POLYCYCLIC AROMATIC COMPOUNDS, TOTAL (PACs) 5800

MW: Variable CAS: None RTECS: None

METHOD: 5800, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: PACs are multi-numbered benzenoid-ring compounds. PACs contain polycyclic aromatic hydrocarbons (PAHs), substituted PAHs, and PAH heterocyclic derivatives.

NAMES & SYNONYMS: Total PACs as a class.

SAMPLING

SAMPLER: FILTER + SOLID SORBENT (2-µm, 37-mm, PTFE filter + washed XAD-2 resin, 100/50 mg)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 5 L @ 0.01 mg/m^3
-MAX: 1000 L

SHIPMENT: Ship at @ 0 °C

SAMPLE STABILITY: at least 30 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: FLOW INJECTION, FLUORESCENCE DETECTOR

ANALYTE: Polycyclic aromatic compounds as a chemical class

EXTRACTION: 4 mL hexane, rotated for at least 12 hours.

INJECTION VOLUME: 25 µL

MOBILE PHASE: 100% acetonitrile at 1.5 mL/min.

CALIBRATION: standard solutions of PACs based on Supelco QTM test mixture.

DETECTOR 1: fluorescence excitation 254 nm; emission 370 nm
RANGE: 0.04 to 250 µg/sample
ESTIMATED LOD: 0.012 µg/sample
PRECISION ($\bar{S}_r$): 0.042 @ 0.13 to 17 µg/sample [1]

DETECTOR 2: fluorescence excitation 254 nm; emission 400 nm
RANGE: 0.15 to 250 µg/sample
ESTIMATED LOD: 0.05 µg/sample
PRECISION ($\bar{S}_r$): 0.065 @ 0.13 to 17 µg/sample [1]

APPLICABILITY: This method is applicable for comparison of environments using the same fume source. The speciation of the PACs as a chemical class is accomplished by solid phase extraction followed by liquid-liquid extraction.

INTERFERENCES: All compounds producing detectable fluorescence at the chosen wavelengths and contained in the DMSO fraction after the sample preparation are identified as PACs.

OTHER METHODS: None identified for PACs as a class. Related methods are 2550, Benzothiazole in Asphalt Fume, by GC/sulfur chemiluminescence [2], and a gravimetric method 5042, Benzene Solubles and Total Particulate (Asphalt Fume) [3].

REAGENTS:

1. Hexane, HPLC grade.
2. Methanol, HPLC grade.
3. Methylene chloride, HPLC grade.
4. Dimethyl sulfoxide (DMSO), HPLC grade.
5. Calbration stock: Supelco QTM PAH mixture*

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Filter: PTFE-laminate membrane filter, 2-µm pore size, 37-mm, (Zefluor, Gelman Sciences, Ann Arbor, MI, or equivalent), backed by a gasket (37-mm OD, 32-mm ID) cut from a cellulose support pad or SKC #225-23, in cassette filter holder.
      NOTE: If sampling in bright sunlight, use opaque or foil-wrapped cassettes to prevent photodegradation.
   b. Solid sorbent: glass tube, 100 mm, 10-mm OD, sealed ends with plastic caps, containing two sections of washed XAD-2 resin (front = 100 mg; back = 50 mg), separated and retained with glass wool plugs (Supelco ORBO-42 Large or equivalent), connected to filter with minimum length PVC tubing.
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Robotics unit or apparatus for solid phase extraction (SPE). (Zymark Benchmate 2 or equivalent).
4. A solvent delivery system capable of delivering 1.5 mL/min of acetonitrile.
5. Autosampler or injection valve.
6. Two fluorescence detectors in series. One set at 254 nm excitation (ex) and 370 nm emission (em). The second set at 254 nm ex and 400 nm em.
7. Cyano solid phase extraction column (Supelco CN-SPE or equivalent).
8. 360° Rotator.
9. Aluminum foil
10. Volumetric flasks, various sizes.
11. Pipettes, various sizes.
12. Syringe or micropipet, various sizes.
13. Test tubes, 16 x 100 mm thin-walled and 16 x 100 mm test tubes with PTFE-lined caps.
14. Vials, autosampler, with PFTE-lined caps.
15. Refrigerant packs.

SPECIAL PRECAUTIONS: Total polycyclic aromatic compounds include the polycyclic aromatic hydrocarbons(PAHs). Some PAHs are irritants while others are carcinogenic. The standard also consists of PAHs. Neat compounds should be weighed out in a glove box. Spent samples and unused standards should be considered toxic waste and disposed of in an appropriate manner.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample 5 to 1000 L of air at 1.0 to 2.0 L/min.
3. Cap the filter and tube and pack securely for shipment with bagged refrigerant.

4. Refrigerate samples upon receipt at the laboratory at 4°C.

SAMPLE PREPARATION:

NOTE: Some applications of the data need only total PACs per sample rather than total PACs per individual medium. In these cases, the filters and sorbent section may be combined into the same screw-capped test tube as a single sample.

5. Remove the samples from the refrigerator and allow to equilibrate to ambient temperature.
6. Extract filters.
   a. Transfer the filter using forceps to a 16 x 100 mm screw capped test tube.
   b. Add 4 mL of hexane.
   c. Rotate the sample for at least 12 hours using a 360° rotator.

   NOTE: Minimize exposure to light during extraction step.
7. Extract solid sorbent tubes.
   a. Transfer front glass wool plug and front sorbent section to a 16 x 100 screw-capped test tube.
   b. Transfer the back sorbent section and remaining glass wool plugs to a separate screw-capped test tube.
   c. Add 4 mL of hexane to each sample.
   d. Rotate the sample for at least 12 hours using a 360° rotator.

   NOTE: Minimize exposure to light during extraction step.
8. Solid phase extraction:
   a. Condition a cyano solid phase extraction column by washing in sequence with 3-mL aliquots of methanol, methylene chloride, and hexane at a flowrate of approximately 0.25 mL/sec.
   b. Transfer 2 mL of the extracted sample in hexane to the head of the cyano-SPE column.
   c. Elute at approximately 0.15 mL/sec and collect in a separate 16 x 100 mm screw capped test tube.
   d. Add 2 mL of hexane and elute through the column at approximately 0.15 mL/sec and combine with the first hexane eluate.
   e. Add 4 mL of DMSO to the hexane eluates, cap, and rotate for at least 12 hours.
   f. Using a Pasteur pipette, transfer an aliquot of the DMSO layer (bottom) to an autosampler vial.

CALIBRATION AND QUALITY CONTROL:

NOTE: This method uses a mixture of 16 PACs as the standard calibration solution to mimic the field samples. The commercial standard chosen was Supelco QTM Test Mixture that contains 2000 µg/mL for each of 16 PACs or 32000 µg/mL total PAC.

9. Calibrate daily with at least six working standards over the range of interest.
   a. Dilute aliquots of calibration stock solution (QTM Test Mixture) with DMSO.
   b. Analyze working standards and blanks (Steps 12 through 15). Intersperse standards among the samples.
   c. Prepare 2 calibration graphs (one for each detector) in terms of mass of total PACs. (Fluorescent peak area vs. µg of total PAC per sample).
10. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes (Steps 5 through 8) in the range of interest (Step 9) at least once for each lot of filters and sorbent tubes used for sampling.
    a. Prepare spiking solutions by making dilutions of the Supelco QTM Test Mixture with hexane.
    b. Using a microliter syringe, spike three filters and three solid sorbent tubes at five concentration levels with the QTM Test mixture. Allow the media to dry in the dark overnight.
    c. Analyze the filters and sorbent tubes (Steps 12 through 15). Prepare graphs of R or DE vs. µg recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration, recovery (R), and desorption efficiency (DE) graphs are in control.

MEASUREMENT:

12. Set solvent delivery system to pump 1.5 mL/min of acetonitrile through the system.

NOTE: A guard column placed between the solvent delivery system and autosampler provides backpressure that aids the pumps in maintaining their prime.

13. Place two fluorescence detectors in series. Set the wavelengths of first detector at 254 nm ex and 370 nm em. Set the wavelengths of the second detector at 254 ex and 400 nm em.
14. Inject 25 µL of the sample into the solvent stream.
15. Measure peak areas.

CALCULATIONS:

NOTE: The mass of total PACs measured at each set of wavelengths is considered a separate analysis. Therefore, the establishment of calibration curves and data analysis are independent for each detector.

16. From the calibration graphs, read the mass (µg corrected for R or DE) of total PACs measured at each wavelength setting found on the filter (W_{fil}), front sorbent section (W_{sf}), and back sorbent section (W_{sb}) and on the average media blank filter (B_{fil}) and sorbent tube sections (B_{sf} and B_{sb}).
17. Calculate concentration of PACs at each wavelength setting (C 254ex/370em or C 254ex/400em) in the air volume sampled V(L) as the sum of the particulate concentration (filter) and the vapor concentration (sorbent tube). A dilution factor of 2 is applied since 2 mL of the original 4 mL of sample is processed through the SPE and liquid/liquid extraction.

$$\mathbf{C\ (ex/em)} = \frac{\mathbf{2\ (W_{fil} + W_{sf} + W_{sb} - B_{fil} - B_{sf} - B_{sb})}}{\mathbf{V}}\ \mathbf{,\ mg/m^3}$$

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

The method gives an indication of exposure to PACs as measured by two separate sets of spectrofluorometric wavelengths. The 254 nm ex/370 nm em response is used as an indication of the lower (2 to 4) ringed PACs that are usually considered irritants. The 254 nm ex/400 nm em response is used as an indication of the higher ringed (4 to 6) PACs that may be mutagenic or carcinogenic. As these measurements are only indications, the data are only applicable to exposures using the same asphalt fume source. No direct correlation of the data to adverse health effects can be made.

Recovery studies for the filter and tube were determined using sampling media spiked with known amounts of the Supelco QTM standard. A set of six filters and sorbent tubes were fortified with known amounts of the QTM Test mixture at four different concentrations per set. The efficiency for recovery from the sampling media, fractionation, and flow-injection analysis was shown to be about 90% for the 254 nm ex/370 nm em analysis and about 95% for the 254 nm ex/400 nm em analysis.

A 30-day storage study, consisting of sets of six filters and sorbent tubes spiked at four concentration levels with Supelco QTM standard, showed no loss when stored under refrigeration. This is reflected by approximately 90% recovery for the 254 nm ex/370 nm em analysis and about 95% for the 254 nm ex/400 nm em analysis. No collection studies were performed, but the sampling train was adopted from NMAM Method 5506 [4].

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METHOD WRITTEN BY:

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