.5) must be documented during the initial calibration. Table 10 summarizes GC operating conditions known to produce acceptable results with the column listed. The GC conditions must be established by each analyst for the particular instrumentation by injecting aliquots of the calibration check standard (7.2.8). It may be necessary to adjust the operating conditions slightly based on observations from analysis of these solutions. Other columns and/or conditions may be used as long as column performance criteria of Section 7.3.5 are satisfied.

Thereafter the calibration check standard must be analyzed daily to verify the performance of the system (Section 7.4).

7.3.3 GC/MS Tuning Criteria

A. Low Resolution Mass Spectrometry

Use a compound such perfluorotributylamine (PFTBA) to verify that the intensity of the peaks is acceptable. If PFTBA is used, mass spectral peak profiles for m/z 69, 219 and 264 must be recorded, plotted, and reported. The scan should include a minimum of +/- two peaks (i.e, m/z 67-71 for the m/z 69 profile).

B. High Resolution Mass Spectrometry

Tune the instrument to meet the minimum required resolving power of 8,000 at 192.9888 or any other PFK reference signal close to 128.0626 (naphthalene). Use peak matching and the chosen PFK reference peak to verify that the exact mass of m/z 242.9856 is within 5 ppm of the required value. The selection of the low and high mass ions must be such that they provide the largest voltage jump performed in any of the three mass descriptors.

7.3.4 MS Operating Conditions

A. Low Resolution Mass Spectrometry

Analyze standards and samples with the mass spectrometer operating in the Selected Ion Monitoring (SIM) mode with a total cycle time of 1 second or less.

B. High Resolution Mass Spectrometry

Analyze standards and samples with the mass spectrometer operating in the SIM mode with a total cycle time (including the voltage reset time) of one second or less.

A reference compound such as Perfluorokerosene (PFK) must be used to calibrate the SIM mass range. One PFK ion per mass descriptor is used as a lock-mass ion to correct for mass drifts that occur during the analysis. In addition to the lock-mass ion, several ions characteristic of PFK are monitored as QC check ions (Table 13).

7.3.5 GC Column Performance Criteria

A. The height of the valley between anthracene and phenanthrene at m/z 178 or the ^{2}H-analogs at m/z 188 shall not exceed 50 percent of the taller of the two peaks.

B. The height of the valley between benzo(b)fluoranthene and benzo(k)fluoranthene shall not exceed 60 percent of the taller of the two peaks.

If these criteria are not met and normal column maintenance procedures are not successful, the column must be replaced and the initial calibration repeated.

7.3.6 Mass Spectrometer Performance

A. Low Resolution Mass Spectrometry

Verify acceptable sensitivity during initial calibration. Demonstrate that the instrument will achieve a minimum signal-to-noise ratio of 10:1 for the quantitation and confirmation ions when the calibration standard with the lowest concentration is injected into the GC/MS system.

B. High Resolution Mass Spectrometry

Record the peak profile of the high mass reference signal (m/z 242.9856) obtained during peak matching by using the low-mass PFK ion at m/z 192.9888 (or lower in mass) as a reference. The minimum resolving power of 8,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity.

The format of the peak profile representation must allow manual determination of the resolution, that is, the horizontal axis must be a calibrated mass scale (amu or ppm per division).

The peak width of the high mass ion at 5 percent of the peak height must not exceed 125 ppm in mass.

7.3.7 Calibration Procedure

Using stock standards, prepare at least five calibration standard solutions, using the same solvent that was used in the final sample extract. Keep the recovery standards and the internal standards at fixed concentrations. Adjust the concentrations recommended in Tables 5 and 6, if necessary, to ensure that the sample analyte concentration falls within the calibration range. The calibration curve must be described within the linear range of the method.

Calibrate the mass spectrometer response using a 2 µL aliquot of each calibration solution. Analyze each solution once.

Calculate:

A. the relative response factors (RRFs) for each analyte as described in Sections 7.7.1.1, 7.7.1.2, and 7.7.1.3.

B. the mean RRFs as required by Section 7.7.1.4.

C. the standard deviation (SD) and relative standard deviation (RSD) as required by Section 7.7.2.

Report all results as required by Section 10.2.

7.3.8 Criteria for Acceptable Initial Calibration

An acceptable initial calibration must satisfy the following performance criteria:

A. The requirements of Sections 7.3.5 and 7.4.6 must be met.

B. The signal to noise ratio (S/N) for the GC signals present in every selected ion current profile (SICP) must be > 10:1 for the labelled standards and unlabelled analytes.

C. The percent relative standard deviation for the mean relative response factors must be no greater than 30 percent for both the unlabelled analytes and internal standards (Section 7.7.2). Otherwise, take corrective action as required by Section 7.7.2.

7.4 CONTINUING CALIBRATION

The continuing calibration consists of an analysis of the calibration check standard (Section 7.2.8) once during each 12-hour shift as described in Section 7.4.1.

The criteria for acceptable continuing calibration are given in Section 7.4.2. These must be satisfied or else corrective action must be taken as required by Section 7.4.2.

7.4.1 Calibration Check

The calibration check standard (Section 7.2.8) must be analyzed at the beginning and end of each analysis period, or at the beginning of every 12-hour shift if the laboratory operates during consecutive 12 hour shifts.

Inject a 2-µL aliquot of the calibration check standard (Section 7.2.8) into the GC/MS. Use the same data acquisition parameters as those used during the initial calibration.

Check the retention time windows for each of the compounds. They must satisfy the criterion of Section 7.4.2C

Check for GC resolution and peak shape. Document acceptable column performance as described in Section 7.3.5. If these criteria are not met, and normal column maintenance procedures are unsuccessful, the column must be replaced and the calibration repeated.

Calculate the continuing RRF and ΔRRF, the relative percent difference (RPD) between the daily RRF and the initial calibration mean RRF as described in Section 7.7.1.5.

Report the results as required by Section 10.2.

7.4.2 Continuing Calibration Performance Criteria

An acceptable continuing calibration must satisfy the following performance criteria:

A. The signal to noise ratio (S/N) for the GC signals present in the selected ion current profile (SICP) for all labelled and unlabelled standards must be ≥ 10:1.

B. The measured RRFs of all analytes (labelled and unlabelled) must be within 30 percent of the mean values established during the initial calibration. If this criterion is not satisfied, a new initial calibration curve must be established before sample extracts can be analyzed.

C. The retention time for any internal standard must not change by more than 30 seconds from the most recent calibration check. Otherwise, inspect the chromatographic system for malfunctions and make the necessary corrections. Document acceptable performance with a new initial calibration curve.

7.5 GC/MS ANALYSIS

The laboratory may proceed with the analysis of samples and blanks only after demonstrating acceptable performance as specified in Sections 7.3 and 7.4.

Analyze standards, field samples and QA samples (Section 8.1) with the gas chromatograph and mass spectrometer operating under the conditions recommended in Sections 7.3.2 and 7.3.4.

Approximately l hr before HRGC/LRMS or HRGC/HRMS analysis, adjust the sample extract volume to approximately 500 µL. This is done by adding 50 µL of the recovery standard spike solution (Section 7.2.5, and Table 4 or 4A) to the 450 µL final volume (Section 6.6.2) of the

concentrated sample extract give the sample extract concentration required by Table 8 or 8A. If the sample volume must be changed to achieve a desired detection limit, the recovery spike solution concentration must be adjusted accordingly to achieve the target concentrations of Table 8 or 8A.

Inject a 2 µL aliquot of the sample extract (Section 6.6.2) on to the DB-5 column. Use the same volume as that used during calibration. Recommended GC/MS operating conditions are described in Section 7.3.

The presence of a given PAH is qualitatively confirmed if the criteria of Section 7.6.1 are satisfied.

The response for any quantitation or confirmation ion in the sample extract must not exceed the response of the highest concentration calibration standard.

Collect, record, and store the data for the calculations required by Sections 9.1.7, 9.1.8, 9.1.9, and 9.1.10. Report the results as required by Section 10.2.

7.6 QUALITATIVE ANALYSIS

7.6.1 Identification Criteria

7.6.1.1 Ion Criteria

For LRMS analysis, all quantitation and confirmation ions (Table 13) must be present.

7.6.1.2 Relative Retention Time (RRT) Criteria

The relative retention time (RRT) of the analyte compared to the RRT for the ^{2}H-standards must be within ±0.008 RRT units of the relative retention times obtained from the continuing calibration (or initial calibration if this applies).

7.6.1.3 Signal to Noise Ratio

The signal to mean noise ratio must be 10:1 for the internal standards. This ratio for the unlabelled compounds must be greater than 2.5 to 1 for the quantitation ions for HRMS and for both quantitation and confirmation ions for LRMS.

If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst must employ additional cleanup on the archive sample and reanalyze.

7.7 QUANTITATIVE ANALYSIS

7.7.1 Relative Response Factors (RRFs)

7.7.1.1 RRF for Unlabelled PAH and Surrogate Standards from Initial Calibration Data

Use the results of the calibration and Equation 429-13 to calculate the relative response factors (RRFs) for each calibration compound and surrogate standard in each calibration

solution (Tables 5 or 5A). Table 11 shows the assignments of the internal standards for calculation of the RRFs for the calibration solution shown in Table 5. Table 11A shows the assignments of the internal standards for calculation of the RRFs for the calibration solution shown in Table 5A. Report the results as required by Section 10.2.

7.7.1.2 RRF for Determining Internal Standard Recovery

Use the results of the calibration in Equation 429-18 to calculate the relative response factor for each internal standard relative to an appropriate recovery standard. Table 11 shows the assignments of the recovery standards for calculating internal standard recoveries for the calibration solution shown in Table 5. Table 11A shows the assignments of the recovery standards for calculating internal standard recoveries for the calibration solution shown in Table 5A. Report the results as required by Section 10.2.

7.7.1.3 RRF for Determining Alternate Standard Recovery

Use the calibration results and Equation 429-19 to calculate the response factor for the alternate standard relative to the appropriate recovery standard. Table 11 shows the assignment of the recovery standards for calculating alternate standard recovery for the calibration solution shown in Table 5. for the calibration solution shown in Table 5. Report the results as required by Section 10.2.

7.7.1.4 Mean Relative Response Factor

Use Equation 429-20 to calculate the mean RRF for each compound (unlabelled calibration standards, surrogate standards, internal standards and alternate standard). This is the average of the five RRFs calculated for each compound (one RRF calculated for each calibration solution). The mean RRF may be used if the linearity criterion of Section 7.7.2 is satisfied.

Report the results as required by Section 10.2.

7.7.1.5 RRF from Continuing Calibration Data

Analyze one or more calibration standards (one must be the medium level standard) on each work shift of 12 hours or less. Use Equations 429-17, 429-18, and 429-19 to calculate the RRFs for each analyte. Use Equation 429-22 to calculate ΔRRF, the relative percent difference between the daily RRF and the mean RRF calculated during initial calibration. Check whether the performance criterion of Section 7.4.2B is satisfied. Report the results as required by Section 10.2.

7.7.2 Relative Standard Deviation of Relative Response Factors

For each analyte, calculate the sample standard deviation (SD) of the RRFs used to calculate the mean RRF. Use Equation 429-21 to calculate the percent relative standard deviation (%RSD) for each analyte. The analyst may use the mean RRF if the percent relative standard deviation of the RRFs is 30% or less. If the RSD requirement is not satisfied, analyze additional aliquots of appropriate calibration solutions to obtain an acceptable RSD of RRFs over the entire

concentration range, or take action to improve GC/MS performance. Otherwise, use the complete five point calibration curve for that compound.

8 QUALITY ASSURANCE/QUALITY CONTROL

Each laboratory that uses this method is required to operate a formal quality control program. The minimum quality control requirements of this program consists of an initial demonstration of laboratory capability (according to Sections 7.3 and 8.1.3.1), and periodic analysis of blanks and spiked samples as required in Sections 8.1.1 and 8.1.3.2 as a continuing check on performance.

The laboratory must maintain performance records to document the quality of data that are generated. The results of the data quality checks must be compared with the method performance criteria to determine if the analytical results meet the performance requirements of the method. The laboratory must generate accuracy statements as described in Section 8.4.1.

8.1 QA SAMPLES

8.1.1 Laboratory Method Blank

The analyst must run a laboratory method blank with each set of 15 or fewer samples. The method blank must be a resin sample from the same batch used to prepare the sampling cartridge and the laboratory control samples. The method blank must be prepared and stored as described in Sections 4.3.4 and 4.3.5.

The analyst shall perform all of the same procedures on the method blank as are performed on the solid samples (Section 6.5.2.1) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

8.1.2 Performance Evaluation Samples

The laboratory should analyze performance evaluation samples quarterly when these samples become available. These samples must be prepared and analyzed by the same methods used for the field samples. Performance for the most recent quarter should be reported with the results of the sample analysis.

8.1.3 Laboratory Control Sample (LCS)

8.1.3.1 Initial Demonstration of Laboratory Capability

Before performing sample analyses for the first time, the analyst shall demonstrate the ability to generate results of acceptable precision and accuracy by using the following procedures.

Prepare spiking solutions from stock standards prepared independently from those used for calibration. Spike at least four resin samples cleaned as described in Section 4.2.2 with each of the target unlabelled analytes as indicated in Table 9. Blank resin contamination levels must be no greater than 10 percent of the levels of the spiked analytes. Add the amounts of

internal standards required by Table 7 or 7A. Add the alternate standard to the extract to monitor the efficiency of the cleanup procedure.

The LCS spikes shall undergo all of the same procedures as are performed on the solid samples (Section 6.5.1.2) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

Calculate:

(A) percent recoveries for the internal standards and alternate standard,
(B) the mass of each target analyte in µg/sample or ng/sample,
(C) the average of the results for the four analyses in µg/sample or ng/sample,
(D) the average recovery (R) as a percentage of the amount added, and
(E) the relative standard deviation S_R.

Report the results as required by Section 10.2.4.

If all the acceptance criteria of Section 8.2.6 are satisfied for all of the target PAH, the analyst may begin analysis of blanks and samples. Otherwise, corrective action must be taken as required by Section 8.2.6.

8.1.3.2 Ongoing Analysis of LCS

The analyst must run two laboratory control samples with each set of 15 or fewer samples. The resin for the LCS must be taken from the same batch used to prepare the sampling cartridge and the laboratory method blank. The LCS resin must be prepared and stored as described in Sections 4.3.4 and 4.3.5.

Prepare spiking solutions from stock standards prepared independently from those used for calibration. Spike each resin sample with each of the target unlabelled analytes as indicated in Table 9. Blank resin contamination levels must be no greater than 10 percent of the levels of the spiked analytes. Add the amounts of internal standards required by Table 7 or 7A. Add the alternate standard to the extract to monitor the efficiency of the cleanup procedure.

The LCS spikes shall undergo all of the same procedures as are performed on the solid samples (Section 6.5.1.2) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

Calculate:

(A) percent recoveries for the internal standards and alternate standard,
(B) the mass of each target analyte in µg/sample or ng/sample,
(C) the average of the results for the two analyses in µg/sample or ng/sample,
(D) the average recovery as a percentage of the amount added, and
(E) the relative percent difference for the two analyses.

Report the results as required by Section 10.2.

Add the results which satisfy the performance requirements of Section 8.2.6 to the results of the initial LCS analyses (8.1.3.1) and previous ongoing data for each compound in the LCS sample.

Update the charts as described in Section 8.4.1.

8.2 ACCEPTANCE CRITERIA

8.2.1 Blank Trains

The levels of any unlabelled analyte quantified in the blank train must not exceed 20 percent of the level of that analyte in the sampling train. If this criterion cannot be met, calculate a reporting limit that is five times the blank value (Equations 429-32 and 429-33). Do not subtract the blank value from the sample value.

8.2.2 Surrogate Standard Recovery

Acceptable surrogate (field spike) recoveries should range from 50 to 150 percent. If field spike recoveries are not within the acceptable range, this must be clearly indicated in the laboratory report. The affected sampling run must be identified in the report of the calculated emissions data.

8.2.3 Internal Standard Recovery

Recoveries for each of the internal standards must be greater than 50 percent and less than 150 percent of the known value.

If internal standard recoveries are outside of the acceptable limits, the signal to noise ratio of the internal standard must be greater than 10. Otherwise the analytical procedure must be repeated on the stored portion of the extract.

NOTE: This criterion is used to assess method performance. As this is an isotope dilution technique, it is, when properly applied, independent of internal standard recovery. Lower recoveries do not necessarily invalidate the analytical results for PAH, but they may result in higher detection limits than are desired.

If low internal standard recoveries result in detection limits that are unacceptable, the cleanup and GC/MS analysis must be repeated with the stored portion of the extract. If the analysis of the archive sample gives low recoveries and high detection limits, the results of both analyses must be reported.

8.2.4 Laboratory Method Blank

The laboratory method blank must not contain any of the target analytes listed in Table 1 at levels exceeding the PQL or 5 percent of the analyte concentration in the field sample.

If the method blank is contaminated, check solvents, reagents, standard solutions apparatus and glassware to locate and eliminate the source of contamination before any more samples are

analyzed. Table 3 shows those compounds that commonly occur as contaminants in the method blank, and the ranges of concentrations that have been reported.

If field samples were processed with a laboratory method blank that showed PAH levels greater than 5 percent of the field sample, they must be re-analyzed using the archived portion of the sample extract.

Recoveries of the internal standards must satisfy the requirements of 8.2.3. If the internal standard recoveries are less than 50%, the S/N ratio must be greater than 10 for the internal standard.

8.2.5 Performance Evaluation Sample

The following will be a requirement when performance evaluation samples become available, and performance criteria have been established:

Performance for the most recent quarter must be reported with the results of the sample analysis. If the performance criteria (to be established) are not achieved, corrective action must be taken and acceptable performance demonstrated before sample analysis can be resumed.

8.2.6 Laboratory Control Samples

8.2.6.1 Initial and Ongoing Analysis

The signal of each analyte in the initial and ongoing laboratory control samples must be at least 10 times that of the background.

Acceptable accuracy is a percent recovery between 50 and 150 percent. Acceptable precision for the initial LCS samples is a relative standard deviation (RSD) of 30 percent or less.

Acceptable precision for the ongoing analysis of duplicate samples is a relative percent difference of 50 percent or less.

If the RSD for the initial demonstration exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.

If the RPD for any ongoing duplicate analyses exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.

Beginning with Section 8.1.3.1, repeat the test for those analytes that failed to meet the performance criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.1.3.1 for the initial analysis and Section 8.3.1.2 for the ongoing analysis.

8.3 ESTIMATION OF THE METHOD DETECTION LIMIT (MDL) AND PRACTICAL QUANTITATION LIMIT (PQL)

8.3.1 Initial Estimate of MDL and PQL

The analyst shall prepare a batch of XAD-2 resin as described in Sections 4.2.2.1 to 4.2.2.3, then check for contamination as required by Section 4.2.2.4. Identify those PAH analytes present at background levels that are too high for the MDL determination. Use the procedure of Appendix A to calculate MDLs for the remaining target PAH compounds. The analyst may use any of the five approaches described in Appendix A (A1.1) to estimate an initial spike level for the MDL determination. One of the suggested approaches is based on a theoretical method quantitation limit (TMQL) estimated according to Equation 429-16.

$$TMQL = C \times \frac{V}{P} \times 100 \times 2 \qquad \text{429-16}$$

Where:

C = the concentration of the PAH in the lowest concentration calibration standard used in the initial calibration, (ng/µL)

V = the final extract volume, (µL)

P = the assumed percent recovery (50%) of the internal standard

2 = a factor to account for the fact that the final extract volume (V) contains one half of the analyte in the sample. The other half is archived.

8.3.2 Ongoing Estimation of MDL and PQL

Once every quarter in which this method is used, the analytical laboratory must analyze one spiked resin sample as described in Appendix A. Include all initial and quarterly results in the calculation of the standard deviation and MDL for each analyte that has not been identified as a common contaminant of the XAD-2 resin.

If the MDL for any analyte exceeds the MDL established during the initial determination, take corrective action as necessary, and repeat the monthly analysis. If any MDL still exceeds the initial MDL, then the initial standard deviation estimation procedure (Appendix A) must be repeated.

8.4 LABORATORY PERFORMANCE

The analyst must have documented standard operating procedures (SOPs) that contain specific stepwise instructions for carrying out this method. The SOPs must be readily available and followed by all personnel conducting the work. The SOP must be made available for review upon request by

the Executive Officer, the tester or reviewer of the analytical results. The analyst may impose restrictions on the dissemination of the information in the SOP.

The analyst must have documented precision and accuracy statements (Section 8.4.1) readily available.

The analyst must have results of the initial and ongoing estimates of the MDL (Sections 8.3.1 and 8.3.2) readily available.

8.4.1 Precision and Accuracy Statement

The precision and accuracy statements for the analytical procedure shall be based on the results of the initial and ongoing LCS analyses. The frequency of analysis is stated in Section 8.1.3.

Prepare a table of the recoveries and the relative percent difference for each ongoing analysis of the LCS and LCS duplicate. Figure 15A is an example of such a table. This must be included in the analytical data package submitted for each set of sample analyses.

Prepare a quality control chart for each target analyte that provides a graphic representation of continued laboratory performance for that target analyte. Figure 15B is an example QC chart for benzo(a)pyrene.

9 CALCULATIONS

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

9.1 ANALYST'S CALCULATIONS

The analyst shall carry out the calculations described in Sections 9.1.1 to 9.1.11.

9.1.1 Relative Response Factors (RRF) for Unlabelled PAH and Surrogate Standards

Calculate the RRF for each target unlabelled PAH analyte and surrogate standard in each calibration solution . Use Equation 429-17 and the data obtained during initial calibration (7.3.7) or continuing calibration (7.4.1).

$$RRF_s = \frac{A_s \times Q_{is}}{A_{is} \times Q_s} \qquad 429\text{-}17$$

Where:

A_s = Area of the response for characteristic ions of the unlabelled analyte or surrogate standard (Tables 11 or 11A, 13, and 14).

A_{is} = Area of the response for characteristic ions of the appropriate internal standard (Tables 11 or 11A, 13, and 14).

Q_s = Amount of the unlabelled PAH calibration analyte or surrogate standard injected on to GC column, ng.

Q_{is} = Amount of the appropriate internal standard injected on to GC column, ng.

9.1.2 RRF for Determination of Internal Standard Recovery

Calculate RRF_{is} according to Equation 429-18, using data obtained from the analysis of the calibration standards.

$$RRF_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times Q_{is}} \qquad 429\text{-}18$$

Where:

A_{rs} = Area of the response for characteristic ions of the appropriate recovery standard (Tables 11 or 11A, 13, and 14).

Q_{rs} = Amount of the appropriate recovery standard injected on to GC column, ng.

9.1.3 RRF for Determination of Alternate Standard Recovery

Calculate RRF_{as} according to Equation 429-19, using data obtained from the analysis of the calibration standards.

$$RRF_{as} = \frac{A_{as} \times Q_{rs}}{A_{rs} \times Q_{as}} \qquad 429\text{-}19$$

Where:

A_{as} = Area of the response for characteristic ions of the alternate standard (Tables 13 and 14).

Q_{as} = Amount of alternate standard injected on to the GC column, ng.

9.1.4 Mean Relative Response Factors ($\overline{RRF}$)

Calculate the mean RRF for each target unlabelled PAH, surrogate standard, internal standard and alternate standard using Equation 429-20 and the RRFs calculated according to Sections 9.1.1, 9.1.2, and 9.1.3.

$$\overline{RRF} = \frac{1}{n} \sum_{i=1}^{n} (RRF)_i \qquad 429\text{-}20$$

Where:

RRF_i = RRF calculated for calibration solution "i" using one of Equations 429-17, 429-18 or 429-19.

n = The number of data points derived from the calibration. The minimum requirement is a five-point calibration (Section 7.2.3, Tables 5 and 6 or 6A)

9.1.5 Percent Relative Standard Deviation (%RSD) of Relative Response Factors

Use Equation 429-21 to calculate the relative standard deviation of the Relative Response Factors for each analyte.

$$\%RSD = \frac{SD}{\overline{RRF}} \times 100\% \qquad 429\text{-}21$$

Where:

$\overline{RRF}$ = Mean relative response factor of a given analyte as defined in Sections 7.7.1.4 and 9.1.4.

SD = The sample standard deviation of the relative response factors used to calculate the mean RRF.

9.1.6 Continuing Calibration ΔRRF

Use Equation 429-22 to calculate ΔRRF, the relative percent difference (RPD) between the daily RRF and the mean RRF calculated during initial calibration.

$$\Delta RRF = \frac{RRF_c - \overline{RRF}}{\overline{RRF}} \times 100\% \qquad 429\text{-}22$$

Where:

RRF_c = The RRF of a given analyte obtained from the continuing calibration (Section 7.4).

9.1.7 Percent Recovery of Internal Standard, R_{is}

Calculate the percent recovery, R_{is} for each internal standard in the sample extract, using Equation 429-23.

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times \overline{RRF_{is}} \times Q_{is}} \times 100\% \qquad 429\text{-}23$$

Where:

$\overline{RRF}_{is}$ = Mean relative response factor for internal standard (Equations 429-18 and 429-20).

9.1.8 Percent Recovery of Surrogate Standard, R_{ss}

Calculate the percent recovery, R_{ss} for each surrogate standard in the sample extract, using Equation 429-24.

$$R_{ss} = \frac{A_{ss} \times Q_{is}}{A_{is} \times \overline{RRF_{s}} \times Q_{ss}} \times 100\% \qquad 429\text{-}24$$

Where:

A_{ss} = Area of the response for characteristic ions of the surrogate standard (Tables 13 and 14).

Q_{ss} = Amount of the surrogate standard added to resin cartridge before sampling, ng.

$\overline{RRF}_{s}$ = Mean relative response factor for surrogate standard (Equations 429-17 and 429-20).

9.1.9 Percent Recovery of Alternate Standard, R_{as}

Calculate the percent recovery, R_{as} for the alternate standard in the sample extract, using Equation 429-25.

$$R_{as} = \frac{A_{as} \times Q_{rs}}{A_{rs} \times \overline{RRF_{as}} \times Q_{as}} \times 100\% \qquad 429\text{-}25$$

Where:

$\overline{RRF}_{as}$ = Mean relative response factor for alternate standard (Equations 429-19 and 429-20).

9.1.10 Mass of the Target Analytes and Surrogate Standards in Emissions Sample or Blank Train

Use Equation 429-26 to determine the total mass of each PAH compound or surrogate standard in the sample:

Report the PQL (9.1.11) for those analytes that were not present at levels higher than the PQL provided to the tester prior to testing (2.3.3).

$$M = \frac{Q_{is} \times A_s}{A_{is} \times \overline{RRF}} \qquad 429\text{-}26$$

Where:

M = Mass (ng) of surrogate standard (M_s) or target analyte (M_t) detected in the sample.

Q_{is} = Amount of internal standard or surrogate standard added to each sample.

A_s = Area of the response for characteristic ions of the unlabelled analyte or surrogate standard (Tables 13 and 14).

A_{is} = Area of the response for characteristic ions of the appropriate internal standard (Tables 13, and 14).

$\overline{RRF}$ = Mean relative response factor of a given analyte calculated as required by Sections 7.7.1.4 and 9.1.4.

9.1.11 Analytical Reporting Limit

The analyst shall report the PQL (Section 2.3.3) for those analytes that were not present in the emissions sample or blank train at levels higher than the pre-test estimate of the PQL.

9.2 TESTER'S CALCULATIONS

9.2.1 Sample/Blank Train PAH Mass Ratio

Use Equation 429-27 to calculate the sample/blank train mass ratio for each PAH detected at levels above the MDL in both the field sample and the blank train.

$$RATIO = \frac{M_t}{M_{BT}} \qquad 429\text{-}27$$

Where:

M_t = Mass of target PAH analyte detected in the sampling train (Equation 429-26).

M_{BT} = Mass of the same PAH analyte detected in the blank train.

If the sample to blank train PAH mass ratio is less than five, calculate the reporting limit for the tested source as required by Section 9.2.4.2. Do not calculate M_c (Section 9.2.2) or M_e (Section 9.2.3) for the emissions report.

9.2.2 PAH Concentration in Emissions

Use Equation 429-28 to calculate the concentration in the emissions of 1) the PAH analytes detected in the sampling train but not in the blank train, and 2) the PAH analytes that satisfy the minimum sample to blank train mass ratio required by Section 9.2.1.

$$M_c = \frac{M_t}{V_{m(std)}} \times \frac{1}{0.028317} \qquad 429\text{-}28$$

Where:

M_c = Concentration of PAH in the gas, ng/dscm, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

M_t = Mass of PAH compound in gas sample, ng (Equation 429-26)

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscf (Equation 429-10)

0.028317 = Factor for converting dscf to dscm.

9.2.3 PAH Mass Emission Rate

Use Equation 429-29 to calculate the mass emission rate for each PAH compound that satisfies the minimum sample/blank train PAH mass ratio (Section 9.2.1).

$$M_e = \frac{M_s}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad 429\text{-}30$$

Where:

M_e = Mass emission rate for PAH analyte, ng/second

M_t = Mass of PAH compound in the gas sample, ng (Equation 429-26)

Q_{std} = Average stack gas dry volumetric flow rate corrected to standard conditions, dscf/min.

60 = Factor for converting minutes to seconds

9.2.4 Source Reporting Limit

9.2.4.1 PAH Not Detected in Either Sampling or Blank Train

Use Equation 429-30 or 429-31 to calculate the reporting limit for those analytes that were not detected at levels above the PQL in either the sampling or blank train.

$$RL_{cs} = \frac{PQL}{V_{m(std)}} \times \frac{1}{0.028317} \qquad 429\text{-}30$$

$$RL_{es} = \frac{PQL}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad 429\text{-}31$$

Where:

Rl_{cs} = Reporting limit for the tested source, (ng/dscm), corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29-92 in. Hg) on dry basis.

Rl_{es} = Reporting limit for the tested source, (ng/sec.).

0.028317 = Factor for converting dscf to dscm.

60 = Factor for converting minutes to seconds.

9.2.4.2 PAH Detected in Blank Train and Sample/Blank Train Ratio <5

If the sample to blank train PAH mass ratio is less than five, then Equation 429-32 or 429-33 shall be used to calculate the reporting limit for that PAH.

$$RL_{cb} = \frac{5 \times M_{BT}}{V_{m(std)}} \times \frac{1}{0.028317} \qquad 429\text{-}32$$

$$RL_{eb} = \frac{5 \times M_{BT}}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad 429\text{-}33$$

Where:

Rl_{cb} = Reporting limit for the tested source, (ng/dscm), corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29-92 in. Hg) on dry basis.

Rl_{eb} = Reporting limit for the tested source, (ng/sec.).

M_{BT} = The total mass of that PAH analyte in the field blank train.

10 REPORTING REQUIREMENTS

The source test protocol must contain all the sampling and analytical data required by Sections 2.2 to 2.5, 4.2.1.1, and 4.2.2.4, as well as the information listed in Sections 10.1 and 10.2 that pertain to identification and quantitation of the samples.

The emissions test report must contain all of the sampling and analytical data necessary to calculate emissions values for the target analytes or to demonstrate satisfactory performance of the method.

The end user or reviewer should be able to obtain from the source test report all information necessary to recalculate all reported test method results or to verify that all required procedures were performed.

Any deviations from the procedures described in this method must be documented in the analytical and sampling report.

10.1 SOURCE TEST PROTOCOL

At a minimum, the source test protocol must include all of the data required by Section 2.2 and the information listed in Sections 10.1.1 through 10.1.4.

10.1.1 Preparation of Filters

A. Manufacturer's lot number for the batch of filters to be used in the test.

B. Contamination check of filter (Section 4.2.1.1)

(i) Date of cleaning.
(ii) Date of PAH analysis.
(iii) Table of results of PAH analysis required by Section 4.2.1. The analytical report must include all of the data listed in Section 10.2.

C. Storage conditions prior to the test (4.3.3)

10.1.2 Preparation of XAD-2 resin

A. ID for the batch to be used in the test. The same batch must be used for the sampling train and the laboratory QC samples.

B. Contamination check of resin (Sections 4.2.2.1 to 4.2.2.4)

(i) Date of cleaning.
(ii) Date of PAH analysis.

(iii) Table of results of PAH analysis required by Section 4.2.2.4. The analytical report must include all of the data listed in Section 10.2.

C. Addition of surrogate standards to the resin cartridge.

(i) Amount of each compound.
(ii) Date of spiking.

D. Storage conditions prior to the test (Section 4.3.3)

10.1.3 Method Detection Limits and Practical Quantitation Limits

The MDL and PQL for each target analyte determined as required by Sections 2.3.2 and 2.3.3.

10.1.4 Target Sampling Parameters

A. Source target concentration of each emitted PAH of interest.

B. Results of calculations required by Sections 2.5.2 to 2.5.5.

Figure 9 shows the minimum required calculations of target sampling parameters.

10.2 LABORATORY REPORT

The analyst must generate a laboratory report for each pre-test analysis of the sampling media (Sections 2.3, 4.2.2.1, and 4.2.2.4) and each post-test analysis of the sampling trains and laboratory QC samples.

A minimum of 7 post-test analyses are required to determine the emissions from the source and to document the quality of the emissions data. These are the analyses of three sampling runs, one blank train, one laboratory method blank and two laboratory control samples.

At a minimum, any report (data package) from the analyst to the tester shall contain the information listed in Sections 10.2.1 to 10.2.6 pertaining to identification and PAH quantitation of all samples.

10.2.1 Five-point Initial Calibration

The report of the results of the initial five-point calibration must include the data listed in A, B, and C below:

A. Mass chromatograms for each initial calibration solution that show at a minimum:

(i) Instrument ID,
(ii) laboratory sample ID on each chromatogram.
(iii) date and time of GC/MS analysis,
(iv) mass of monitored ions for each compound in the calibration solution - unlabelled PAH, internal standard, surrogate standard, alternate standard and recovery standard,
(v) retention time for each compound in the calibration solution, and

(vi) either peak height or area of the signals observed for the monitored ion masses.

B. A summary table of the data obtained for each initial calibration solution that shows at a minimum:

(i) Instrument ID,
(ii) laboratory sample ID,
(iii) date and time of GC/MS analysis,
(iv) retention time for each compound - unlabelled PAH, internal standard, surrogate standard, alternate standard and recovery standard,
(v) relative retention time for each unlabelled PAH,
(vi) either peak height or area of the signals observed for the monitored ion masses,
(vii) the relative response factors for each unlabelled PAH, internal standard, surrogate standard, and alternate standard, and
(viii) analyst's signature

Figure 14A is an example of a summary table that contains the minimum required information for the analysis of a single calibration solution.

C. A summary table that shows at a minimum:

(i) Instrument ID,
(ii) the date and time of the GC/MS analysis,
(iii) the relative response factor (RRF) calculated for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in each calibration solution,
(iv) the average relative response factor ($\overline{RRF}$) calculated for the five point calibration,
(v) the relative standard deviation of the relative response factors, and
(vi) the recovery of each internal standard in percent.

Figure 14B is an example of a report that contains the minimum required information for a five point calibration summary.

10.2.2 Continuing Calibration

The report of the results of a continuing calibration must include the data listed in 10.2.2 A, B, and C below:

A. Mass chromatogram that shows at a minimum the information listed in 10.2.1 A.

B. A summary table of the raw data obtained for the continuing calibration that shows at a minimum, the information listed in 10.2.1 B.

C. A summary table that shows at a minimum:

(i) the relative response factor (RRF) for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in the continuing calibration solution,
(ii) the average relative response factor ($\overline{RRF}$) for each compound calculated for the five point calibration,

(iii) ΔRRF for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in the continuing calibration solution,
(iv) the recovery of each internal standard in percent.

Figure 14C is an example of a summary report that contains the minimum information required by Section 10.2.2C for the analysis of the continuing calibration solution.

10.2.3 Laboratory Method Blank

The laboratory report of the results of the analysis of the method blank must include at a minimum the data listed in 10.2.3 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A.

B. A summary table of the data obtained for each method blank that shows at a minimum, the information listed in 10.2.5 B.

C. A summary table that reports the same data as listed in 10.2.5 C below.

10.2.4 Laboratory Control Samples

The report of the results of the analysis of the LCS samples must include at a minimum the data listed in 10.2.4 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A.

B. A summary table of the raw data for each sample that shows at a minimum, the information listed in 10.2.1 B, and in addition:

(i) Client's sample ID
(ii) mass of each analyte,
(iii) the recovery of each internal standard, and alternate standard,

Figure 16A is an example of a summary table that contains the minimum information required by 10.2.4 B.

C. A summary table that reports for the two LCS analyses:

(i) client's sample ID,
(ii) sample matrix description,
(iii) date of cleaning of the XAD-2 resin,
(iv) lot number for the resin (resin for all field samples and QA samples must come from the same lot),
(v) date of extraction of LCS samples,

Figure 15A is an example of a summary table that contains the minimum information required by 10.2.4 C.

10.2.5 Emissions Samples

The report of the results of the analyses of the three sampling trains and the blank train must include the data listed in 10.2.5 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A, and in addition,

   (i) client's sample ID

B. A summary table of the data for the analysis of each sample that shows at a minimum, the information listed in 10.2.1 B, and in addition,

   (i) client's sample ID
   (ii) Date of five point initial calibration (ICAL)
   (iii) ICAL ID,
   (iv) mass of each analyte,
   (v) the recovery of each internal standard, alternate standard and surrogate standards in percent.

Figure 16A is an example of a summary table that contains the minimum information required by 10.2.5 B.

C. A summary table that reports:

   (i) client's sample ID (from a chain of custody record submitted by the tester),
   (ii) sample matrix description,
   (iii) date of cleaning of the XAD-2 resin,
   (iv) lot number for the resin (resin for all field samples and QA samples must come from the same lot),
   (v) date of submittal of the tester's samples
   (vi) date of extraction of samples,
   (vii) Initial calibration Run ID,
   (viii) Continuing calibration ID

Figure 16B is an example of a summary table that contains the minimum information required by 10.2.5C.

10.2.6 Data Flags

The laboratory report must include an explanation of any qualifiers that are used to indicate specific qualities of the data.

10.3 EMISSIONS TEST REPORT

The emissions test report should include narrative that describes how the test was done. The tester's report must also include all the appropriate sections used in a report from a Method 5 test such as a description of the plant process, sampling port locations, control equipment, fuel being used, general

plant load conditions during the test (description of plant production equipment problems, etc.), and anything else necessary to characterize the condition being tested.

The tester's report must also include all of the information listed in Sections 10.3.1 to 10.3.4.

10.3.1 Tester's Summary of Analytical Results

The tester must summarize the results of the minimum seven analyses required for each source test. At a minimum, the summary must contain the information listed in Figure 17A including all data flags.

The tester must obtain the detailed analytical results (Section 10.2) from the laboratory and include them in the appendices as required below.

10.3.2 Field Data Summary

The report from the tester to the end user must contain a field data summary. This summary must include at a minimum a table of the results of the calculations required by Section 4.5. as well as the values which were used to calculate the reported results. Figure 17B is an example of a field data summary that contains the minimum required information.

10.3.3 PAH Emissions Results

Figure 17C show the calculations of the concentrations and mass emission rates of the target PAH. The reviewer should be able to use the data in Figures 17A and 17B to check the calculations in Figure 17C. The reviewer should also be able to check the appendix to the report to determine the accuracy and the quality of the data summarized by the tester in Figures 17A and 17B.

10.3.4 Appendix to the Emissions Test Report

At a minimum, the following raw data or signed copies must be included in an appendix to the emissions test report.

A. Record of data for sample site selection and minimum number of traverse points.

B. Moisture determination for isokinetic settings.

C. Velocity traverse data.

D. Gas analysis for determination of molecular weight.

E. Calibration records.

F. Method 429 sampling run sheets.

G. PAH laboratory reports listed in Section 10.2

The information listed above is to be considered as the minimum that should be included to characterize a given operating condition. The end user or the executive officer may require additional information for any given project.

11 BIBLIOGRAPHY

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11.3 U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 3630B. Silica Gel Cleanup. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

11.4 Thomason, J.R., ed., Cleaning of Laboratory Glassware. Section 3, A, pp 1-7 in "Analysis of Pesticide Residues in Human and Environmental Samples", Environmental Protection Agency, Research Triangle Park, N.C. (1974).

11.5 ARB Method 428. Determination of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Emissions From Stationary Sources. September, 1990.

11.6 U. S. Environmental Protection Agency, Method 1625 Revision B - Semivolatile Organic Compounds by Isotope Dilution. 40 CFR Ch.1 (7-1-95 Edition) Pt. 136, App. A.

11.7 Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March, 1972.

11.8 Shigehara, R.T., Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News, 2: 4-11. October, 1974

11.9 "Prudent Practices in the Laboratory. Handling and Disposal of Chemicals," National Academy Press. Washington D.C. 1995.

TABLE 1

METHOD 429 TARGET ANALYTES

Naphthalene
2-Methylnaphthalene
Acenaphthene
Acenaphthylene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-cd)pyrene
Dibenz(a,h)anthracene
Benzo(ghi)perylene

TABLE 2

PRACTICAL QUANTITATION LIMITS FOR TARGET PAHs

	LRMS (µg/sample)	HRMS (ng/sample)	
Naphthalene	244	480	370
2-Methylnaphthalene	1.25	66	19
Acenaphthene	0.210	5.0	5.0
Acenaphthylene	0.104	5.0	5.0
Fluorene	0.207	16.5	5.5
Phenanthrene	0.85	22	14
Anthracene	0.146	5.0	5.0
Fluoranthene	0.346	5.0	5.0
Pyrene	0.191	5.0	5.0
Benzo(a)anthracene	0.167	5.0	5.0
Chrysene	0.272	5.0	5.0
Benzo(b)fluoranthene	1.119	5.0	5.0
Benzo(k)fluoranthene	0.738	5.0	5.0
Benzo(e)pyrene	0.146	5.0	5.0
Benzo(a)pyrene	0.191	5.0	5.0
Perylene	0.143	5.0	5.0
Indeno(1,2,3-cd)pyrene	0.798	5.0	5.0
Dibenz(a,h)anthracene	0.465	5.0	5.0
Benzo(ghi)perylene	0.305	5.0	5.0

TABLE 3
PAH ANALYSIS BY HRMS OF DIFFERENT LOTS OF CLEANED RESIN

PAH ANALYTES	CONCENTRATION (ng/sample)												
	SAMPLE IDENTIFICATION												
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13
Naphthalene	480	220	198	120	350	340	320	360	370	380	340	520	220
2-Methylnaphthalene	65	32	38	15.6	32	15.6	32	26	19	45	15	32	48
Acenaphthylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Acenaphthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Fluorene	16.5	9.8	13	< 5.0	5.7	5.4	7.4	5.8	5.5	10	5.5	6.8	5.0
Phenanthrene	22	16	32	<12.5*	14	14.8	16	12	14	24	13	<13.0*	14
Anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(a)anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Chrysene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(b)fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(k)fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(e)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(a)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Perylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Indeno(1,2,3-cd)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Dibenzo(a,h)anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(g,h,i)perylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0

* 5 x the concentration of the lowest calibration standard

TABLE 4

COMPOSITION OF THE SAMPLE SPIKING SOLUTIONS

Spiking Solutions	Analytes	Concentration ng/µl LRMS	Concentration pg/µl HRMS
1.	**Surrogate Standards**		
	d_{10}-Fluorene	1.0	250
	d_{14}-Terphenyl	1.0	250
2.	**Internal Standards**		
	d_8-Naphthalene	1.0	100
	d_{10}-2-Methylnaphthalene	1.0	100
	d_8-Acenaphthylene	1.0	100
	d_{10}-Phenanthrene	1.0	100
	d_{10}-Fluoranthene	1.0	100
	d_{12}-Benzo(a)anthracene	1.0	100
	d_{12}-Chrysene	1.0	100
	d_{12}-Benzo(b)fluoranthene	1.0	200
	d_{12}-Benzo(k)fluoranthene	1.0	200
	d_{12}-Benzo(a)pyrene	1.0	200
	d_{12}-Perylene	1.0	200
	d_{12}-Indeno(1,2,3,c-d)pyrene	1.0	200
	d_{14}-Dibenz(a,h)anthracene	1.0	200
	d_{12}-Benzo(ghi)perylene	1.0	200
3.	**Alternate Standard**		
	d_{10}-Anthracene	1.0	100
4.	**Recovery Standards**		
	d_{10}-Acenaphthene	20.0	2000
	d_{10}-Pyrene	20.0	2000
	d_{12}-benzo(e)pyrene	20.0	2000

TABLE 4A

COMPOSITION OF ALTERNATIVE SAMPLE SPIKING SOLUTIONS

Spiking Solutions	Analytes	Concentration pg/µl HRMS
1A.	**Surrogate Standards**	
	d_{12}-Benzo(e)pyrene	250
	d_{14}-Terphenyl	250
2A.	**Internal Standards**	
	d_8-Naphthalene	100
	d_8-Acenaphthylene	100
	d_{10}-Acenaphthene	100
	d_{10}-Fluorene	100
	d_{10}-Phenanthrene	100
	d_{10}-Fluoranthene	100
	d_{12}-Benzo(a)anthracene	100
	d_{12}-Chrysene	100
	d_{12}-Benzo(b)fluoranthene	200
	d_{12}-Benzo(k)fluoranthene	200
	d_{12}-Benzo(a)pyrene	200
	d_{12}-Indeno(1,2,3,c-d)pyrene	200
	d_{14}-Dibenz(a,h)anthracene	200
	d_{12}-Benzo(ghi)perylene	200
3A.	**Alternate Standard**	
	d_{10}-Anthracene	100
4A.	**Recovery Standards**	
	d_{10}-2-Methylnaphthalene	2000
	d_{10}-Pyrene	2000
	d_{12}-Perylene	2000

TABLE 5

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR LOW RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (ng/µL)				
	Solutions				
	1	2	3	4	5
Calibration Standards					
Naphthalene	0.25	0.5	1.0	2.5	5.0
2-Methylnaphthalene	0.25	0.5	1.0	2.5	5.0
Acenaphthene	0.25	0.5	1.0	2.5	5.0
Acenaphthylene	0.25	0.5	1.0	2.5	5.0
Fluorene	0.25	0.5	1.0	2.5	5.0
Phenanthrene	0.25	0.5	1.0	2.5	5.0
Anthracene	0.25	0.5	1.0	2.5	5.0
Fluoranthene	0.25	0.5	1.0	2.5	5.0
Pyrene	0.25	0.5	1.0	2.5	5.0
Benzo(a)anthracene	0.25	0.5	1.0	2.5	5.0
Chrysene	0.25	0.5	1.0	2.5	5.0
Benzo(b)fluoranthene	0.25	0.5	1.0	2.5	5.0
Benzo(k)fluoranthene	0.25	0.5	1.0	2.5	5.0
Benzo(e)pyrene	0.25	0.5	1.0	2.5	5.0
Benzo(a)pyrene	0.25	0.5	1.0	2.5	5.0
Perylene	0.25	0.5	1.0	2.5	5.0
Indeno(1,2,3-cd)pyrene	0.25	0.5	1.0	2.5	5.0
Dibenz(a,h)anthracene	0.25	0.5	1.0	2.5	5.0
Benzo(ghi)perylene	0.25	0.5	1.0	2.5	5.0
Internal Standards					
d_8-Naphthalene	1.0	1.0	1.0	1.0	1.0
d_{10}-2-Methylnaphthalene	1.0	1.0	1.0	1.0	1.0
d_8-Acenaphthylene	1.0	1.0	1.0	1.0	1.0
d_{10}-Phenanthrene	1.0	1.0	1.0	1.0	1.0
d_{10}-Fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(a)anthracene	1.0	1.0	1.0	1.0	1.0
d_{12}-Chrysene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(b)fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(k)fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(a)pyrene	1.0	1.0	1.0	1.0	1.0
d_{12}-Perylene	1.0	1.0	1.0	1.0	1.0
d_{12}-Indeno(1,2,3,c-d)pyrene	1.0	1.0	1.0	1.0	1.0
d_{14}-Dibenz(a,h)anthracene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(ghi)perylene	1.0	1.0	1.0	1.0	1.0

TABLE 5 (CONT)

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR LOW RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (ng/µL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{10}-Fluorene	1.0	1.0	1.0	1.0	1.0
d_{14}-Terphenyl	1.0	1.0	1.0	1.0	1.0
Alternate Standard					
d_{10}-Anthracene	1.0	1.0	1.0	1.0	1.0
Recovery Standards					
d_{10}-Acenaphthene	1.0	1.0	1.0	1.0	1.0
d_{10}-Pyrene	1.0	1.0	1.0	1.0	1.0
d_{12}-benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0

TABLE 6

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/µL)				
	Solutions				
	1	2	3	4	5
Calibration Standards					
Naphthalene	10	50	100	200	500
2-Methylnaphthalene	10	50	100	200	500
Acenaphthylene	10	50	100	200	500
Acenaphthene	10	50	100	200	500
Fluorene	10	50	100	200	500
Phenanthrene	10	50	100	200	500
Anthracene	10	50	100	200	500
Fluoranthene	10	50	100	200	500
Pyrene	10	50	100	200	500
Benzo(a)anthracene	10	50	100	200	500
Chrysene	10	50	100	200	500
Benzo(b)fluoranthene	10	50	100	200	500
Benzo(k)fluoranthene	10	50	100	200	500
Benzo(e)pyrene	10	50	100	200	500
Benzo(a)pyrene	10	50	100	200	500
Perylene	10	50	100	200	500
Indeno(1,2,3-cd)pyrene	10	50	100	200	500
Dibenz(a,h)anthracene	10	50	100	200	500
Benzo(ghi)perylene	10	50	100	200	500
Internal Standards					
d_8-Naphthalene	100	100	100	100	100
d_8Methylnaphthalene	100	100	100	100	100
d_8-Acenaphthylene	100	100	100	100	100
d_{10}-Phenanthrene	100	100	100	100	100
d_{10}-Fluoranthene	100	100	100	100	100
d_{12}-Benzo(a)anthracene	100	100	100	100	100
d_{12}-Chrysene	100	100	100	100	100
d_{12}-Benzo(b)fluoranthene	200	200	200	200	200
d_{12}-Benzo(k)fluoranthene	200	200	200	200	200
d_{12}-Benzo(a)pyrene	200	200	200	200	200
d_{12}-Perylene	200	200	200	200	200
d_{12}-Indeno(1,2,3,c-d)pyrene	200	200	200	200	200
d_{14}-Dibenz(a,h)anthracene	200	200	200	200	200
d_{12}-Benzo(ghi)perylene	200	200	200	200	200

TABLE 6 (CONT)

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/µL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{10}-Fluorene	100	100	100	100	100
d_{14}-Terphenyl	100	100	100	100	100
Alternate Standard					
d_{10}-Anthracene	100	100	100	100	100
Recovery Standards					
d_{10}-Acenaphthene	200	200	200	200	200
d_{10}-Pyrene	200	200	200	200	200
d_{12}-benzo(e)pyrene	200	200	200	200	200

TABLE 6A

CONCENTRATIONS OF PAHs IN ALTERNATIVE WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/µL)				
	Solutions				
	1	2	3	4	5
Calibration Standards					
Naphthalene	10	50	100	200	500
2-Methylnaphthalene	10	50	100	200	500
Acenaphthylene	10	50	100	200	500
Acenaphthene	10	50	100	200	500
Fluorene	10	50	100	200	500
Phenanthrene	10	50	100	200	500
Anthracene	10	50	100	200	500
Fluoranthene	10	50	100	200	500
Pyrene	10	50	100	200	500
Benzo(a)anthracene	10	50	100	200	500
Chrysene	10	50	100	200	500
Benzo(b)fluoranthene	10	50	100	200	500
Benzo(k)fluoranthene	10	50	100	200	500
Benzo(e)pyrene	10	50	100	200	500
Benzo(a)pyrene	10	50	100	200	500
Perylene	10	50	100	200	500
Indeno(1,2,3-cd)pyrene	10	50	100	200	500
Dibenz(a,h)anthracene	10	50	100	200	500
Benzo(ghi)perylene	10	50	100	200	500
Internal Standards					
d_8-Naphthalene	100	100	100	100	100
d_8-Acenaphthylene	100	100	100	100	100
d_{10}-Acenaphthene	100	100	100	100	100
d_{10}-Fluorene	100	100	100	100	100
d_{10}-Phenanthrene	100	100	100	100	100
d_{10}-Fluoranthene	100	100	100	100	100
d_{12}-Benzo(a)anthracene	100	100	100	100	100
d_{12}-Chrysene	100	100	100	100	100
d_{12}-Benzo(b)fluoranthene	200	200	200	200	200
d_{12}-Benzo(k)fluoranthene	200	200	200	200	200
d_{12}-Benzo(a)pyrene	200	200	200	200	200
d_{12}-Indeno(1,2,3,c-d)pyrene	200	200	200	200	200
d_{14}-Dibenz(a,h)anthracene	200	200	200	200	200
d_{12}-Benzo(ghi)perylene	200	200	200	200	200

TABLE 6A (CONT)

CONCENTRATIONS OF PAHs IN ALTERNATIVE WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/µL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{12}-benzo(e)pyrene	100	100	100	100	100
d_{14}-Terphenyl	100	100	100	100	100
Alternate Standard					
d_{10}-Anthracene	100	100	100	100	100
Recovery Standards					
d_{10}-2-Methylnaphthalene	200	200	200	200	200
d_{10}-Pyrene	200	200	200	200	200
d_{12}-Perylene	200	200	200	200	200

TABLE 7

SPIKE LEVELS FOR LABELLED STANDARDS

Time of Addition	Analyte	LRMS (µg/sample)	HRMS (ng/sample)
Before sampling	**Surrogate Standards**		
	d_{10}-Fluorene	2.0	500
	d_{14}-Terphenyl	2.0	500
Before extraction	**Internal Standards**		
	d_8-Naphthalene	2.0	200
	d_{10}-2-Methylnaphthalene	2.0	200
	d_8-Acenaphthylene	2.0	200
	d_{10}-Phenanthrene	2.0	200
	d_{10}-Fluoranthene	2.0	200
	d_{12}-Benzo(a)anthracene	2.0	200
	d_{12}-Chrysene	2.0	200
	d_{12}-Benzo(b)fluoranthene	2.0	400
	d_{12}-Benzo(d)fluoranthene	2.0	400
	d_{12}-Benzo(a)pyrene	2.0	400
	d_{12}-Perylene	2.0	400
	d_{12}-Indeno(1,2,3,c-d)pyrene	2.0	400
	d_{14}-Dibenz(a,h)anthracene	2.0	400
	d_{12}-Benzo(ghi)perylene	2.0	400
Before extraction	**Alternate Standard**		
	d_{10}-Anthracene	2.0	200
Before GC/MS	**Recovery Standards**		
	d_{10}-Acenaphthene	1.0	100
	d_{10}-Pyrene	1.0	100
	d_{12}-benzo(e)pyrene	1.0	100

TABLE 7A

SPIKE LEVELS FOR LABELLED STANDARDS FOR ALTERNATIVE HRMS SPIKING SCHEME

Time of Addition	Analyte	HRMS (ng/sample)
Before sampling	**Surrogate Standards**	
	d_{12}-benzo(e)pyrene	500
	d_{14}-Terphenyl	500
Before extraction	**Internal Standards**	
	d_8-Naphthalene	200
	d_8-Acenaphthylene	200
	d_{10}-Acenaphthene	200
	d_{10}-Fluorene	200
	d_{10}-Phenanthrene	200
	d_{10}-Fluoranthene	200
	d_{12}-Benzo(a)anthracene	200
	d_{12}-Chrysene	200
	d_{12}-Benzo(b)fluoranthene	400
	d_{12}-Benzo(d)fluoranthene	400
	d_{12}-Benzo(a)pyrene	400
	d_{12}-Indeno(1,2,3,c-d)pyrene	400
	d_{14}-Dibenz(a,h)anthracene	400
	d_{12}-Benzo(ghi)perylene	400
Before extraction	**Alternate Standard**	
	d_{10}-Anthracene	200
Before GC/MS	**Recovery Standards**	
	d_{10}-2-Methylnaphthalene	100
	d_{10}-Pyrene	100
	d_{12}-Perylene	100

TABLE 8

TARGET CONCENTRATIONS FOR LABELLED STANDARDS IN SAMPLE EXTRACT[1]

	ng/µl LRMS	pg/µl HRMS
Surrogate Standards		
d_{10}-Fluorene	2.0	500
d_{14}-Terphenyl	2.0	500
Internal Standards		
d_8-Naphthalene	2.0	200
d_{10}-2-Methylnaphthalene	2.0	200
d_8-Acenaphthylene	2.0	200
d_{10}-Phenanthrene	2.0	200
d_{10}-Fluoranthene	2.0	200
d_{12}-Benzo(a)anthracene	2.0	200
d_{12}-Chrysene	2.0	200
d_{12}-Benzo(b)fluoranthene	2.0	400
d_{12}-Benzo(k)fluoranthene	2.0	400
d_{12}-Benzo(a)pyrene	2.0	400
d_{12}-Perylene	2.0	400
d_{12}-Indeno(1,2,3,c-d)pyrene	2.0	400
d_{14}-Dibenz(a,h)anthracene	2.0	400
d_{12}-Benzo(ghi)perylene	2.0	400
Alternate Standard		
d_{10}-Anthracene	1.0	200
Recovery Standards		
d_{10}-Acenaphthene	1.0	200
d_{10}-Pyrene	1.0	200
d_{12}-benzo(e)pyrene	1.0	200

[1] Assuming 100 percent recovery.

TABLE 8A

TARGET CONCENTRATIONS FOR LABELLED STANDARDS IN SAMPLE EXTRACT OBTAINED WITH ALTERNATIVE HRMS SPIKING SCHEME[1]

	pg/µl HRMS
Surrogate Standards	
d_{12}-benzo(e)pyrene	500
d_{14}-Terphenyl	500
Internal Standards	
d_8-Naphthalene	200
d_8-Acenaphthylene	200
d_{10}-Acenaphthene	200
d_{10}-Fluorene	200
d_{10}-Phenanthrene	200
d_{10}-Fluoranthene	200
d_{12}-Benzo(a)anthracene	200
d_{12}-Chrysene	200
d_{12}-Benzo(b)fluoranthene	400
d_{12}-Benzo(k)fluoranthene	400
d_{12}-Benzo(a)pyrene	400
d_{12}-Indeno(1,2,3,c-d)pyrene	400
d_{14}-Dibenz(a,h)anthracene	400
d_{12}-Benzo(ghi)perylene	400
Alternate Standard	
d_{10}-Anthracene	200
Recovery Standards	
d_{10}-2-Methylnaphthalene	200
d_{10}-Pyrene	200
d_{12}-Perylene	200

[1] Assuming 100 percent recovery.

TABLE 9

CONCENTRATIONS OF COMPOUNDS IN LABORATORY CONTROL SPIKE SAMPLE

	ng/sample	
	LRMS	HRMS
Unlabelled Compounds		
Naphthalene	2.0	1000
2-Methylnaphthalene	2.0	200
Acenaphthylene	2.0	200
Acenaphthene	2.0	200
Fluorene	2.0	200
Phenanthrene	2.0	500
Anthracene	2.0	200
Fluoranthene	2.0	200
Pyrene	2.0	200
Benzo(a)anthracene	2.0	200
Chrysene	2.0	200
Benzo(b)fluoranthene	2.0	200
Benzo(k)fluoranthene	2.0	200
Benzo(e)pyrene	2.0	200
Benzo(a)pyrene	2.0	200
Perylene	2.0	200
Indeno(1,2,3,c-d)pyrene	2.0	200
Dibenz(a,h)anthracene	2.0	200
Benzo(ghi)perylene	2.0	200
Alternate Standard		
d_{10}-Anthracene	2.0	200

TABLE 10

RECOMMENDED GAS CHROMATOGRAPHIC OPERATING CONDITIONS FOR PAH ANALYSIS

Column Type	DB-5
Length (m)	30
ID (mm)	0.25
Film Thickness (µm)	0.32
Helium Linear Velocity (cm/sec)	30
Injection mode	Splitless
Splitless Time (sec)	30
Initial Temperature (^{o}C)	45
Initial Time (min)	4
Program Rate (^{o}C/min)	8
Final Temperature (^{o}C)	300
Final Hold Time	until benzo(ghi) perylene has eluted
Injector Temperature (^{o}C)	320

TABLE 11

ASSIGNMENTS OF INTERNAL STANDARDS FOR CALCULATION OF RRFs
AND QUANTITATION OF TARGET PAHs AND SURROGATE STANDARDS

Analyte	Internal Standards
Unlabeled PAH	
Naphthalene	d_8-Naphthalene
2-Methylnaphthalene	d_{10}-2-Methylnaphthalene
Acenaphthylene	d_8-Acenaphthylene
Acenaphthene	d_8-Acenaphthylene
Fluorene	d_{10}-Phenanthrene
Phenanthrene	d_{10}-Phenanthrene
Anthracene	d_{10}-Phenanthrene
Fluoranthene	d_{10}-Fluoranthene
Pyrene	d_{10}-Fluoranthene
Benzo(a)anthracene	d_{12}-Benzo(a)anthracene
Chrysene	d_{12}-Chrysene
Benzo(b)fluoranthene	d_{12}-Benzo(b)fluoranthene
Benzo(k)fluoranthene	d_{12}-Benzo(k)fluoranthene
Benzo(e)pyrene	d_{12}-Benzo(a)pyrene
Benzo(a)pyrene	d_{12}-Benzo(a)pyrene
Perylene	d_{12}-Perylene
Indeno(1,2,3-cd)pyrene	d_{12}-Indeno(1,2,3,c-d)pyrene
Dibenz(a,h)anthracene	d_{14}-Dibenz(a,h)anthracene
Benzo(ghi)perylene	d_{12}-Benzo(ghi)perylene
Surrogate Standards	
d_{10}-Fluorene	d_{10}-Phenanthrene
d_{14}-Terphenyl	d_{10}-Fluoranthene

TABLE 11A

ASSIGNMENTS OF INTERNAL STANDARDS FOR CALCULATION OF RRFs AND QUANTITATION OF TARGET PAHs AND SURROGATE STANDARDS USING ALTERNATIVE HRMS SPIKING SCHEME

Analyte	Internal Standards
Unlabeled PAH	
Naphthalene	d_8-Naphthalene
2-Methylnaphthalene	d_{10}-Acenaphthene
Acenaphthylene	d_8-Acenaphthylene
Acenaphthene	d_{10}-Acenaphthene
Fluorene	d_{10}-Fluorene
Phenanthrene	d_{10}-Phenanthrene
Anthracene	d_{10}-Phenanthrene
Fluoranthene	d_{10}-Fluoranthene
Pyrene	d_{10}-Fluoranthene
Benzo(a)anthracene	d_{12}-Benzo(a)anthracene
Chrysene	d_{12}-Chrysene
Benzo(b)fluoranthene	d_{12}-Benzo(b)fluoranthene
Benzo(k)fluoranthene	d_{12}-Benzo(k)fluoranthene
Benzo(e)pyrene	d_{12}-Benzo(a)pyrene
Benzo(a)pyrene	d_{12}-Benzo(a)pyrene
Perylene	d_{12}-Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene	d_{12}-Indeno(1,2,3,c-d)pyrene
Dibenz(a,h)anthracene	d_{14}-Dibenz(a,h)anthracene
Benzo(ghi)perylene	d_{12}-Benzo(ghi)perylene
Surrogate Standards	
d_{14}-Terphenyl	d_{10}-Fluoranthene
d_{12}-Benzo(e)pyrene	d_{12}-Benzo(a)pyrene

TABLE 12

ASSIGNMENTS OF RECOVERY STANDARDS FOR DETERMINATION OF PERCENT RECOVERIES OF INTERNAL STANDARDS AND THE ALTERNATE STANDARD

Analyte	Recovery Standard
Internal Standards	
d_8-Naphthalene	d_{10}-Acenaphthene
d_{10} -2-Methylnaphthalene	d_{10}-Acenaphthene
d_8-Acenaphthylene	d_{10}-Acenaphthene
d_{10}-Phenanthrene	d_{10}-Pyrene
d_{10}-Fluoranthene	d_{10}-Pyrene
d_{12}-Benzo(a)anthracene	d_{10}-Pyrene
d_{12}-Chrysene	d_{10}-Pyrene
d_{12}-Benzo(b)fluoranthene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(k)fluoranthene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(a)pyrene	d_{12}-Benzo(e)pyrene
d_{12}-Perylene	d_{12}-Benzo(e)pyrene
d_{12}-Indeno(1,2,3,c-d)pyrene	d_{12}-Benzo(e)pyrene
d_{14}-Dibenz(a,h)anthracene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(ghi)perylene	d_{12}-Benzo(e)pyrene
Alternate Standard	
d_{10}-Anthracene	d_{10}-Pyrene

TABLE 12A

ASSIGNMENTS OF RECOVERY STANDARDS FOR DETERMINATION OF PERCENT RECOVERIES OF INTERNAL STANDARDS AND THE ALTERNATE STANDARD USING ALTERNATIVE HRMS SPIKING SCHEME

Analyte	Recovery Standard
Internal Standards	
d_8-Naphthalene	d_{10}-2-Methylnaphthalene
d_{10} -2-Methylnaphthalene	d_{10}-2-Methylnaphthalene
d_8-Acenaphthylene	d_{10}-2-Methylnaphthalene
d_{10}-Phenanthrene	d_{10}-Pyrene
d_{10}-Fluoranthene	d_{10}-Pyrene
d_{12}-Benzo(a)anthracene	d_{10}-Pyrene
d_{12}-Chrysene	d_{10}-Pyrene
d_{12}-Benzo(b)fluoranthene	d_{12}-Perylene
d_{12}-Benzo(k)fluoranthene	d_{12}-Perylene
d_{12}-Benzo(a)pyrene	d_{12}-Perylene
d_{12}-Perylene	d_{12}-Perylene
d_{12}-Indeno(1,2,3,c-d)pyrene	d_{12}-Perylene
d_{14}-Dibenz(a,h)anthracene	d_{12}-Perylene
d_{12}-Benzo(ghi)perylene	d_{12}-Perylene
Alternate Standard	
d_{10}-Anthracene	d_{10}-Pyrene

TABLE 13

QUANTITATION AND CONFIRMATION IONS FOR SELECTED
ION MONITORING OF PAHs BY HRGC/LRMS

Analyte	Quant. Ion	Confirm. Ion	%Relative Abundance of Confirm. Ion
Naphthalene	128	127	10
d_8-Naphthalene	136	68	80
2-Methylnaphthalene	142	141	80
d_{10}-2-Methylnaphthalene	152		
Acenaphthylene	152	153	15
d_8-Acenaphthylene	160		
Acenaphthene	154	153	86
d_{10}-Acenaphthene	164		
Fluorene	166	165	80
d_{10}-Fluorene	176		
Phenanthrene	178	176	15
d_{10}-Phenanthrene	188	94	
Anthracene	178	176	15
d_{10}-Anthracene	188	94	
Fluoranthene	202	101	15
d_{10}-Fluoranthene	212	106	
Pyrene	202	101	15
d_{10}-Pyrene	212	106	
Benzo(a)anthracene	228	114	15
d_{12}-Benzo(a)anthracene	240	120	
Chrysene	228	114	15
d_{12}-Chrysene	240	120	
d_{14}-Terphenyl	244	122	15

TABLE 13 (CONT)

QUANTITATION AND CONFIRMATION IONS FOR SELECTED
ION MONITORING OF PAHs BY HRGC/LRMS

Analyte	Quant. Ion	Confirm. Ion	%Relative Abundance of Confirm. Ion
Benzo(b)fluoranthene	252	126	25
d_{12}-Benzo(b)fluoranthene	264	132	
Benzo(k)fluoranthene	252	126	25
d_{12}-Benzo(k)fluoranthene	264	132	
Benzo(e)pyrene	252	126	25
d_{12}-Benzo(e)pyrene	264	132	
Benzo(a)pyrene	252	126	25
d_{12}-Benzo(a)pyrene	264	132	
Perylene	252	126	26
d_{12}-Perylene	264	132	
Indeno(1,2,3-cd)pyrene	276	138	28
d_{12}-Indeno(1,2,3-cd)pyrene	288		
Dibenz(ah)anthracene	278	139	24
d_{14}-Dibenz(ah)anthracene	292		
Benzo(ghi)perylene	276	138	37
d_{12}-Benzo(ghi)perylene	288		

TABLE 14

MASS DESCRIPTORS USED FOR SELECTED ION MONITORING FOR HRGC/HRMS

Descriptor No.	Analyte Type	Ion m/z	Accurate
1	Naphthalene	M	128.0626
	PFK	LOCK	130.9920
	d_8-Naphthalene	IS	136.1128
	2-Methylnaphthalene	M	142.0782
	d_{10}-2-Methylnaphthalene	IS	152.1410
	Acenaphthylene	M	152.0626
	d_8-Acenaphthylene	IS	160.1128
	Acenaphthene	M	154.0782
	d_{10}-Acenaphthene	RS	164.1410
	PFK	QC	169.9888
2	Fluorene	M	166.0782
	d_{10}-Fluorene	SS	176.1410
	Phenanthrene	M	178.0782
	d_{10}-Phenanthrene	IS	188.1410
	Anthracene	M	178.0782
	d_{10}-Anthracene	AS	188.1410
	Fluoranthene	M	202.0782
	d_{10}-Fluoranthene	IS	212.1410
	Pyrene	M	202.0782
	PFK	QC	204.9888
	d_{10}-Pyrene	RS	212.1410
	Benzo(a)anthracene	M	228.0939
	d_{12}-Benzo-a-Anthracene	IS	240.1692
	Chrysene	M	228.0939
	d_{12}-Chrysene	IS	240.1692
	PFK	LOCK	230.9856
	d_{14}-Terphenyl	SS	244.1974

IS = Internal Standard
SS = Surrogate Standard
AS = Alternate Standard
RS = Recovery Standard
LOCK = Lock-Mass Ion
QC = Quality Control Check Ion

TABLE 14 (CONT)

MASS DESCRIPTORS USED FOR SELECTED ION MONITORING FOR HRGC/HRMS

Descriptor No.	Analyte Type	Ion m/z	Accurate
3	Perylene	M	252.0939
	d_{12}-Perylene	IS	264.1692
	PFK	QC	268.9824
	Benzo(b)fluoranthene	M	252.0939
	d_{12}-Benzo(b)fluoranthene	IS	264.1692
	Benzo(k)fluoranthene	M	252.0939
	d_{12}-Benzo-k-fluoranthene	IS	264.1692
	Benzo(e)pyrene	M	252.0939
	d_{12}-Benzo(e)pyrene	RS	264.1692
	Benzo(a)pyrene	M	252.0939
	d_{12}-Benzo(a)pyrene	IS	264.1692
	Benzo(ghi)perylene	M	276.0939
	d_{12}-Benzo(ghi)perylene	IS	288.1692
	Indeno(1,2,3-cd)pyrene	M	276.0939
	d_{12}-Indeno(1,2,3-cd)pyrene	IS	288.1692
	Dibenzo(ah)anthracene	M	278.1096
	PFK	LOCK	280.9824
	d_{14}-Dibenzo(ah)anthracene	IS	292.1974

The following nuclidic masses were used:

H = 1.007825 ^{2}H = 2.014102 C = 12.000000

IS = Internal Standard
SS = Surrogate Standard
AS = Alternate Standard
RS = Recovery Standard
LOCK = Lock-Mass Ion
QC = Quality Control Check Ion

FIGURE 1

METHOD 429 FLOWCHART

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§1.3.9	*The end user is identified*
§1.3.10	*The tester is designated*

35

	The end user chooses:	
§2.1.1	!	source target concentration

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§2.1.2	*The tester selects analyst with documented*
§8.4	*experience in satisfactory performance of analytical*
§8.4.1	*procedures*

37

		Tester and laboratory coordinate:
§4.3.2	!	pre-test cleaning of glassware
§4.2	!	pre-test cleaning, contamination checks, and
§4.3.3		storage of sampling materials and reagents
§4.3.4	!	preparation of filter, sorbent cartridges, method blanks, and LCS

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		Tester requests pre-test analytical results from laboratory:
§10.1.1	!	contamination check of filters
§10.1.2	!	contamination check of XAD-2 resin
§10.1.3	!	Method detection limits (MDLs) and Practical quantitation limits (PQLs)

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		Tester calculates and plans:
§2.5	!	≥3 sampling runs and ≥1 blank sampling train
	!	sample volume
	!	sampling time
	!	source reporting limit
	!	chain of custody

40

		Tester performs:
§4.3.1	!	calibration of equipment

41

		Tester writes:
§2.2	!	pre-test protocol

42

		Tester performs:
§4.4.1	!	preliminary field sampling determinations
§4.4.2	!	sampling train preparation
§4.4.3	!	leak-checks
§4.4.4	!	sampling procedure
	!	≥3 sampling runs
	!	≥1 blank sampling train
§5	!	recovery of all runs and blank sampling train

43

		Tester delivers:
§5.3	!	recovered sampling runs and blank train(s)
§5.4	!	chain of custody record

44

		Laboratory performs:
§6	!	extraction of field samples
§7	!	analyses
§8	!	QA/QC procedures
§9	!	chain of custody
§10.2	!	reporting requirements

45

		Tester performs:
§4.3.1	!	post-test calibrations
§9.2	!	calculations
§10.3	!	data recording and chain of custody
	!	reporting requirements

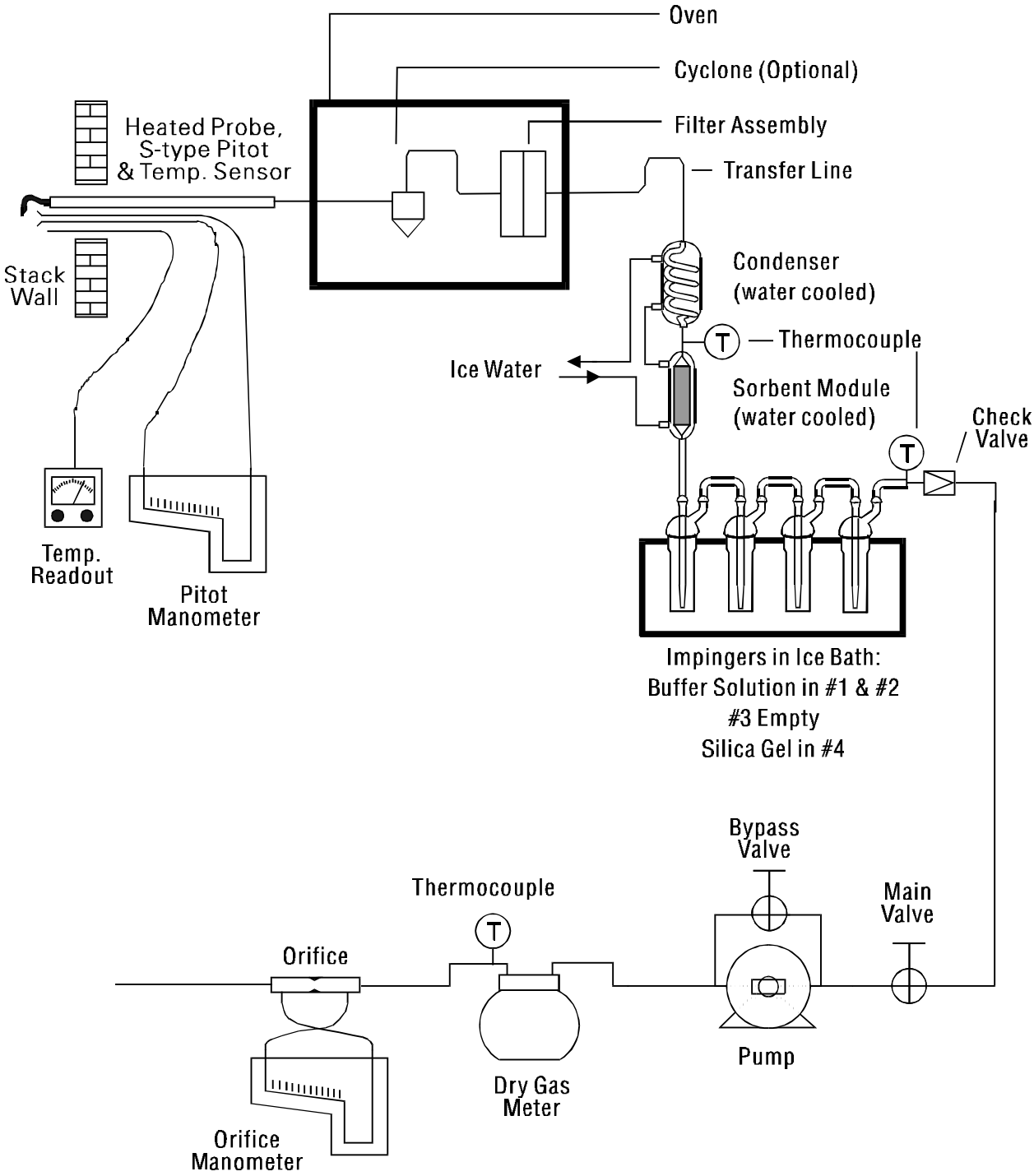

Figure 2
PAH Sampling Train

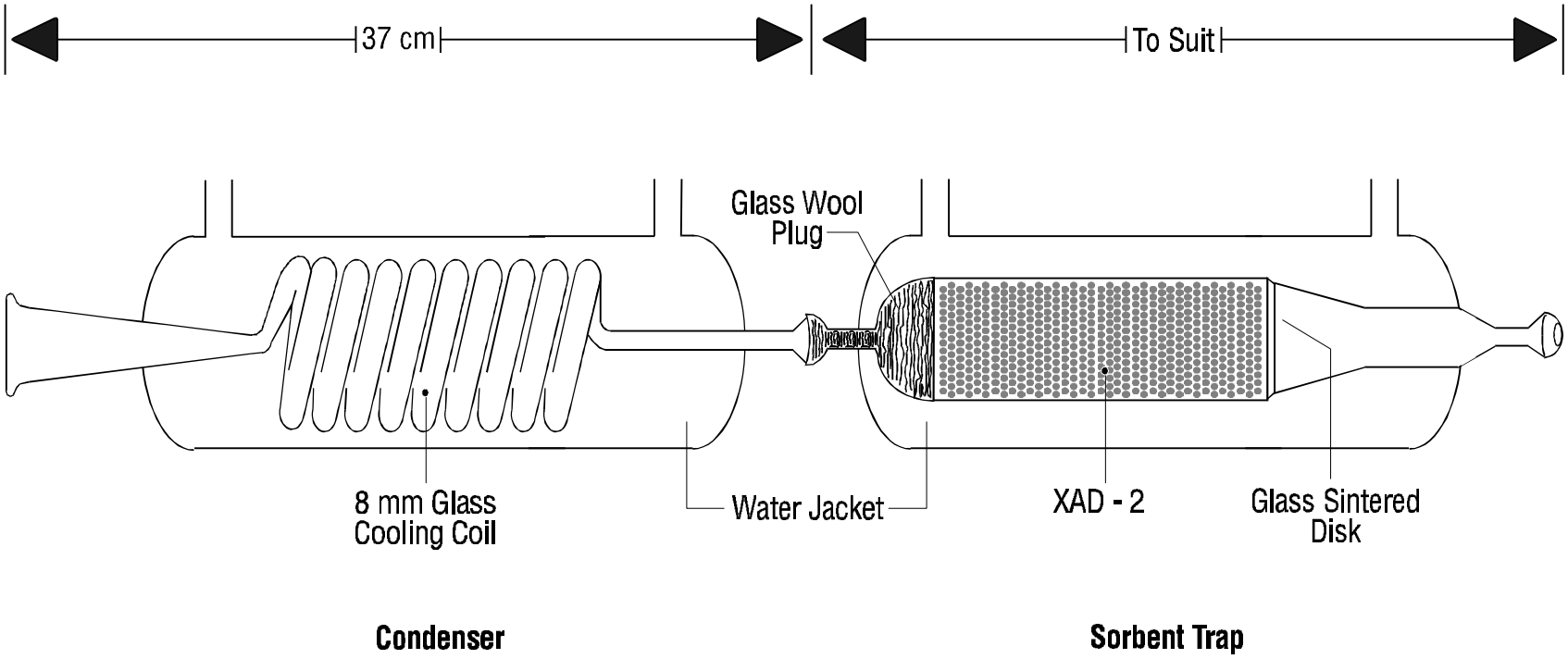

Figure 3

Condenser and Sorbent Trap for Collection
of Gaseous PAHs

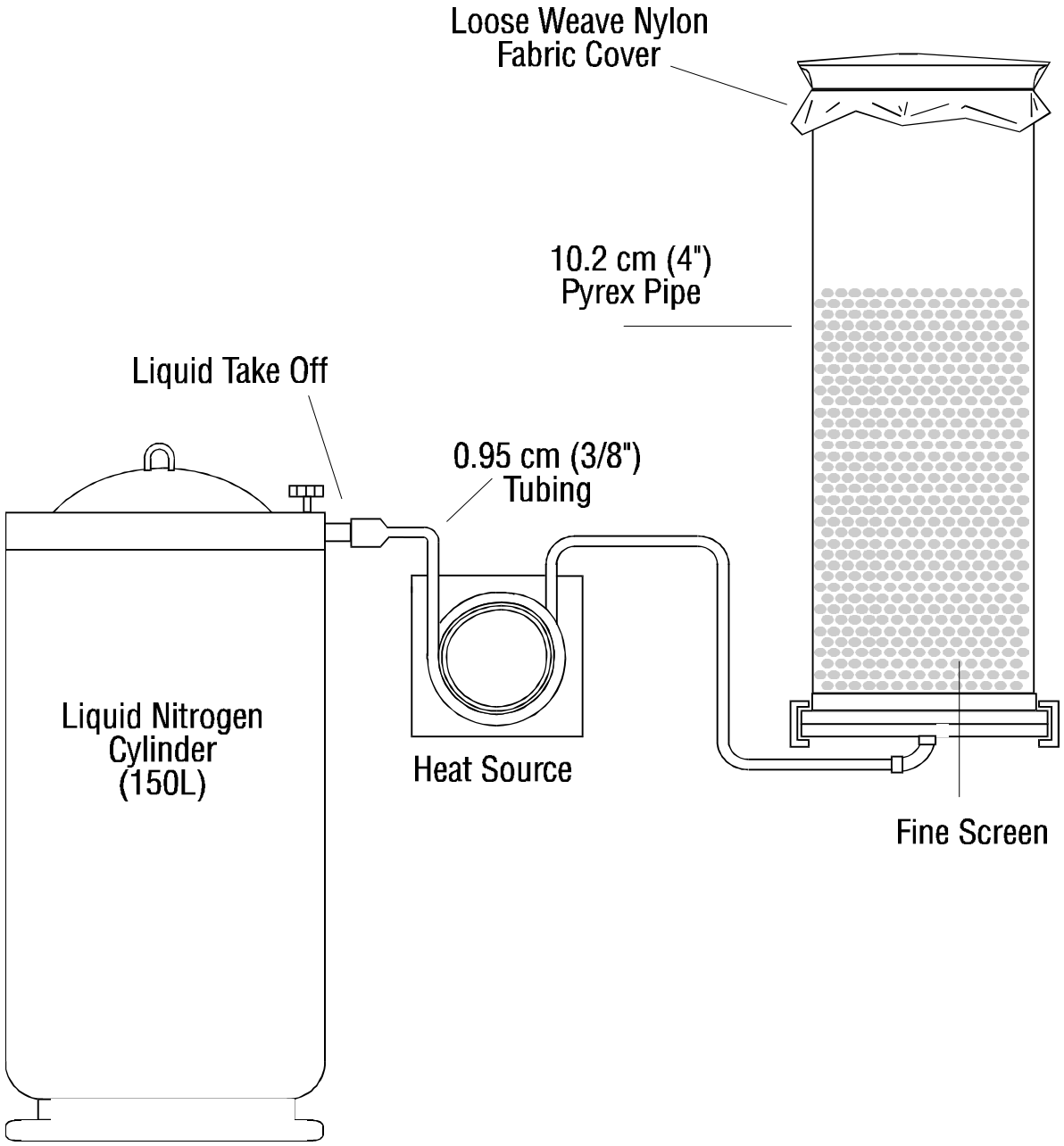

Figure 4

XAD-2 Fluidized Bed Drying Apparatus

FIGURE 5

METHOD 429 FIELD DATA RECORD

Run No. _____
Location _____
Date _____
Operator_____
Meter Box No. _____
Local Time
Start/Stop _____
ΔH@ _____
Stack Diameter _____
Meter Box Calibration
Factor (Y) _____

Pitot Tube Factor _____
Probe Tip Dia, in. _____
Probe Length _____
Sampling Train Leak Test Leak Rate
Before _____ in. Hg _____ cu.ft/min
After _____ in. Hg _____ cu.ft/min
Leak-Check Volume _____cu. ft.
Pitot Tube Leak-Check
Before _____ After _____

Project No. _____
Plant Name _____
Ambient Temp ^{o}F _____
Meter Temp ^{o}F _____
Bar. Press, "Hg _____
Stack Press, "H_2O _____
Assumed Moisture, % _____
Heater Box Setting, ^{o}F _____
Probe Heater Setting, ^{o}F _____
Assumed M.W. (wet%) _____
Assumed M.W. (dry%) _____

Sampling Point	Clock Time	Dry Gas Meter, cu, ft.	Pitot ΔP in. H_2O	Orifice ΔH "H_2O		Temperature (^{o}F)			Pump Vacuum
				Desired	Actual	Impinger	Filter box	Stack	in. Hg
Start									

Figure 6

Recovery of PAH Sampling Train

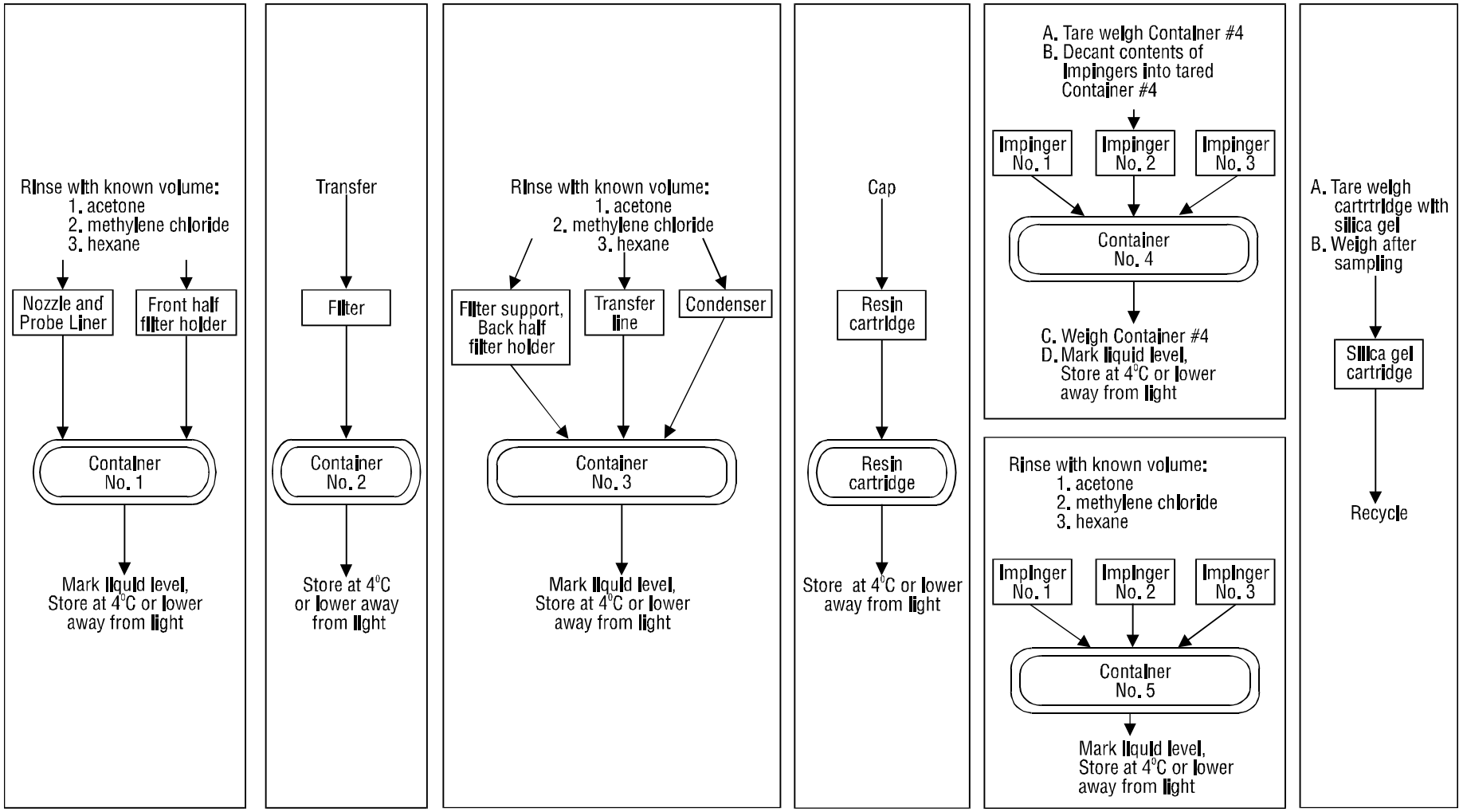

Figure 7

Flow Chart for Sampling, Extraction and Cleanup for Determination of PAH in a Split Sample

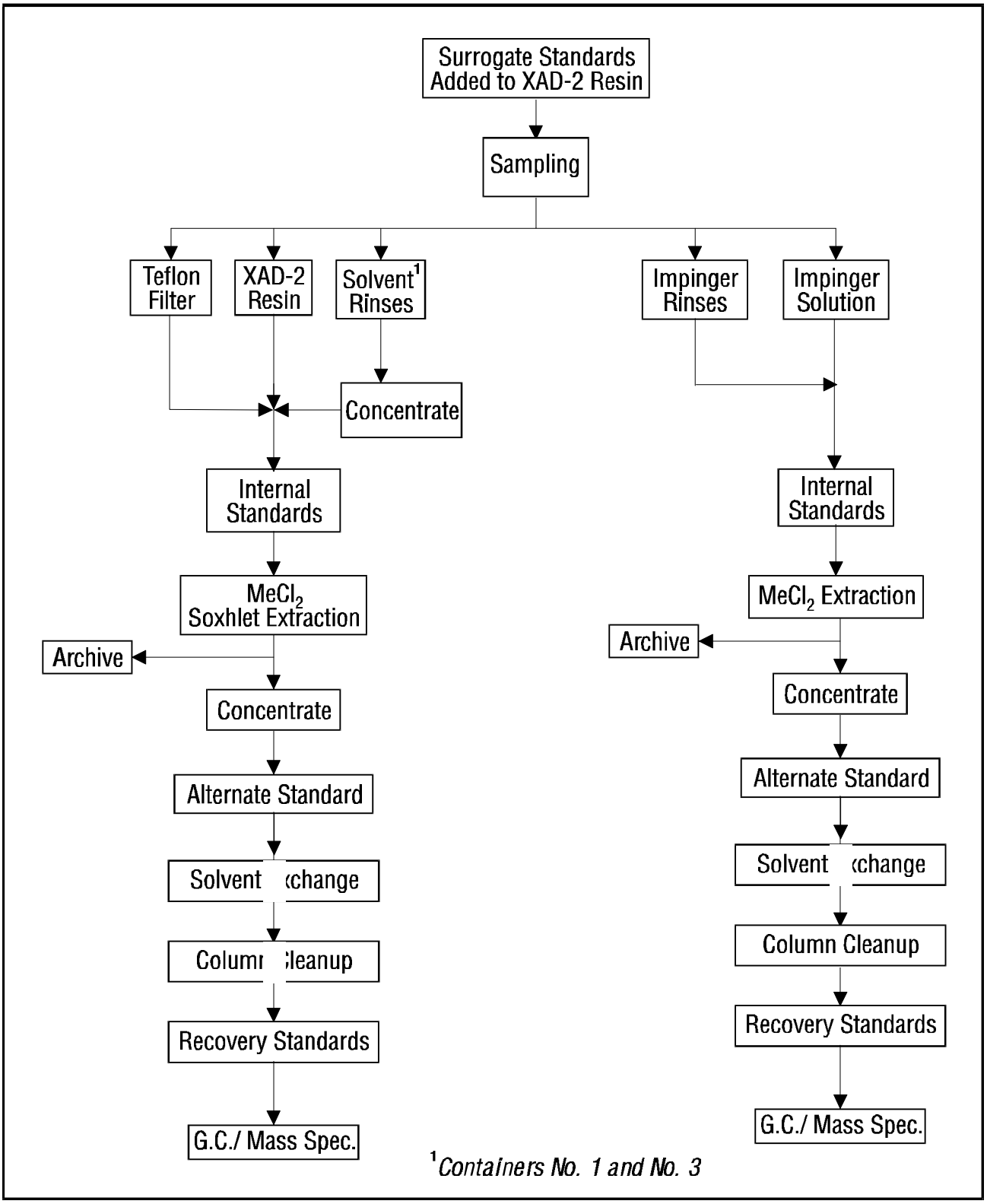

Figure 8
Flow Chart for Sampling, Extraction and Cleanup for Determination of PAH in a Composite Sample

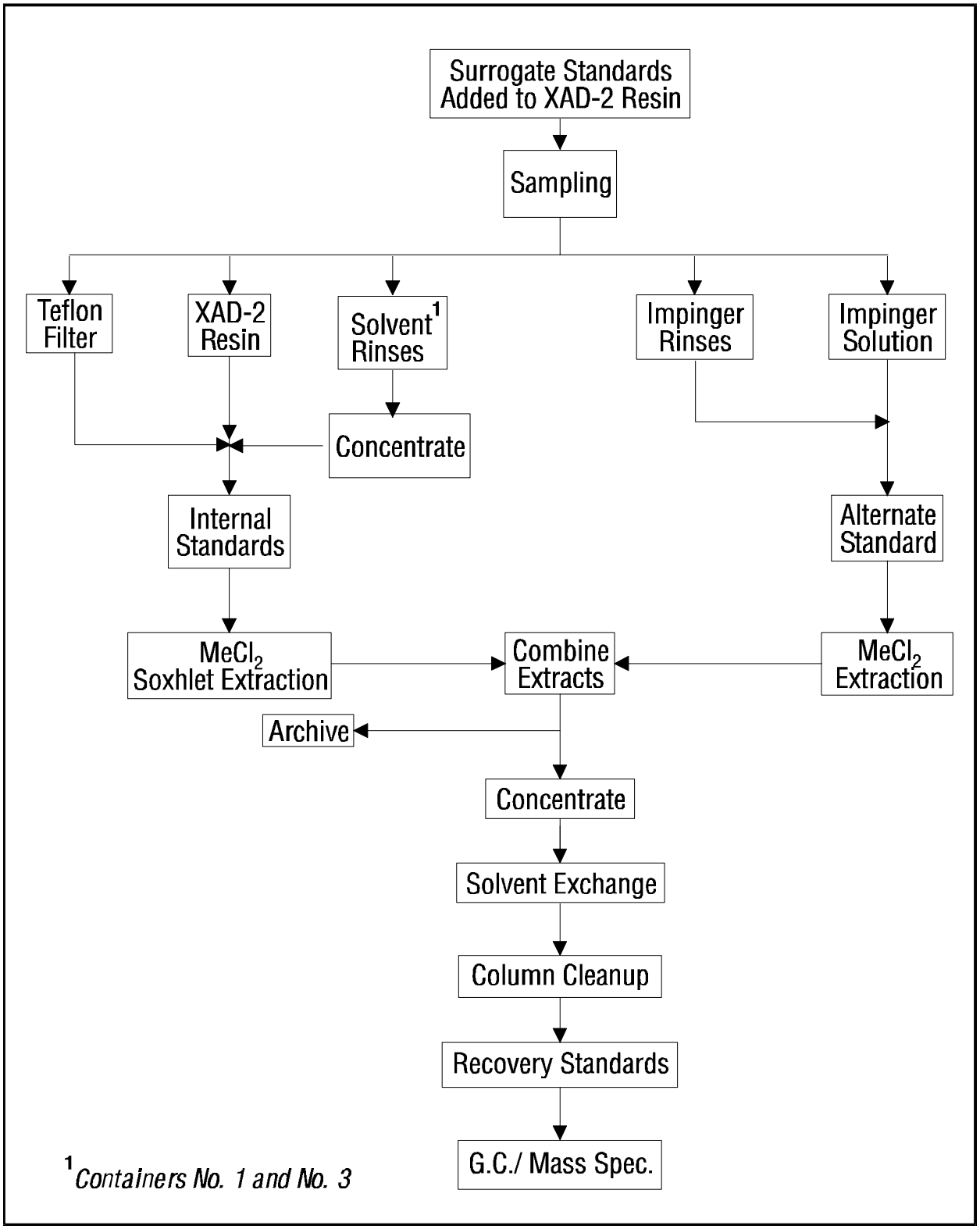

FIGURE 9

EXAMPLE OF PRE-TEST CALCULATIONS FOR PAH EMISSIONS TEST

					PST = 6 hours PSV = 180 dscf	
	PQL (ng/sample)	STC (ng/dscm)	MSV (dscf)	MST (hours)	F	SRL (ng/dscm)
Naphthalene	2400	<1500	>56.5	>1.89	NA	471
2-Methylnaphthalene	330	NA	NA	NA	NA	64.7
Acenaphthylene	5.0	180	0.98	0.03	183	0.98
Acenaphthene	5.0	6	29.4	0.98	6	0.98
Fluorene[1]	83	<6	>489	>16.3	NA	16.3
Phenanthrene	110	120	32.4	1.08	6	21.6
Anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Fluoranthene	5.0	46	3.8	0.13	47	0.98
Pyrene	5.0	46	3.8	0.13	47	0.98
Benzo(a)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Chrysene	5.0	42	4.2	0.14	43	0.98
Benzo(b)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(k)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(e)pyrene	5.0	NA	NA	NA	NA	0.98
Benzo(a)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Perylene	5.0	NA	NA	NA	NA	0.98
Indeno(1,2,3-c,d)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Dibenzo(a,h)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Benzo(g,h,i)perylene	5.0	<6	>29.4	>0.98	NA	0.98
Average Volumetric Sampling Rate (VSR) = 0.5 dscfm = 30 dscf/hr						

PQL = Practical quantitation limit for analyte (based on pre-test analysis of XAD-2 resin)

STC = Source target concentration for analyte. (From previous emissions test. Samples were analyzed by HRGC/LRMS).

MSV = Minimum sample volume required to collect detectable levels of target analyte. (MSV = PQL ÷ STC) *Equation 429-1*

MST = Minimum sample time required to collect detectable levels of target analyte at VSR. (MST = MSV ÷ VSR) *Equation 429-2*

PST = Planned sampling time (6 hours chosen as the longest practical sampling time for the planned emissions test)

PSV = Planned sample volume (PSV = PST × VSR) *Equation 429-4*

F = Safety factor (>1) that allows for deviation from ideal sampling and analytical conditions. (F = PSV ÷ MSV) *Equation 429-5*

SRL = Source reporting limit if the target analyte cannot be detected with the planned test parameters. (SRL = PQL ÷ PSV) *Equation 429-7*

NA This calculation is not applicable either because there is no STC value available or the STC is a detection limit.

[1] PSV is lower than the MSV. Therefore, the analyte is not expected to be detected if it is present at the target concentrations. It will only be detected if the actual concentration is higher than the indicated SRL.

FIGURE 10

CARB METHOD 429 (PAHs) SAMPLING TRAIN SET-UP RECORD

RUN NO.	_____	PROJECT NO.	_____
PLANT NAME	_____	PLANT LOCATION	_____
SET-UP DATE	_____	SET-UP BY	_____
RECEIVED BY	_____	DATE/TIME	_____

	COMPONENTS	COMPONENT ID	OTHER INFORMATION	
1.	NOZZLE	_____	Material	_____
			Diameter	_____
2.	PROBE	_____	Liner material	_____
			Length	_____
3.	FILTER HOLDER	_____	Before set-up, all openings sealed with	_____
			Filter support type	_____
4.	FILTER	Lot # _____	Filter Type	_____
			Size	_____
			Contamination check?	_____
5.	TRANSFER LINE AND CONDENSER	_____	Transfer line material	_____
	Fittings	_____		_____
6.	XAD-2 RESIN CARTRIDGE	_____	Both ends sealed in lab prior to set-up	_____
			Fittings	_____
			Contamination check?	_____
			Spiked?	_____
7.	IMPINGERS: No. 1	_____	Charge with 100 mL impinger solution and weigh	_____ g
	U-Connector	_____		
	No. 2	_____	Charge with 100 mL impinger solution and weigh	_____ g
	U-Connector	_____		
	No. 3	_____		
	U-Connector	_____	Weigh empty	_____ g
8.	SILCA GEL CARTRIDGE	_____	Tare weight	_____ g
			Appearance	_____

FIGURE 11

CARB METHOD 429 (PAHs) SAMPLING TRAIN RECOVERY RECORD

RUN NO. _____ PROJECT NO. _____
PLANT NAME _____ PLANT LOCATION _____
RECOVERY DATE _____ RECOVERED BY _____

1. CHECK whether openings were covered. RINSE 3x each with Acetone, $MeCl_2$, Hexane. MARK liquid level and STORE containers at temp. <4°C away from light.

Component	Openings covered?	Rinse volume (mL) Acetone	$MeCl_2$	Hexane	Storage Container(s) IDs
Nozzle					
Probe liner					
Filter holder front					

2. STORE filter(s) at temp. <4°C away from light. RECORD ALL sample storage information.

Component	Appearance after sampling	Storage (Temperature & light)	Storage Container(s) ID
Filter			
Filter			
Filter			

3. CHECK whether openings were covered. RINSE 3x each with Acetone, $MeCl_2$, Hexane. MARK liquid level and STORE containers at temp. <4°C away from light.

Component	Openings covered?	Rinse volume (mL) Acetone	$MeCl_2$	Hexane	Storage Temp. & light	Storage Container ID
Filter support and filter holder back						
Transfer line						
Condenser						

4. STORE Resin cartridges at temp. <4°C away from light. RECORD ALL storage information.

ID	Appearance after sampling	Storage temperature & light conditions

5. WEIGH impinger contents and silica gel cartridge. MARK liquid level and STORE impinger contents at temp. <4°C away from light.

Weight	No. 1	No. 2	No. 3	Additional impingers No. 4	No. 5	Silica gel cartridge
Final (g)						
Before sampling (g)						
Gain (g)	(A)	(B)	(C)	(D)	(E)	(F)

Total condensate (A) + (B) + (C) + (D) + (E) + (F) _____ (g)

STORAGE CONTAINER ID(s) _____ _____ _____ _____

6. RINSE impingers 3x each with Acetone, $MeCl_2$, Hexane. MARK liquid level and STORE impinger rinses at temp. <4°C away from light.

Rinse volumes (mL)	Acetone					
	$MeCl_2$					
	Hexane					
STORAGE CONTAINER ID(s)						

FIGURE 12

CHAIN OF CUSTODY SAMPLE RECORD

Project # _____ Date:_____ Start: _____
Stop: _____
Source name: _____ Sample/Run # : _____
Sampling location: _____ Sample type: _____
Chain of Custody Log Record # (s) _____ Operator: _____

SAMPLE STORAGE INFORMATION

SAMPLE PRESERVATION	Comments
Ice/Dry ice?	

CHAIN OF CUSTODY

ACTION	DATE	TIME	GIVEN BY	TAKEN BY

RELATED IDs	DESCRIPTION/COMMENTS	Log #s
FR	Front rinse (nozzle, probe,filter holder front)	
F	Filter in sealed storage container	
BR	Back rinse (filter support, filter holder, sample line & condenser	
C	Resin cartridge	
I	Impinger contents	
IR	Impinger rinses	

FIGURE 13

CHAIN OF CUSTODY LOG RECORD

PROJECT NO. _____ **Page _____ of _____**

Log #	Sample ID	Date	Time	Comments	Given by	Taken by

Sample Identifier **Sample Description**

FR	Rinses of probe and front half of filter holder
F	Filter in sealed storage container
BR	Rinses of filter support, back half of filter holder, sample transfer line and condenser
C	Aluminum foil wrapped, capped resin cartridge
I	Impinger contents
IR	Impinger rinses

FIGURE 14A

EXAMPLE GC/MS SUMMARY REPORT (HRMS) FOR INITIAL CALIBRATION SOLUTION #1
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

ICAL ID: ST1120A1 ACQUIRED: 12/3/94 16:23:24 INSTRUMENT: W
RUN #: PAHCS1 PROCESSED: 12/3/94 OPERATOR: MPA

	RT	RRT	Area	RRF
Naphthalene	8:20	1.006	6.66 E+07	0.75
2-Methylnaphthalene	9:42	1.007	1.44 E+07	1.30
Acenaphthylene	11:04	1.003	1.57 E+07	1.44
Acenaphthene	11:20	1.004	1.05 E+07	0.94
Fluorene	12:06	1.003	8.15 E+06	1.05
Phenanthrene	13:20	1.003	1.99 E+07	1.15
Anthracene	13:23	1.001	7.07 E+06	1.02
Fluoranthene	14:38	1.001	3.18 E+07	1.26
Pyrene	14:55	1.001	3.31 E+07	1.31
Benzo(a)anthracene	16:34	1.002	2.08 E+07	1.13
Chrysene	16:39	1.003	2.26 E+07	1.13
Benzo(b)fluoranthene	18:54	1.004	2.35 E+07	1.69
Benzo(k)fluoranthene	18:58	1.004	2.50 E+07	1.24
Benzo(e)pyrene	19:42	1.004	2.41 E+07	1.20
Benzo(a)pyrene	19:51	1.003	2.11 E+07	1.07
Perylene	20:06	1.004	1.38 E+07	0.70
Indeno(1,2,3-c,d)pyrene	23:60	1.006	2.07 E+07	2.19
Dibenzo(a,h)anthracene	24:01	1.006	1.49 E+07	1.66
Benzo(g,h,i)perylene	25:15	1.005	1.84 E+07	2.23
d_8-Naphthalene	8:17	1.000	3.54 E+08	4.22
d_8-Acenaphthylene	11:02	1.000	1.09 E+08	1.29
d_{10}-Acenaphthene	11:17	1.000	1.11 E+08	1.32
d_{10}-Fluorene	12:04	1.000	7.78 E+07	0.93
d_{10}-Phenanthrene	13:18	1.000	6.92 E+07	0.82
d_{10}-Fluoranthene	14:37	1.000	2.53 E+08	1.03
d_{12}-Benzo(a)anthracene	16:32	1.000	1.83 E+08	0.75
d_{12}-Chrysene	16:36	1.000	2.00 E+08	0.82
d_{12}-Benzo(b)fluoranthene	18:50	1.000	2.77 E+08	1.35
d_{12}-Benzo(k)fluoranthene	18:54	1.000	4.03 E+08	1.95
d_{12}-Benzo(a)pyrene	19:47	1.000	3.93 E+08	1.91
d_{12}-Indeno(1,2,3-c,d)pyrene	23:52	1.000	1.89 E+08	0.92
d_{14}-Dibenzo(a,h)anthracene	23:52	1.000	1.80 E+08	0.87
d_{12}-Benzo(g,h,i)perylene	25:07	1.000	1.65 E+08	0.80
d_{14}-Terphenyl	14:59		2.65 E+08	0.52
d_{12}-Benzo(e)pyrene	19:37	1.000	1.44 E+08	0.37
d_{10}-Anthracene	13:22	1.000	5.82 E+07	0.69
d_{10}-2-Methylnaphthalene	9:38	1.000	8.40 E+07	---
d_{10}-Pyrene	14:54	1.000	2.45 E+08	---
d_{12}-Perylene	20:01	1.000	1.03 E+08	---

FIGURE 14B

EXAMPLE OF INITIAL CALIBRATION (ICAL) RRF SUMMARY
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

ICAL ID:	ST1120	ACQUIRED:	3-DEC-94	INSTRUMENT:	W
RUN #:	NA	PROCESSED:	3-DEC-94	OPERATOR:	MPA

	RRF #1	RRF #2	RRF #3	RRF #4	RRF #5	Mean RRF	SD	%RSD
Naphthalene	0.75	0.66	0.61	0.64	0.71	0.67	0.056	8.29%
2-Methylnaphthalene	1.30	1.15	1.10	1.12	1.26	1.19	0.089	7.47%
Acenaphthylene	1.44	1.27	1.24	1.28	1.43	1.33	0.096	7.19%
Acenaphthene	0.94	0.84	0.80	0.83	0.94	0.87	0.067	7.72%
Fluorene	1.05	0.94	0.88	0.92	1.07	0.97	0.082	8.43%
Phenanthrene	1.15	1.06	1.01	1.05	1.23	1.10	0.088	8.00%
Anthracene	1.02	1.00	0.98	0.95	1.14	1.02	0.074	7.25%
Fluoranthene	1.26	1.15	1.08	1.13	1.28	1.18	0.085	7.21%
Pyrene	1.31	1.27	1.13	1.15	1.41	1.25	0.115	9.22%
Benzo(a)anthracene	1.13	1.05	1.05	1.04	1.23	1.10	0.082	7.43%
Chrysene	1.13	1.02	0.97	0.98	1.11	1.04	0.073	7.00%
Benzo(b)fluoranthene	1.69	1.45	1.46	1.42	1.86	1.58	0.194	12.33%
Benzo(k)fluoranthene	1.24	1.25	1.14	1.18	1.26	1.21	0.052	4.32%
Benzo(e)pyrene	1.20	1.12	1.06	1.06	1.19	1.12	0.066	5.89%
Benzo(a)pyrene	1.07	0.99	0.96	0.96	1.14	1.02	0.080	7.81%
Perylene	0.70	0.63	0.58	0.60	0.70	0.64	0.059	9.12%
Indeno(1,2,3-c,d)pyrene	2.19	2.01	1.92	1.99	2.26	2.07	0.143	6.90%
Dibenzo(a,h)anthracene	1.66	1.60	1.56	1.61	1.87	1.66	0.122	7.35%
Benzo(g,h,i)perylene	2.23	2.05	1.96	2.00	2.32	2.11	0.154	7.28%
d_8-Naphthalene	4.22	4.15	4.16	4.18	4.10	4.16	0.044	1.05%
d_8-Acenaphthylene	1.29	1.29	1.28	1.27	1.30	1.29	0.012	0.91%
d_{10}-Acenaphthene	1.32	1.34	1.32	1.30	1.32	1.32	0.013	1.00%
d_{10}-Fluorene	0.93	0.95	0.94	0.95	0.95	0.94	0.011	1.21%
d_{10}-Phenanthrene	0.82	0.82	0.82	0.86	0.88	0.81	0.026	3.09%
d_{10}-Fluoranthene	1.03	1.00	1.07	1.07	0.99	1.03	0.038	3.71%
d_{12}-Benzo(a)anthracene	0.75	0.70	0.70	0.72	0.70	0.71	0.022	3.09%
d_{12}-Chrysene	0.82	0.79	0.81	0.83	0.84	0.82	0.021	2.56%
d_{12}-Benzo(b)fluoranthene	1.35	1.39	1.46	1.27	1.32	1.36	0.072	5.32%
d_{12}-Benzo(k)fluoranthene	1.95	1.95	2.14	1.84	2.11	2.00	0.124	6.23%
d_{12}-Benzo(a)pyrene	1.91	1.96	2.11	1.82	1.99	1.96	0.107	5.46%
d_{12}-Indeno(1,2,3-c,d)pyrene	0.92	0.88	0.98	0.85	0.98	0.92	0.059	6.40%
d_{14}-Dibenzo(a,h)anthracene	0.87	0.84	0.91	0.78	0.89	0.86	0.049	5.71%
d_{12}-Benzo(g,h,i)perylene	0.80	0.76	0.83	0.73	0.80	0.78	0.042	5.36%
d_{14}-Terphenyl	0.52	0.52	0.49	0.48	0.51	0.51	0.018	3.59%
d_{12}-Benzo(e)pyrene	0.37	0.37	0.37	0.36	0.36	0.36	0.005	1.50%
d_{10}-Anthracene	0.69	0.73	0.74	0.80	0.90	0.77	0.080	10.40%
d_{10}-2-Methylnaphthalene	---	---	---	---	---	---	---	---
d_{10}-Pyrene	---	---	---	---	---	---	---	---
d_{12}-Perylene	---	---	---	---	---	---	---	---

FIGURE 14C

EXAMPLE OF CONTINUING CALIBRATION (CONCAL) SUMMARY
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

CONCAL ID:	CC1202	ICAL ID:	ST1120	INSTRUMENT:	W
CONCAL DATE:	12/3/94	ICAL DATE:	3-DEC-94	OPERATOR:	MPA

	RRF	ICAL RRF	ΔRRF	RPD %
Naphthalene	0.68	0.67	0.01	1.5
2-Methylnaphthalene	1.42	1.19	0.23	17.6
Acenaphthylene	1.42	1.33	0.09	6.6
Acenaphthene	0.91	0.87	0.04	4.5
Fluorene	0.98	0.97	0.01	1.0
Phenanthrene	1.10	1.10	0.00	0.0
Anthracene	0.98	1.02	-0.04	4.0
Fluoranthene	1.12	1.18	-0.06	5.2
Pyrene	1.18	1.25	-0.07	5.8
Benzo(a)anthracene	1.08	1.10	-0.02	1.8
Chrysene	1.04	1.04	0.00	0.0
Benzo(b)fluoranthene	1.46	1.58	-0.12	7.9
Benzo(k)fluoranthene	1.12	1.21	-0.09	7.7
Benzo(e)pyrene	1.04	1.12	-0.08	7.4
Benzo(a)pyrene	0.95	1.02	-0.07	7.1
Perylene	0.62	0.64	-0.02	3.2
Indeno(1,2,3-c,d)pyrene	2.04	2.07	-0.03	1.5
Dibenzo(a,h)anthracene	1.61	1.66	-0.05	3.1
Benzo(g,h,i)perylene	2.11	2.11	0.00	0.0
d_8-Naphthalene	4.78	1.16	0.68	15.3
d_8-Acenaphthylene	1.20	1.29	-0.09	7.2
d_{10}-Acenaphthene	1.25	1.32	-0.07	5.5
d_{10}-Fluorene	0.85	0.94	-0.09	10.1
d_{10}-Phenanthrene	0.79	0.81	-0.02	2.5
d_{10}-Fluoranthene	1.05	1.03	0.02	1.9
d_{12}-Benzo(a)anthracene	0.69	0.71	-0.02	2.9
d_{12}-Chrysene	0.82	0.82	0.00	0.0
d_{12}-Benzo(b)fluoranthene	1.24	1.36	-0.12	9.2
d_{12}-Benzo(k)fluoranthene	1.91	2.00	-0.09	4.6
d_{12}-Benzo(a)pyrene	1.87	1.96	-0.09	4.7
d_{12}-Indeno(1,2,3-c,d)pyrene	0.84	0.92	-0.08	9.1
d_{14}-Dibenzo(a,h)anthracene	0.80	0.86	-0.06	7.2
d_{12}-Benzo(g,h,i)perylene	0.76	0.78	-0.02	2.6
d_{14}-Terphenyl	0.50	0.51	-0.01	2.0
d_{12}-Benzo(e)pyrene	0.37	0.36	0.01	2.7
d_{10}-Anthracene	0.71	0.77	-0.06	8.1
d_{10}-2-Methylnaphthalene	---	---		
d_{10}-Pyrene	---	1.000		
d_{12}-Perylene	---	1.000		

FIGURE 15A.

EXAMPLE OF SUMMARY REPORT OF LCS RESULTS
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Client ID: CARB
Lab ID: 1412 9/LCS1/LCS2
Instrument: W
Operator: MPA
Reviewer: JCM

Sample Matrix: XAD-2
Date Received: NA
Date Extracted: 11/30/94
Date Analyzed: 12/3/94
Sample amount: Sample

ICAL ID: ST1120
ICAL DATE: 12/3/94
CONCAL ID: NA
CONCAL DATE: NA
Units: NA

Resin Lot #: LC1130M
LCS IDs: NA
LCS DATE: NA

COMPOUND:	LCS1 %R	LCS2 %R	RPD %
Naphthalene	100	103	3.0
2-Methylnaphthalene	96	95	1.0
Acenaphthylene	95	97	2.1
Acenaphthene	92	94	2.2
Fluorene	94	96	2.1
Phenanthrene	93	94	1.1
Anthracene	91	89	2.2
Fluoranthene	90	92	2.2
Pyrene	87	89	2.3
Benzo(a)anthracene	87	86	1.2
Chrysene	83	89	7.0
Benzo(b)fluoranthene	92	93	1.1
Benzo(k)fluoranthene	92	95	3.2
Benzo(e)pyrene	97	99	2.0
Benzo(a)pyrene	89	92	3.3
Perylene	89	89	0.0
Indeno(1,2,3-c,d)pyrene	87	90	3.4
Dibenzo(a,h)anthracene	88	90	2.2
Benzo(g,h,i)perylene	89	91	1.2
Internal Standards (%R)			
d_8-Naphthalene	67	64	
d_8-Acenaphthylene	73	70	
d_{10}-Acenaphthene	76	75	
d_{10}-Fluorene	79	81	
d_{10}-Phenanthrene	88	93	
d_{10}-Fluoranthene	84	80	
d_{12}-Benzo(a)anthracene	96	98	
d_{12}-Chrysene	96	91	
d_{12}-Benzo(b)fluoranthene	88	85	
d_{12}-Benzo(k)fluoranthene	85	84	
d_{12}-Benzo(a)pyrene	92	90	
d_{12}-Indeno(1,2,3-c,d)pyrene	104	105	
d_{14}-Dibenzo(a,h)anthracene	96	96	
d_{12}-Benzo(g,h,i)perylene	102	103	
Alternate Standard (%R)			
d_{10}-Anthracene	83	85	

FIGURE 15B

LCS RECOVERIES FOR BENZO(a)PYRENE

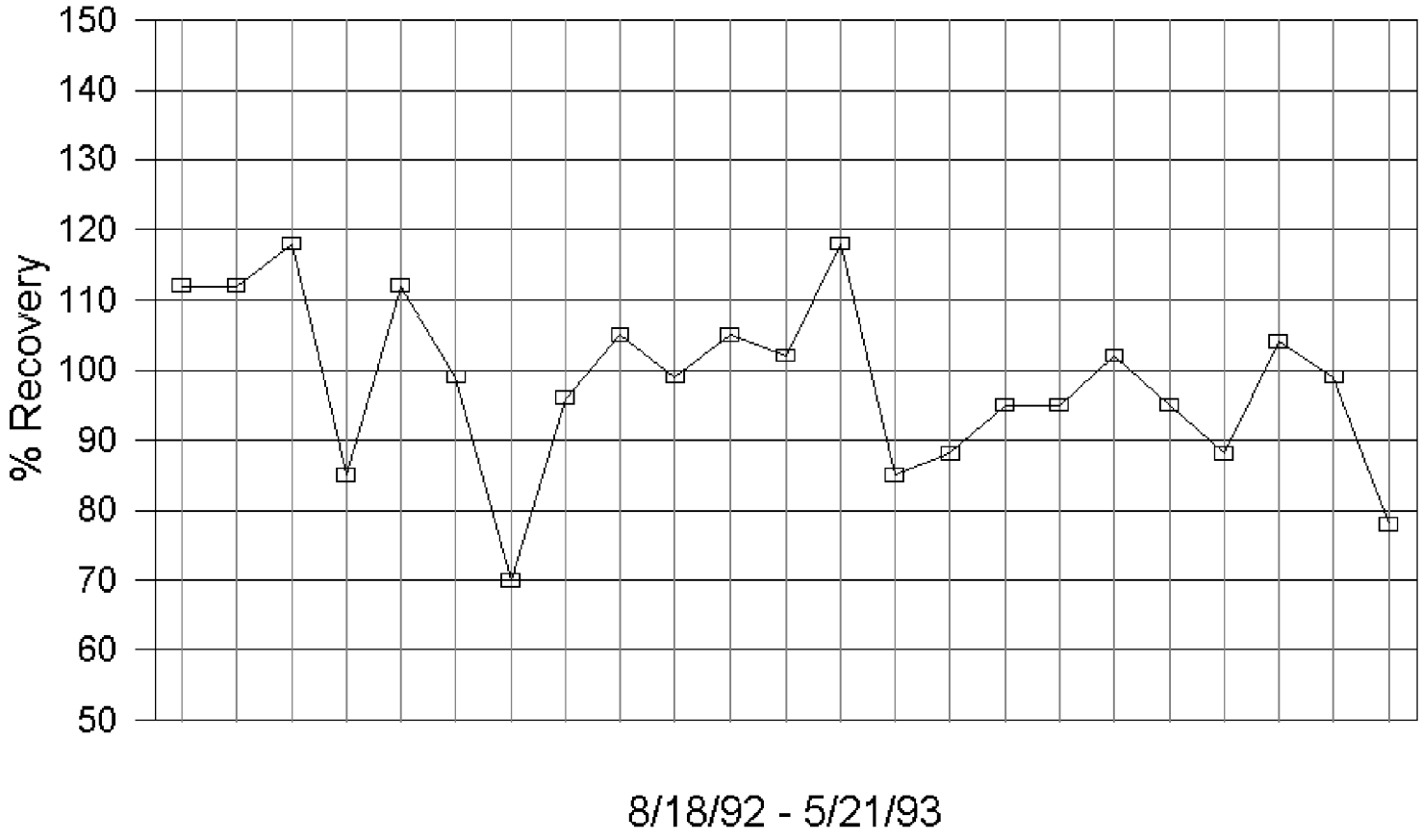

FIGURE 16A

EXAMPLE GC/MS SUMMARY REPORT (HRMS) FOR SAMPLE RUN #32
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Lab ID: 14129-02 ICAL ID: 12/3/94 16:23:40 Instrument: W
Acquired: 12/3/94 16:23:40 ICAL DATE: 12/3/94 Operator: MPA
Client ID: M429-32 Reviewer: JCM

	RT	RRT	Area	RRF	Amt. (ng)	% REC
Naphthalene	8:21		1.053 E+10	0.67	10,478.37	
2-Methylnaphthalene	9:41		1.790 E+08	1.19	140.98	
Acenaphthylene	11:03		9.371 E+08	1.33	712.59	
Acenaphthene	11:19		7.649 E+06	0.87	8.21	
Fluorene	12:05		2.417 E+07	0.97	30.02	
Phenanthrene	13:17		8.402 E+08	1.10	925.53	
Anthracene	13:21		2.905 E+07	1.02	34.54	
Fluoranthene	14:36		5.932 E+08	1.18	254.36	
Pyrene	14:52		7.611 E+08	1.25	307.62	
Benzo(a)anthracene	16:32		3.120 E+06	1.10	1.9	
Chrysene	16:32		9.620 E+06	1.04	6.2	
Benzo(b)fluoranthene	18:49		1.030 E+06	1.58	7.6	
Benzo(k)fluoranthene	Not found		0.0	1.21		
Benzo(e)pyrene	19:36		1.646 E+07	1.12	13.61	
Benzo(a)pyrene	19:46		4.936 E+06	1.02	3.95	
Perylene	20:01		1.823 E+06	0.64	2.32	
Indeno(1,2,3-c,d)pyrene	23:54		5.728 E+06	2.07	4.37	
Dibenzo(a,h)anthracene	23:56		5.875 E+05	1.66	0.59	
Benzo(g,h,i)perylene	25:09		1.584 E+07	2.11	14.95	
d_8-Naphthalene	8:18	1.000	4.794 E+08	1.16	124.92	62.5
d_8-Acenaphthylene	11:01	1.000	1.972 E+08	1.29	166.07	83.0
d_{10}-Acenaphthene	11:16	1.000	2.142 E+08	1.32	176.19	88.1
d_{10}-Fluorene	12:02	1.000	1.658 E+08	0.94	190.71	95.4
d_{10}-Phenanthrene	13:16	1.000	1.652 E+07	0.81	213.39	106.7
d_{10}-Fluoranthene	14:34	1.000	3.955 E+08	1.03	116.22	58.1
d_{12}-Benzo(a)anthracene	16:28	1.000	2.835 E+08	0.71	121.18	60.6
d_{12}-Chrysene	16:31	1.000	2.987 E+08	0.82	111.08	55.5
d_{12}-Benzo(b)fluoranthene	18:45	1.000	3.439 E+08	1.36	165.79	41.4
d_{12}-Benzo(k)fluoranthene	18:50	1.000	4.304 E+08	2.00	141.02	35.3
d_{12}-Benzo(a)pyrene	19:41	1.000	4.895 E+08	1.96	163.67	40.9
d_{12}-Indeno(1,2,3-c,d)pyrene	23:46	1.000	2.529 E+08	0.92	179.71	44.9
d_{14}-Dibenzo(a,h)anthracene	23:45	1.000	2.400 E+08	0.86	182.65	45.7
d_{12}-Benzo(g,h,i)perylene	24:60	1.000	2.006 E+08	0.78	167.24	41.8
d_{14}-Terphenyl	14:55		7.988 E+08	0.51	523	105
d_{12}-Benzo(e)pyrene	19:32	1.000	3.011 E+08	0.36	676.33	135.3
d_{10}-Anthracene	13:20	1.000	6.795 E+07	0.77	95.29	47.6
d_{10}-2-Methylnaphthalene	9:38	1.000	1.844 E+07	---	100	
d_{10}-Pyrene	14:51	1.000	6.576 E+08	---	100	
d_{12}-Perylene	19:56	1.000	3.057 E+08	---	100	

FIGURE 16B

EXAMPLE LABORATORY REPORT OF PAH RESULTS FOR SAMPLE RUN #32
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Client ID M429-32	Sample Matrix: M429	ICAL ID: ST1120	Resin Lot #: LC1130M
Lab ID: 14129-02	Date Received: 11/18/94	ICAL DATE: 12/3/94	LCS IDs: 14129-LCS1/LCS2
Instrument: W	Date Extracted: 11/30/94	CONCAL ID: NA	LCS DATE: 12/3/94
Operator: MPA	Date Analyzed: 12/3/94	CONCAL DATE: NA	
Reviewer: JCM	Sample amount: Sample	Units: ng/sample	

COMPOUND:	Conc.	R.L.	Flags
Naphthalene	10478	1600	
2-Methylnaphthalene	141	94	
Acenaphthylene	712	5.0	
Acenaphthene	8.2	5.0	
Fluorene	30	27	
Phenanthrene	930	80	
Anthracene	35	5.0	
Fluoranthene	254	5.0	
Pyrene	307	5.0	
Benzo(a)anthracene	ND	5.0	
Chrysene	6.2	5.0	
Benzo(b)fluoranthene	7.6	5.0	
Benzo(k)fluoranthene	ND	5.0	
Benzo(e)pyrene	14	5.0	
Benzo(a)pyrene	ND	5.0	
Perylene	ND	5.0	
Indeno(1,2,3-c,d)pyrene	ND	5.0	
Dibenzo(a,h)anthracene	ND	5.0	
Benzo(g,h,i)perylene	15	5.0	
Internal Standards (%R)			
d_8-Naphthalene	62		
d_8-Acenaphthylene	83		
d_{10}-Acenaphthene	88		
d_{10}-Fluorene	95		
d_{10}-Phenanthrene	107		
d_{10}-Fluoranthene	58		
d_{12}-Benzo(a)anthracene	61		
d_{12}-Chrysene	56		
d_{12}-Benzo(b)fluoranthene	41		H
d_{12}-Benzo(k)fluoranthene	35		H
d_{12}-Benzo(a)pyrene	41		H
d_{12}-Indeno(1,2,3-c,d)pyrene	45		H
d_{14}-Dibenzo(a,h)anthracene	46		H
d_{12}-Benzo(g,h,i)perylene	42		H
Alternate Standard (%R)			
d_{10}-Anthracene	48		
Surrogate Standard (%R)			
d_{14}-Terphenyl	105		
d_{12}-Benzo(e)pyrene	135		

FIGURE 17A
EXAMPLE OF TESTER'S SUMMARY OF LABORATORY REPORTS

Run #:	31	32	33	Field Blank	Method Blank	LCS #1	LCS #2
	ng/sample					**percent recovery**	
Naphthalene	4300	10000	460000 *	<1600	<1700	100	103
2-Methylnaphthalene	< 94	140	6400 *	< 94	<78	96	95
Acenaphthylene	140	710	85000 *	9.1	< 5.0	95	97
Acenaphthene	9.2	8.2	500	< 5.0	< 5.0	92	94
Fluorene	27	30	180	< 27	< 27	94	96
Phenanthrene	310	930	43000 *	< 80	< 74	93	94
Anthracene	26	35	2400	5.3	< 5.0	91	89
Fluoranthene	83	250	16000 *	16	< 5.0	90	92
Pyrene	110	310	20000 *	19	< 5.0	87	89
Benzo(a)anthracene	< 5.0	< 5.0	170	< 5.0	< 5.0	87	86
Chrysene	< 5.0	6.2	300	< 5.0	< 5.0	83	89
Benzo(b)fluoranthene	< 5.0	7.6	340	< 5.0	< 5.0	92	93
Benzo(k)fluoranthene	< 5.0	< 5.0	89	< 5.0	< 5.0	92	95
Benzo(e)pyrene	35	< 35	530	6.9	< 5.0	97	99
Benzo(a)pyrene	< 5.0	< 5.0	240	< 5.0	< 5.0	89	92
Perylene	< 5.0	< 5.0	110	< 5.0	< 5.0	89	89
Indeno(1,2,3-c,d)pyrene	< 5.0	< 5.0	100	< 5.0	< 5.0	87	90
Dibenzo(a,h)anthracene	< 5.0	< 5.0	6.4	< 5.0	< 5.0	88	90
Benzo(g,h,i)perylene	< 85	< 85	440	17.0	< 5.0	89	91
Internal Standards (%R)							
d_8-Naphthalene	66	62	57 *	53	55	67	64
d_8-Acenaphthylene	82	83	85 *	73	69	73	70
d_{10}-Acenaphthene	85	88	80 *	81	75	76	75
d_{10}-Fluorene	91	95	102	90	82	79	81
d_{10}-Phenanthrene	106	107	79 *	107	93	88	93
d_{10}-Fluoranthene	79	58	75 *	83	80	84	80
d_{12}-Benzo(a)anthracene	100	61	108	114	93	96	98
d_{12}-Chrysene	91	56	99	102	88	96	91
d_{12}-Benzo(b)fluoranthene	69	41 H	60	85	84	88	85
d_{12}-Benzo(k)fluoranthene	62	35 H	50	78	84	85	84
d_{12}-Benzo(a)pyrene	70	41 H	58	86	89	92	90
d_{12}-Indeno(1,2,3-c,d)pyrene	82	45 H	58	106	106	104	105
d_{14}-Dibenzo(a,h)anthracene	72	42 H	58	92	92	96	96
d_{12}-Benzo(g,h,i)perylene	84	46 H	58	107	104	102	103
Surrogate Standards (%R)							
d_{14}-Terphenyl	125	105	90	123	130		
d_{12}-Benzo(e)pyrene	72	135	112	103	112		
Alternate Standard (%R)							
d_{10}-Anthracene	67	48 H	115	116	101	83	85
Test Date	11/15/94	11/16/94	11/17/94	11/16/94	NA	NA	NA
Date received by lab.	11/18/94	11/18/94	11/18/94	11/18/94	NA	NA	NA
Date extracted	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94
Date analyzed	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94

"<" denotes that the compound was not detected at levels above the indicated reporting limit.
"H" indicates internal Standard Recovery Results below 50%, but signal-to-noise greater than 10:1.
"*" indicates compounds reanalyzed at 1:50 dilution due to saturation.

FIGURE 17B
FIELD DATA SUMMARY FOR PAH EMISSIONS TEST

	RUN ID	31	32	33	
	DATE	11-15-95	11-16-95	11-17-95	
	START/STOP TIME	1015/1435	1020/1645	0855/1525	
	LOCATION	STACK	STACK	STACK	
	STACK DIAMETER	35.5 in.	35.5 in.	35.5 in.	
	NOZZLE DIAMETER	0.3105	0.313 in.	0.3125 in.	
	METER BOX ID	5419	5419	5419	
STANDARD DRY GAS VOLUME	$V_{m(std)}$	145.19	235.57	250.76	DSCF(68° F)
	V_m	132.65	213.67	228.10	cubic ft
	P_{bar}	29.78	29.98	29.88	inches Hg
	ΔH_{avg}	1.15	1.35	1.56	inches H_2O
	T_m	60.0	60.0	60.0	° F
	K_1	17.64	17.64	17.64	
	Y	1.08	1.08	1.08	
PERCENT MOISTURE	B_{ws}	12.9	15.0	18.4	percent
	Impinger + tare	2183.3	2092.3	2063	grams
	Final wt.	2609.8	2934.9	3210.2	grams
	Net imp. catch	426.5	842.6	1147.2	grams
	Silica gel tare	1561.8	1788.8	1585.7	grams
	Post sampling wt.	1590.0	1826.9	1536.2	grams
	Moisture gain	28.2	38.1	49.5	grams
	Total moisture (V_{1c})	454.7	880.7	1196.7	grams
	$V_{w(std)}$	21.43	41.50	56.39	DSCF(68° F)
	$V_{m(std)}$	145.19	235.57	250.76	DSCF(68° F)
	K_2	0.0471	0.0471	0.0471	
MOLECULAR WEIGHT	M_d	29.93	29.95	30.08	lb/lbmole
	M_s	28.40	28.16	27.86	lb/lbmole
	O_2	11.25	10.75	10.00	percent
	CO	0.00	0.00	0.00	percent
	CO_2	9.25	9.50	10.50	percent
	N_2	79.50	79.75	79.50	percent
	B_{ws}	12.86	14.98	18.36	percent
GAS VELOCITY	v_s	38.4	40.88	43.2	feet/second
	Δp	0.530	0.56	0.59	inches H_2O
	T_s	420	428	427	° F
	P_g	-0.27	-0.27	-0.27	inches H_2O
	P_s	29.76	29.96	29.86	inches Hg
	M_s	28.40	28.16	27.86	lb/lbmole
	K_p	85.49	85.49	85.49	
	C_p	0.83	0.83	0.83	
VOLUMETRIC FLOW RATE	Q_{std}	8241	8531	8641	DSCF(68° F)
	B_{ws}	12.86	14.98	18.36	percent
	v_s	38.38	40.88	43.23	feet/second
	A	6.8736	6.8736	6.8736	sq. feet
	sec/min	60	60	60	
	K_1	17.64	17.64	17.64	
ISOKINETIC RATIO	I	96	99	104	percent
	T_s	420	428	427	° F
	$V_{m(std)}$	145.19	235.57	250.76	DSCFM(68° F)
	P_s	29.76	29.96	29.86	inches Hg
	v_s	38.38	40.88	43.23	feet/second
	θ	240	360	360	minutes
	B_{ws}	12.86	14.98	18.36	percent
	A_n	0.00053	0.00053	0.00053	sq. feet
	K_4	0.09450	0.09450	0.09450	

FIGURE 17C

EXAMPLE OF EMISSIONS TEST REPORT

	Run #31	Run #32	Run #33
(ng/dscm)			
Naphthalene	1046	1499	64782
2-Methylnaphthalene	<23	21.0	901
Acenaphthylene	34	106	11971
Acenaphthene	2.2	1.2	70
Fluorene	6.6	4.5	25
Phenanthrene	75	139	6056
Anthracene	<6.3	5.3	338
Fluoranthene	20	38	2253
Pyrene	27	47	2817
Benzo(a)anthracene	<1.2	<0.75	24
Chrysene	<1.2	0.92	42
Benzo(b)fluoranthene	<1.2	1.1	48
Benzo(k)fluoranthene	<1.2	<0.75	13
Benzo(e)pyrene	<8.5	<5.3	75
Benzo(a)pyrene	<1.2	<0.75	34
Perylene	<1.2	<0.75	16
Indeno(1,2,3-c,d)pyrene	<1.2	<0.75	14
Dibenzo(a,h)anthracene	<1.2	<0.75	0.90
Benzo(g,h,i)perylene	<21	<13	62
(ng/sec)			
Naphthalene	4068	6036	264180
2-Methylnaphthalene	<89	85	3676
Acenaphthylene	132	429	48816
Acenaphthene	8.7	5.0	287
Fluorene	26	18	103
Phenanthrene	293	561	24695
Anthracene	<25	21	1378
Fluoranthene	79	151	9189
Pyrene	104	187	11486
Benzo(a)anthracene	<4.7	<3.0	99
Chrysene	<4.7	3.7	172
Benzo(b)fluoranthene	<4.7	4.6	195
Benzo(k)fluoranthene	<4.7	<3.0	51
Benzo(e)pyrene	<33	<21	304
Benzo(a)pyrene	<4.7	<3.0	138
Perylene	<4.7	<3.0	63
Indeno(1,2,3-c,d)pyrene	<4.7	<3.0	57
Dibenzo(a,h)anthracene	<4.7	<3.0	3.7
Benzo(g,h,i)perylene	<80	<51	253

Standard Conditions: 68 deg.F (20 deg.C) & 29.92 in. Hg. (760 mm Hg)
"<" indicates that the compound was not detected above the reporting limit.

METHOD 429 - APPENDIX A

DETERMINATION OF THE METHOD DETECTION LIMIT

This procedure is based on the approach adopted by the EPA and included as Appendix B to Title 40, Part 136 of the Code of Federal Regulations (40 CFR 136). The samples shall be subjected to the same extraction, concentration, cleanup, and analytical procedures as those required for the field samples.

A1 Procedure

A1.1 Make an estimate of the detection limit (MDL) of each target compound using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent methylene chloride.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

(e) The concentration equivalent to five times the theoretical quantitation limit (Section 8.3.1 of the test method)

The experience of the analyst is important to this process, but one of the above considerations must be included in the initial estimate of the detection limit.

A1.2 Prepare according to the procedures described in Sections 4.2.2.1 to 4.2.2.4 enough XAD-2 resin to provide, at a minimum, eight aliquots each with mass equal to that required to pack a Method 429 sorbent cartridge. A contamination check must be conducted to identify those PAH for which a MDL cannot be determined by this method.

A1.3 To each of seven (7) aliquots of the clean resin, add an amount of each target analyte equal to the estimated detection limit. The mass of each resin aliquot must be known, and should be approximately 40 grams, the amount required to pack a Method 429 sorbent cartridge. The eighth aliquot shall be a blank.

A1.4 Process each of the eight samples through the entire PAH analytical method. All quality criteria requirements of the analytical method must be satisfied.

A1.5 Report the analytical results. The laboratory report must satisfy all of the reporting requirements of Section 10 of the test method.

A1.6 It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with step A1.3. This will: (1) prevent repeating this entire procedure and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure a good estimate of the method detection, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in step A1.3. Evaluate these data:

(1) If the sample levels are in a desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL according to Section A2.

(2) If these measurements indicate the selected analyte level is not in correct range, re-estimate the MDL with a new sample as in A1.2 and repeat steps A1.3 to A1.5.

A2 CALCULATION

A2.1 Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i^2\right)}{n}\right] \qquad \text{429-(A)-(1)}$$

$$S = \sqrt[2]{S^2}$$

Where:

X_i, i = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i = 1 to n.

A2.2 (a) Compute the MDL as follows:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ 0.99)} \times (S) \qquad \text{429(A)-(2)}$$

Where:

MDL = the method detection limit

$t_{(n-1, 1-\alpha = 0.99)}$ = Students' t-value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table 429(A)-1.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in A2.2(a) are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL
UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

A3 OPTIONAL ITERATIVE PROCEDURE

A3.1 This is to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step A1.1, take the MDL as calculated in Step A2.2, spike the matrix at this calculated MDL and repeat the procedure starting with Step A1.3.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with

the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right] \qquad 429(A)\text{-}(3)$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step A1.3. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in Equation 429(A)-3 to compute the final MDL according to the following equation:

$$MDL = 2.681(S_{pooled}) \qquad 429(A)\text{-}(4)$$

Where: 2.681 is equal to $t_{(12,\ 1-\alpha\ =\ .99)}$.

(d) The 95% confidence limits for MDL calculated using Equation 429(A)-4 are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL
UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLE 429(A)-1

SELECTED STUDENT'S t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of Replicates	Degrees of Freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390