p-TOLUENESULFONIC ACID 5043

$C_7H_8O_3S$ MW: 172.20 CAS: 104-15-4 RTECS: XT6300000

METHOD: 5043, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA : no PELs
NIOSH: no RELs
ACGIH: no TLVs
(1 ppm = 7.03 mg/m^3 @ NTP)

PROPERTIES: solid; MP 106 to 107 °C when anhydrous; d 1.20 g/mL @ 20 °C; BP 140 °C @ 20 mm Hg; VP not significant @ 25 °C

NAMES & SYNONYMS: 4-methylbenzenesulfonic acid; *p*-methylphenylsulfonic acid; tosic acid

SAMPLING

SAMPLER: FILTER (13-mm glass fiber)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 29 days @ 25 °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: HPLC, UV DETECTOR

ANALYTE: *p*-toluenesulfonic acid

EXTRACTION: 2 mL 2% isopropanol in water v/v; ultrasonic bath, 10 min

INJECTION VOLUME: 100 µL

MOBILE PHASE: 21% acetonitrile/79% water containing 0.005 M Pic® A v/v; 1 mL/min

COLUMN: 3.9-mm ID x 15 cm stainless steel packed with 10-µm µ-Bondapak C_{18}

DETECTOR: UV @ 222 nm

CALIBRATION: standard solutions of p-toluenesulfonic acid in isopropanol: water

RANGE: 0.27 to 120 µg/sample [1]

ESTIMATED LOD: 0.08 µg/sample [1]

PRECISION ($\hat{S}_r$): 0.046 @ 3 to 15 µg/sample [1]

APPLICABILITY: *p*-Toluenesulfonic acid at 0.0027 to 1.2 mg/m^3 can be determined in a 100-L air sample by this method. This method has been used to analyze samples collected at a foundry & machining company where *p*-toluenesulfonic acid was a catalyst in a process to produce a resin from resorcinol and furfuryl alcohol [2].

INTERFERENCES: None identified.

OTHER METHODS: Chromatographic methods for determination of *p*-toluenesulfonic acid in solution have been published [3-7]. None has been published for air analysis. An alternative air sampler for the present method is a midget impinger containing isopropanol [1,2].

REAGENTS:

1. *p*-Toluenesulfonic acid,* >98% pure.
2. Water, distilled.
3. Acetonitrile,* chromatographic quality.
4. Isopropanol, chromatographic quality.
5. PIC®A, "paired-ion chromatography," low UV reagent (Waters Corp., or equivalent). PIC®A contains water, tetrabutylammonium hydrogen sulfate, and phosphoric acid. Add entire vial of PIC®A to 1 L of distilled water to make 0.005*M* solution.
6. Extraction solution: 2% Isopropanol/98% water (v/v). Add 20 mL of isopropanol to distilled water to make 1 L of solution.
7. *p*-Toluenesulfonic acid calibration stock solution, 4.0 mg/mL. Dissolve 200 mg *p*-toluenesulfonic acid in extraction solution to make 50 mL of solution.

* **See SPECIAL PRECAUTIONS**

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter in 2-piece filter holder (Swinnex, Millipore Corp., or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. HPLC, UV detector, 222 nm, integrator, and column (page 5043-1).
4. Vials, 4-mL, with PTFE-lined caps.
5. Graduated cylinder, 1-L, readable to 10 mL.
6. Volumetric flasks, 25- and 10-mL.
7. Syringes, 10-mL, 500-µL, and 100-µL.
8. Ultrasonic water bath.
9. Film, plastic, water resistant.
10. Syringe filters, 3-mm PTFE membranes, 0.45-µm pore size, in polypropylene housing.
11. Forceps.

SPECIAL PRECAUTIONS: *p*-Toluenesulfonicacid is highly irritating to the skin and mucous membranes; also, it can cause a potentially explosive reaction of acetic anhydride with water. Acetonitrile is toxic and is a fire hazard (flash point = 12.8°C). Wear protective clothing and work in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach the sampler to the personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 10 to 1000 L.
   NOTE: Limit the maximum loading of particulate matter on the filter to approximately 0.5 mg.
4. Seal ends of sampler with plastic film. Ship to laboratory at room temperature.

SAMPLE PREPARATION:

5. Using the forceps, transfer the 13-mm glass fiber filter to a 4-mL vial.
6. Add 2 mL of the extraction solution to the vial and cap securely.
7. Place the sample vial into an ultrasonic bath and agitate for 10 min.
8. Filter the sample solution through a PTFE membrane syringe filter.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range of interest: 0.04 to 60 µg/mL.
   a. Prepare working standards over the range of interest. Add a known amount of the calibration stock solution to an aliquot of the extraction solution.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph (peak area or height vs. µg of analyte).
10. Determine recovery (R) at least once for each lot of glass fiber filters in the calibration range (step 9).

Prepare three filters at each of five concentration levels plus three media blanks.

a. Place 13-mm glass fiber filters into 4-mL vials.
b. With a microliter syringe, fortify each filter with a known amount of the calibration stock solution.
c. Allow the uncapped vials to stand overnight at room temperature.
d. Prepare and analyze with working standards (steps 5 through 8, and steps 12 and 13).
e. Prepare graph of R vs. µg of analyte recovered.

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

MEASUREMENT:

12. Set high performance liquid chromatograph to manufacturer's recommendations and to conditions given on page 5043-1. Inject 100-µL aliquot manually or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with desorbing solution, reanalyze, and apply appropriate dilution factor in calculations.
13. Measure peak area or height for *p*-toluenesulfonic acid.

CALCULATIONS:

14. Determine the mass, µg (corrected for R), of analyte found on the filter (W) and the average media blank (B).
15. Calculate the concentration, C, of *p*-toluenesulfonic acid in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Average recoveries of *p*-toluenesulfonic acid after fortification of 13-mm glass fiber filters with 3-, 6-, 10-, and 15-µg quantities of the compound were 1.02, 0.96, 1.04 and 0.96, respectively; precision ($\bar{S}_r$) was 0.046 (23 samples, pooled). After 29 days of storage at room temperature, the average recovery of 3-µg quantities of *p*-toluenesulfonic acid from glass fiber filters was 1.03; S_r was 0.023 (5 samples).

The purpose of the 2% isopropanol in samples and standards was to prevent possible deterioration of *p*-toluenesulfonic acid by bacteria during storage.

ALTERNATIVE METHOD:

As an alternative to the glass fiber filters, air samples of *p*-toluenesulfonic acid can be collected in midget impingers containing isopropanol at 1 L/min. After sampling, the impinger solution is transferred to a 20-mL glass vial and transported to the laboratory. The vial is placed onto a heating plate maintained at 80°C, and the isopropanol is evaporated to dryness with a gentle stream of nitrogen (total evaporation time is about 1.5 hours). A 2-mL aliquot of 2% isopropanol in water is added to the vial, and the vial is placed into an ultrasonic bath for 30 seconds. Then the vial is tilted in order to wet the inside wall of the vial. Solution is filtered through a PTFE membrane syringe filter and is ready for analysis according to the method described above.

EVALUATION OF ALTERNATIVE METHOD:

Isopropanol was found to evaporate from the midget impinger during air sampling. Air at room temperature was drawn at 1 L/min through an impinger containing 20 mL of isopropanol. After 1 hour of pump operation,

6 mL of the isopropanol had evaporated, and the remaining 14 mL was cold because of evaporation. Separate recovery experiments were performed. The average recovery of 3-µg quantities of *p*-toluenesulfonic acid from 20-mL volumes of fortified isopropanol was 1.04 (Sr = 0.054 for 6 samples); the average recovery of 6-µg quantities of *p*-toluenesulfonic acid from 20-mL volumes of fortified isopropanol was 1.01 (S_r = 0.028 for 6 samples). After 29 days of storage at room temperature, the average recovery of 3-µg quantities of *p*-toluenesulfonic acid from 20-mL volumes of isopropanol was 0.95 (S_r = 0.050 for 6 samples). This alternative method and the method with glass fiber filters both have the same LOD and LOQ, because final sample solution volumes in the two methods are the same.

REFERENCES:

[1] Tucker SP [1997]. Backup data report for method 5043, *p*-Toluenesulfonic Acid. National Institute for Occupational Safety and Health, DPSE/NIOSH, (Unpublished report).
[2] Tucker SP [1996]. Analytical report for Sequence #8567, DPSE/MRSB. Cincinnati, OH: National Institute for Occupational Safety and Health. (Unpublished report).
[3] Lange FT, Wenz M, Brauch H [1995]. Trace-level determination of aromatic sulfonates in water by on-line ion-pair extraction/ion-pair chromatography and their behavior in the aquatic environment. J High Resolut Chromatogr *18*:243-252.
[4] Altenbach B, Giger W [1995]. Determination of benzene- and naphthalene sulfonates in wastewater by solid-phase extraction with graphitized carbon black and ion-pair liquid chromatography with UV detection. Anal Chem *67*:2325-2333.
[5] Bastian B, Knepper TP, Hoffmann P, Ortner HM [1994]. Fresenius' J Anal Chem *348*: 674-679.
[6] Brouwer ER, Slobodnik J, Lingeman H, Brinkman UAT [1992]. Analusis *20*: 121-126.
[7] Schullerer S, Brauch HJ, Frimmel FH [1990]. Vom Wasser *75*:83-97.

METHOD WRITTEN BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE