BENZENE-SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME) 5042

MW: variable	CAS: 8052-42-4 asphalt; none, asphalt fume	RTECS: CI990000, asphalt; none, asphalt fume

METHOD: 5042, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA: No PEL
NIOSH: C 5 mg/m^3 (15-min) as total particulates
ACGIH: 5 mg/m^3

PROPERTIES: not defined

SYNONYMS: bitumen fumes

SAMPLING

SAMPLER:	FILTER (tared 37-mm, 2-µm, PTFE filter)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	28 L @ 5 mg/m^3
-MAX:	400 L @ 5 mg/m^3
SHIPMENT:	routine
SAMPLE STABILITY:	not determined
BLANKS:	5 field blanks per day

ACCURACY

RANGE STUDIED:	not determined
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	GRAVIMETRIC
ANALYTE:	Airborne total particulate (TP) material and the benzene-soluble fraction (BSF)
EXTRACTION:	3 mL benzene; ultrasonic bath, 20 minutes
BALANCE:	0.001 mg sensitivity; use same balance, if practical, before and after sample collection
CALIBRATION:	Check and maintain calibration of balance according to manufacturer's recommendations
RANGE:	TP: 0.13 to 2 mg per sample BSF: 0.14 to 2 mg per sample
ESTIMATED LOD:	TP: 0.04 mg per sample BSF: 0.04 mg per sample
PRECISION ($\bar{S}_r$):	TP: 0.048 at ≥ 0.10 mg per sample BSF: 0.061 at ≥ 0.21 mg per sample

APPLICABILITY: The working range is 0.14 to 2 mg/m^3 for a 1000-L sample. The method is applicable to 15-minute samples. The method was evaluated for asphalt fume; however, it is nonspecific and determines the concentrations of total particulate and the soluble fraction of the total particulate to which a worker is exposed. Therefore, for each sample matrix collected other than asphalt fume, a surrogate standard must be selected and spiked onto sampling media. These spiked samples will be used to determine recoveries, precision, and accuracy, also LOD and LOQ if necessary; moreover, other solvents besides benzene can be evaluated. The particle size of the particulate should be less than 40 µm, and preferably less than 30 µm. If particle sizes are larger than this, another sampler should be used.

INTERFERENCES: Changes in temperature or humidity during pre- and post-collection weighing may affect accuracy. A controlled laboratory environment is needed to exclude positive interferences due to dust contamination. Losses may occur from air stripping or volatilization of a collected sample during sampling, shipping, or analysis.

OTHER METHODS: The total particulate portion of this method is based on NMAM 0500 [1]. Other methods applicable to asphalt fume are NMAM 5800, Polycyclic Aromatic Compounds [2], and NMAM 2550, Benzothiazole in Asphalt Fume [3].

REAGENTS:

1. Benzene,* ≤ 5 ppm evaporation residue, e.g., Aldrich Chemical Co. Cat. No. 27,070-9 or equivalent.
2. Acetone,* HPLC grade.
3. Hexane,* HPLC grade.
4. Nitrogen,* purified and filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, 2-µm pore size, PTFE membrane filter laminated to PTFE (Zefluor, Pall Gelman Sciences, Cat. No. P5PJ037; Supelco, Cat. No. 2-0043; SKC Cat. No. 225-17-07; or equivalent hydrophobic filter), with cellulose support pad in a 37-mm cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Balance, readable to 0.001 mg.
4. Static neutralizer, ^{210}Po; replace according to manufacturer's recommendations.
5. Environmental chamber or room for balance (e.g., 20 ± 1 °C, constant ± 5% relative humidity, and dust-free).
6. Weighing cups,* PTFE, 2-mL (Fisher Cat. No. 2006529, or equivalent), in a carrying rack.
7. Vacuum oven, equipped with in-line filter on vacuum release valve to remove dust.

   NOTE: Keep the interior of the vacuum oven dust-free for maximum sensitivity, reproducibility, and accuracy.
8. Forceps.
9. Test tubes,** glass, 13-mm x 100 mm, with PTFE-lined screw caps.
10. Pipet,** glass, volumetric, 3-mL, with bulb.
11. Pipet,** glass, Mohr, 2-mL, with bulb.
12. Clarification units, 6-mL PTFE-treated reservoir with 1-µm PTFE frit (Daigger and Company, Inc., Lincolnshire, IL, Cat. No. LID-2102-10US, or equivalent).
13. Pressure regulator, valve, tubing, in-line filter to remove dust and organics, with adapter for applying nitrogen pressure to the clarification unit.
14. Ultrasonic bath.

* Rinse the weighing cups as follows.
   a. Wash with acetone until all visible residue is removed.
   b. Rinse with hexane for several seconds.
   c. Air dry.
   d. Discard any weighing cups that are not visibly clean.

** Rinse all glassware with acetone then hexane; air dry.

SPECIAL PRECAUTIONS: Benzene is a suspect carcinogen [4]. Asphalt fumes are considered a potential occupational carcinogen [4]. Benzene, hexane, and acetone are highly flammable. Prepare samples and standards in a well-ventilated hood and avoid skin contact. Use care when working with compressed gases.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Number the backup pads with a ballpoint pen and place them, numbered side down, in the filter cassette bottom sections.
2. Preweigh the filters by the weighing procedure given in step 3. Record the mean tare weight of sample filters, W_1 and field blanks, B_1 (µg).
3. Weighing procedure:
   - a. Equilibrate the filters or weighing cups in an environmentally controlled weighing area or chamber for at least two hours.
   - b. Zero the balance before each weighing.
   - c. Using forceps, pass each filter or weighing cup over a static neutralizer. Repeat this step if the filter or weighing cup does not release easily from the forceps or attracts the balance pan. Static electricity can cause erroneous weight readings.
   - d. Weigh each filter or weighing cup until a constant weight is obtained (two successive weighings within 10 µg). Record the mean of the last two weighings to the nearest microgram.
4. Assemble the filter in the filter cassette and close firmly to prevent leakage. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

SAMPLING:

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at an accurately known flow rate between 1 to 4 L/min for a total sample volume of 28 L to 400 L. Do not exceed a total filter loading of approximately 2 mg total particulate.
7. Collect five field blanks for each day of sampling for determining the limit of detection (LOD) and the limit of quantitation (LOQ).
8. Replace plugs in cassettes and pack securely for shipment to the laboratory. Recommend samples be refrigerated upon receipt at the laboratory.

CALIBRATION AND QUALITY CONTROL:

9. Use the same balance, if practical, for weighing filters and weighing cups before and after sample collection or benzene evaporation. Check and maintain calibration of balance according to manufacturer’s recommendations. Zero the balance before each weighing.
10. Process three tared media blanks through the measurement procedures for total particulate and benzene-soluble fraction.

TOTAL PARTICULATE MEASUREMENT:

11. After sampling:
    - a. Allow refrigerated sample cassettes to come to room temperature before proceeding.
    - b. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
    - c. Remove the top and bottom plugs from the filter cassette. Equilibrate sampler for at least two hours in the balance room or environmental chamber.
    - d. Remove the shrink band, pry open the cassette, and gently remove the filter to avoid loss of sample.
    - e. Reweigh (step 3) each filter, including field blanks. Record the mean post-sampling weight, W_2 or B_2 (µg). Also, record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.)
    - f. After weighing, transfer the filter carefully with forceps to a clean test tube and cap the tube.

CALCULATIONS FOR TOTAL PARTICULATE:

12. Calculate the concentration of total particulate, C_{TP} (mg/m^3), in the air volume sampled, V (L).

$$C_{TP} = \frac{(W_2 - W_1) - (B_2 - B_1)}{V}, \text{ mg/m}^3$$

where: W_1 = mean tare weight of filter before sampling (µg)
W_2 = mean post-sampling weight of sample-containing filter (µg)
B_1 = mean tare weight of field blank filters (µg)
B_2 = mean post-sampling weight of field blank filters (µg)

BENZENE-SOLUBLE FRACTION MEASUREMENT:

13. Condition clarification unit by rinsing the reservoir with 1.5 mL of benzene. Use nitrogen pressure to force the benzene through the frit. Appropriately dispose of the benzene rinse.
14. Extract benzene-soluble fraction.
    a. Add 3.0 mL benzene via a 3-mL volumetric pipet to the filter-containing test tube (step 11.e.) Recap the test tube.
    b. Place the test tube upright in beaker containing water to the same level as the liquid in the test tube. Place the beaker and test tube in ultrasonic bath and agitate for 20 minutes.
    c. Transfer benzene extract to conditioned clarification unit and force the extract through into a clean test tube, using nitrogen pressure as in step 13. Discard sampling filter and clarification unit.

    NOTE: Be sure the end of the clarification unit is well below the opening of the test tube to prevent sample loss by spattering.
15. Preweigh clean weighing cups by the weighing procedure in step 3. Record the mean tare weight, W_3 or B_3 (µg).

    NOTE: The weighing cup should already be prerinsed and dried as described in the Equipment section.

    a. Identify each tared weighing cup by labeling its place in the carrying rack.
    b. Transfer a 1.5-mL aliquot of the benzene extract via a 2-mL Mohr pipet to the tared weighing cup.

    NOTE: An aliquot may be taken from the remaining extract at this step if other analyses (e.g., polycyclic aromatic compounds) are to be performed on the sample. Apply the appropriate aliquot factor in calculations.
16. Place the weighing cup rack in a vacuum oven preheated to 40C. Apply vacuum until pressure in the oven is 7 to 27 kPa (50 to 200 mm Hg). Allow solvent to evaporate (about two hours). Release the vacuum by slowly opening a release valve that has an in-line filter to remove room dust.
17. Reweigh the weighing cup by the weighing procedure in step 3. Record the mean post-sampling weight, W_4 or B_4 (µg). Also, record anything remarkable about the sample (e.g., overload, leakage, wet, spattering, etc.).
18. After weighing, clean the weighing cup as described in the Equipment section.

CALCULATIONS FOR BENZENE-SOLUBLE FRACTION:

19. Calculate the concentration of benzene-soluble fraction, C_{BSF} (mg/m^3), in the volume of air sampled, V (L):

$$C_{BSF} = \frac{[(W_4 - W_3) - (B_4 - B_3)] \cdot 2}{V}, \text{ mg/m}^3$$

where: W_3 = mean tare weight of sample weighing cup (µg)
W_4 = mean post-sampling weight of sample weighing cup (µg)
B_3 = mean tare weight of field blank weighing cups (µg)
B_4 = mean post-sampling weight of field blank weighing cups (µg)

2 = aliquot factor

EVALUATION OF METHOD:

Asphalt fume collected during a previous NIOSH investigation [5] was spiked on tared PTFE filters, allowed to dry at least overnight, and extracted using benzene. The results are summarized in the table below.

Spiking level (mg)*	**Total Particulates**		**Benzene-Soluble Fraction**	
	Recovery (%)	**S_r**	**Recovery (%)**	**S_r**
1.85	102	5.97	97.9	0.738
1.17	103	3.98	98.8	2.02
0.62	94.0	5.85	94.8	1.85
0.23	91.6	3.50	96.9	6.10
0.12	82.1	3.91	80.9	9.54
0.058	110	16.4	92.1	13.5
0.025	105	11.4	73.1	17.4

*Six replicates per level

The pooled relative standard deviation ($\bar{S}_r$) for the total particulates was 4.8% at loadings greater than or equal to 0.10 mg per sample. For the benzene-soluble fraction, the pooled relative standard deviation was 6.1% at loadings greater than or equal to 0.21 mg per sample.

The accuracy criterion is based on determining the range of analyte loadings and the analyte loading on the sample media that will give at least 95% confidence of obtaining a measurement of the analyte that is within 25% of the true value 95% of the time. Since no independent method for determining the total particulate concentration is available, no estimate of the bias for the total particulate data was made; therefore, the maximum allowable bias was calculated at which the accuracy criterion could still be met. Based on the spiking data, if the total particulate loading was greater than or equal to 0.10 mg per filter, the measurement determination will be within 25% of the true value 95% of the time if the true bias is less than 10.0%. The bias for the benzene-soluble fraction was negative (see the data above), and since the bias for the benzene-soluble fraction varied little, the bias was pooled over the spiking range of 1.85 to 0.20 mg per filter. It was determined that the 25% accuracy criterion was met if the benzene-soluble fraction was greater than or equal to 0.20 mg per filter.

The limit of detection (LOD) and the limit of quantitation (LOQ) were determined using field blanks [6]. The LOD is equal to three times the standard deviation of the field blank weight differences (post-sampling weight - tare weight), and the LOQ is equal to ten times the standard deviation of the field blank weight differences. Field sample values should be compared to the LOD and LOQ values only after the field samples have been blank corrected.

The standard deviations of the field blank weights were 0.013 mg per sample for total particulates and 0.014 mg per sample for the benzene-soluble fraction. Therefore, the LOD and LOQ for total particulates were 0.04 and 0.13 mg per sample, respectively. The LOD and LOQ for the benzene-soluble fraction were 0.04 and 0.14 mg per sample, respectively. These LOD and LOQ values should only be compared to blank corrected field sample data.

A user check of the method was performed in which tared PTFE filters were spiked with 1.08, 0.392, or 0.216 mg of pyrene per filter and then analyzed by an independent chemist [6]. A mean total particulate recovery of 103% (S_r = 5.85%) was obtained, and the mean benzene-soluble fraction recovery was 109% (S_r = 9.91%). Correlation of benzene-soluble mass with total particulate was linear, with R^2 = 0.994, and the mean ratio of benzene-soluble mass to total particulate was 106% ($S_r = 7.80\%$).

In other experiments, three of 60 field blanks (three sets of 20 field blanks each) had a significantly higher than expected benzene-soluble fraction when compared with the other field blanks [6]. This event had two undesirable consequences: (1) Because the average weight of the field blanks was increased, the field samples were over corrected, and (2) the standard deviation of the field blank weights was increased resulting in higher LOD and LOQ values. For example, if the set of twenty field blanks with one high result is randomly assigned to groups of three (repeatedly), the standard deviation of the groups with the high result could exceed the standard deviation of the other groups by more than 1.6 times. Since this event also may occur with field samples, these elevated results were not excluded when the data were evaluated. Although these events were observed with a syringe type clarification unit and not the recommended clarification unit, the cause of this event was not determined. Therefore, it is important to collect as many field blanks as is reasonable (five blanks per day); also, it may be advisable to establish a monitoring program to track the occurrence of elevated field blanks and, if possible, to identify and eliminate the cause(s).

In another experiment, the recommended clarification unit (PTFE-treated reservoir and a PTFE filter) was evaluated along with three syringe type clarification units [6]. The recommended clarification unit gave lower average extractable material than the syringe-type clarification units; also, the recommended clarification unit did not release increasing amounts of extractable material upon prolonged contract with solvent. Prerinsing the recommended clarification unit appeared to lower the average amount of extractable material. Additionally, the recommended clarification unit eliminated the need for using a glass syringe and was more convenient to use than the syringe type clarification units.

In a preliminary asphalt fume spiking experiment, benzene and methylene chloride were evaluated as extraction solvents [6]. Asphalt fume [5] was spiked on tared PTFE filter media at the following concentrations: 3.38, 0.68, 0.14, and 0.034 mg per filter. Benzene gave recoveries greater than 100% for all concentrations of asphalt fume spiked on PTFE filters. While methylene chloride gave recoveries greater than 96% for the two highest levels spiked, at the two lower levels the recoveries were less than 67%.

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