BENZOYL PEROXIDE 5009

$(C_6H_5CO)_2O_2$ MW: 242.22 CAS: 94-36-0 RTECS: DM85750000

METHOD: 5009, Issue 3 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 3:** 26 February 2016

OSHA: 5 mg/m³
NIOSH: 5 mg/m³

PROPERTIES: solid; MP 103 °C; d 1.334 g/mL @ 25 °C; VP not significant; auto ignition temperature 80 °C

SYNONYMS: dibenzoyl peroxide, benzoyl superoxide

SAMPLING

SAMPLER: FILTER (0.8-µm cellulose ester membrane)

FLOW RATE: 1 - 3 L/min

VOL-MIN: 40 L @ 5 mg/m³
-MAX: 400 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 9% loss from filter after 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3 to 9 mg/m³ [1]; (90-L samples)

BIAS: -0.52%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1]

ACCURACY: ± 11.82%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: benzoyl peroxide

EXTRACTION: ethyl ether, 10 mL

PRESSURE-COLUMN: 9000 KPa (1300 psi)

MOBILE PHASE: 70/30 methanol/water; 1.6 mL/min

COLUMN: 250 mm x 3 mm-ID stainless steel; spherical silica particles with 5% bonded coating of octadecyl groups, US Pharmacopeia (USP) L1

DETECTOR: UV photometer @ 254 nm

CALIBRATION: benzoyl peroxide in ethyl ether

RANGE: 0.2 to 1.7 mg per sample [1]

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 2 to 19 mg/m³ for a 90-L air sample.

INTERFERENCES: None identified

OTHER METHODS: This is Method S253 [3] in a revised format. A non-specific gravimetric method and a non-specific colorimetric method appear in the criteria document [4].

REAGENTS:

1. Benzoyl peroxide, 99% pure.*
2. Ethyl ether, purified, without stabilizer.*
3. Methanol, distilled in glass.
4. Water, deionized and distilled.
5. Calibration stock solution, 10 mg/mL. Dissolve 250 mg benzoyl peroxide in ethyl ether and dilute to 25 mL. Stable at least one week at 4 °C.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter, with backup pad in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Refrigerant, water solution, sealed, refreezable, reusable.
4. Vials, 20-mL, polytetrafluoroethylene (PTFE)-lined caps.
5. High performance liquid chromatograph, 254-nm UV detector, sample injection valve with a 20-µL external sample loop, syringe filter, integrator and column (page 5009-1) or autosampler.
6. Tweezers.
7. Microliter syringes, 10- and 100-µL.
8. Volumetric flasks, 10- and 25-mL, assorted sizes.
9. Pipet, 10-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Benzoyl peroxide is a flammable solid and may explode when heated; it will attack some plastics, rubber, and coatings [4]. Ethyl ether is highly flammable and forms explosive peroxides on exposure to air.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 40 to 400 L. Do not exceed 2 mg particulate loading on the filter.
3. Ship samples in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

4. Immediately upon receipt at laboratory, refrigerate the samples.
5. As soon as possible after receipt, transfer each filter to a clean vial with tweezers.
6. Pipet 10 mL ethyl ether into each vial; screw on cap. Swirl to mix.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards covering the range 0.01 to 1.7 mg per sample.
   a. Add calibration stock solution with a microliter syringe to ethyl ether in a 10-mL volumetric flask and dilute to the mark.
   b. Analyze together with samples, blanks and control samples (steps 10 through 12).
   c. Prepare calibration graph of peak area vs. mass (mg) of benzoyl peroxide per sample.
8. Determine recovery of benzoyl peroxide from filters at least once for each lot of samplers in the calibration range (step 7). Prepare three filters at each of five levels plus media blanks.
   a. Add aliquot of calibration stock solution with a microliter syringe directly onto a media blank filter in a vial.
   b. Prepare and analyze together with working standards (steps 5, 6 and 10 through 12).
   c. Prepare a graph of recovery vs. mg benzoyl peroxide recovered.

9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

10. Set high performance liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5009-1.
11. Flush sample loop thoroughly with sample (0.1 mL) and inject sample or autosampler.
12. Measure peak area.

CALCULATIONS:

13. Read mass, mg (corrected for recovery), of benzoyl peroxide found on sample filters, W (mg), and on average blank filters, B (mg), from calibration graph.
14. Calculate concentration, C (mg/m^3), of benzoyl peroxide in the air volume sampled, V (L):

$$C = \frac{(W - B)x10^3}{V}, mg/m^3$$

EVALUATION OF METHOD

Method S253 was issued on January 21, 1977 [3], and validated over the range 3.1 to 19.1 mg/m^3 at 26 °C and 764 mm Hg, using 90-L samples [1, 5]. The collection efficiency of the filter was determined to be 1.00, since no benzoyl peroxide was detected on a backup filter mounted directly behind the front filter. Storage stability studies on the filters held in the filter cassettes indicated a 9.3% decrease in the amount of benzoyl peroxide recovered after one week. Benzoyl peroxide was stable in ethyl ether at room temperature for at least one week. Overall precision, $\widehat{S}_{rT}$, was 0.060. Recovery was 0.97 in the range 0.225 to 0.900 mg per sample for 18 spiked samples.

REFERENCES:

[1] NIOSH [1976]. Backup data report: S253 for Benzoyl Peroxide. In: Ten NIOSH analytical methods (Set 2). Available as order No. PB 271-464 from NTIS. Unpublished.

[2] Wade R [1980]. Memorandum: UBTL analytical laboratory report for benzoyl peroxide, Sequence #2182-J. Salt Lake City, UT: Utah Biomedical Test Laboratory. Unpublished.

[3] NIOSH [1978]. Benzoyl peroxide: Method S253. In: NIOSH manual of analytical methods. 2nd ed. (Vol 4). Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 78-175.

[4] NIOSH [1977]. NIOSH criteria for a recommended standard: occupational exposure to benzoyl peroxide. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-166.

[5] Gunderson EC, Anderson CC [1980]. Development and validation of methods for sampling and analysis of workplace toxic substances. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 80-133.

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