METHYL tert-BUTYL ETHER   1615

$CH_3OC(CH_3)_3$ MW: 88.15   CAS: 1634-04-4   RTECS: KN5250000

METHOD: 1615, Issue 2	EVALUATION: PARTIAL	Issue 1: 15 August 1990
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OSHA : No permissible exposure limit
NIOSH: No recommended exposure limit
ACGIH: No threshold limit value
(1 ppm = 3.6 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.74 g/mL @ 20 °C;
BP 55.2 °C; VP 32.6 kPa (245 mm Hg)
@ 25 °C

SYNONYMS: MTBE; 2-methoxy-2-methyl-propane.

SAMPLING	MEASUREMENT

SAMPLING

SAMPLER: SOLID SORBENT TUBES
(two charcoal tubes in series; front 400 mg; back 200 mg)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 2 L @ 10 ppm
-MAX: 96 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C, 3 weeks @ -7 °C (92% recovery) [1]

BLANKS: 2 to 10 field blanks per set

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl tert-butyl ether (MTBE)

DESORPTION: 2 mL CS_2, 30 min

INJECTION VOLUME: 1 μL, split ratio 60:1

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: 0 °C for 7 min; 5 °C/min to 25 °C, and then 25 °C/min to 250 °C (hold 5 min)

CARRIER GAS: He, 1 to 2 mL/min

COLUMN: fused silica capillary, 50 m x 0.3-mm ID, 0.5-μm film of bonded dimethylsilicone gum (polydimethylsiloxane)

CALIBRATION: standard solutions of MTBE in CS_2

RANGE: 0.06 to >10 mg per sample [1]

ESTIMATED LOD: 0.02 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.033 @ 9 μg to ~10 mg per sample [1]

ACCURACY

RANGE STUDIED: not studied

BIAS: not significant [1]

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

ACCURACY: not determined

APPLICABILITY: The working range is 0.2 to >35 ppm (0.75 to >125 mg/m^3) for an 80-L air sample. This method is designed for the determination of MTBE in gasoline and may be used for the determination of other components of gasoline.

INTERFERENCES: 2,3-Dimethylbutane may interfere if initial chromatographic temperatures are higher than 0 °C.

OTHER METHODS: This is a new method [1].

REAGENTS:

1. Methyl tert-butyl ether,* reagent grade.
2. Carbon disulfide,* reagent grade.
3. Calibration stock solution, 7.41 mg/mL. Dilute 40 µL methyl tert-butyl ether to 4.00 mL with carbon disulfide.
4. Helium, prepurified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.
7. Liquid nitrogen or carbon dioxide for subambient cooling of GC oven.

    * See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Two glass tubes in tandem, each 8 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing activated coconut shell charcoal held by plugs of silated glass wool (front tube = 400 mg, back tube = 200 mg). Pressure drop across tubes at 1 L/min airflow must be less than 3.4 kPa.
2. Personal sampling pump, 0.1 to 0.2 L/min with flexible connecting tubing.
3. Gas chromatograph with sub-ambient cooling, flame ionization detector (page 1615-1).
4. Vials, 5-mL, 2-mL with PTFE-lined crimp caps.
5. Pipettes, TD, 4-, 2- and 1-mL.
6. Syringes, 1-mL, 250-, 100-, 25-, and 10-µL.

SPECIAL PRECAUTIONS: Methyl tert-butyl ether and carbon disulfide are extremely flammable (flash points -28 °C and -30 °C, respectively. Carbon disulfide is also toxic. Work with these compounds in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.1 to 0.2 L/min for a sample size of 2 to 96 L.
4. Separate the tubes, cap, and pack securely for shipment. Chilling of the samples is necessary if they are not expected to be analyzed within five days.

SAMPLE PREPARATION:

5. Add 2.0 mL carbon disulfide to 5-mL vials. Loosely cap vials.
6. Place front and back sorbent sections in separate vials. Discard glass wool and foam plugs. Immediately cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least seven working standards.
   a. Prepare standards in capped vials by mixing various volumes (i.e., 5 to 230 µL) of calibration stock solution with carbon disulfide to a total volume of 4.00 mL to obtain concentrations in the range of 0.010 to 5 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
9. Determine the desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each level plus three media blanks.
   a. Use the 400-mg charcoal tube for DE determination. Hold charcoal in the tube by silanzied glass wool.
   b. Prepare three DE stock solutions by mixing 4, 40, and 160 µL of methyl tert-butyl ether and making up a total volume to 4.00 mL with carbon disulfide to produce corresponding concentrations of 0.741, 7.41 and 29.62 µg/µL.

    c.   Inject 24 µL of the 0.741 µg/µL stock solution, 7 and 19 µL of the 7.41 µg/µL solution, 7, 11, and 14 µL of the 29.62 µg/µL stock solution onto the tubes near the glass wool plug and draw clean air through the tubes at 0.1 L/min for 1 to 2 minutes.

    d.   Seal tube with plastic caps. Allow to stand overnight.

    f.   Prepare a graph of DE vs. mg of MTBE recovered.

10.   Analyze three quality control blind spikes and three analyst spikes to ensure the calibration curve and DE are in control.

MEASUREMENT:

11.   Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1615-1. Inject sample aliquot manually using solvent flush technique or with an autosampler.

    NOTE 1:   If the sample peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in the calculations.

    NOTE 2:   The given conditions are recommendations for the determination of MTBE in gasoline. An initial temperature lower than 0 °C will produce better peak resolution but longer analysis time.

12.   Measure peak area.

CALCULATIONS:

13.   Determine the mass, mg (corrected for DE) of MTBE found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14.   Calculate concentration, C, of MTBE in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

A calibration curve in the concentration range 0.74 to 111 mg/mL MTBE in carbon disulfide indicated a linear correlation with a coefficient of 0.9998 and s_r of 3.3% [1]. Other calibration curves at lower concentrations, covering the recovery/stability range, i.e. 9.3 to 426 µg/mL MTBE in CS_2, indicated linear correlation coefficients >0.998. The LOD and LOQ values varied between 19 to 22 µg/mL and 36 to 73 µg/mL, respectively.

A six-level, 31-day storage stability study, conducted at -7 °C, in the range 17.8 to 415 µg MTBE in gasoline spiked on 400 mg charcoal tubes, indicated recoveries of 99.0 ± 4.3% for the first day, 93.2 ± 2.0% for the 17th day, 91.9 ± 7.1% after 23-day storage and 89.0 ± 5.2% after 31-day storage. A five-day room-temperature stability study at 415 µg MTBE in gasoline spiked in 400 mg charcoal tubes indicated a 100.0 ± 4.6% recovery.

Four charcoal tubes spiked with 415 µg MTBE in gasoline had air drawn for six hours at 100 mL/min and then were stored at -7 °C for five days indicating 103.6 ± 9.0% recovery. No sample loss occurred due to breakthrough at the 415-µg per sample MTBE level.

Charcoal tubes which were spiked with 10 mg MTBE in gasoline and which had 6 to 78 L of air drawn through them did not indicate any breakthrough of MTBE. Light hydrocarbons i.e. n-butane, and isopentane, which are not retained by the charcoal, did break through.

REFERENCES:

[1]   Palassis, J., R.W. Hartle, and J.L. Holtz. Development of a Method for Determination of Methyl tert-Butyl Ether (MTBE) in Gasoline Vapors and Liquid Gasoline Samples,   Appl. Occup. Environ. Hyg. 8(11):964-969 (1993).

METHOD WRITTEN BY:

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