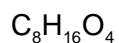


## METHYL ETHYL KETONE PEROXIDE

3508



MW: 176.21

CAS: 1338-23-4

RTECS: EL9450000; 21837

METHOD: 3508, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 August 1987

Issue 2: 15 August 1994

OSHA : no PEL  
 NIOSH: C 0.2 ppm/15 min  
 ACGIH: C 0.2 ppm  
 (1 ppm = 7.2 mg/m<sup>3</sup> @ NTP)

PROPERTIES: liquid; d 1.170 g/mL @ 20 °C; flash  
 point (open cup) 82 °C

SYNONYMS: MEKP; MEK peroxide; 2-butanone peroxide

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	IMPINGER (15 mL dimethyl phthalate)	<b>TECHNIQUE:</b>	VISIBLE ABSORPTION SPECTROPHOTOMETRY
<b>FLOW RATE:</b>	0.5 to 2 L/min	<b>ANALYTE:</b>	diphenylcarbazide oxidation product
<b>VOL-MIN:</b>	52 L @ 0.2 ppm	<b>SAMPLE PREPARATION:</b>	note liquid volume; remove 5 mL aliquot; add 5 mL diphenylcarbazide color reagent; heat at 85 ± 5 °C for 15 min; cool in room temperature water bath exactly 5 min
<b>-MAX:</b>	520 L	<b>ANALYSIS:</b>	color development; absorbance @ 565 nm
<b>SHIPMENT:</b>	transfer to silanized, foil-wrapped vials; ship in dry ice	<b>CALIBRATION:</b>	standard solutions of methyl ethyl ketone peroxide in dimethyl phthalate
<b>SAMPLE STABILITY:</b>	90% recovery after 21 days @ -4 °C [2]	<b>RANGE:</b>	75 to 750 µg per sample [1]
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>ESTIMATED LOD:</b>	75 µg per sample [1]
<b>ACCURACY</b>		<b>PRECISION (<math>\hat{S}_r</math>):</b>	0.052 [2]
<b>RANGE STUDIED:</b>	not studied for generated samples		
<b>BIAS:</b>	not determined		
<b>OVERALL ACCURACY:</b>	not determined		

**APPLICABILITY:** The working range is 0.11 to 1.1 ppm (0.75 to 7.5 mg/m<sup>3</sup>) for a 100-L air sample [1]. This method has not been tested with aerosol generation or field samples. Special care must be taken in the conditioning of the glassware and in the storage of the samples.

**INTERFERENCES:** The diphenylcarbazide color reaction is relatively non-specific. Most ketones, except acetone, will exhibit positive interference at high levels. Other peroxides or any strong oxidant could also interfere with this procedure. Substances which catalyze the decomposition of peroxide may cause a significant decrease in the measurement; in particular, the presence of metal ions adsorbed on the glassware.

**OTHER METHODS:** This revises P&CAM 331 [1].

**REAGENTS:**

1. Acetic acid, glacial, reagent grade.
2. Dimethyl phthalate (DMP), reagent grade.
3. Water, distilled, deionized.
4. Toluene.
5. Methanol.
6. Isopropyl alcohol, reagent grade.
7. Sulfuric acid, conc.
8. Diphenylcarbazide (DPC) solution, 0.25% (w/v). Dissolve 0.25 g  $\pm$  0.01 g reagent grade DPC in DMP in an Al foil-covered 100-mL volumetric flask. Agitate in ultrasonic bath to aid dissolution. Dilute to 100 mL.  
NOTE: This solution is light-sensitive. Prepare immediately before using.
9. Color reagent. Mix 30 mL 0.25% DPC solution with 20 mL glacial acetic acid.
10. Methyl ethyl ketone peroxide (MEKP), 60%, technical grade, in dimethyl phthalate. Standardize as in APPENDIX.
11. Calibration stock solution.\* Pipet ca. 10  $\mu$ L of 60% MEKP into a 50-mL pre-weighed volumetric flask. Accurately weigh the flask plus MEKP; dilute to the mark with dimethyl phthalate. Wrap flask in Al foil. Prepare in duplicate.
12. Sodium thiosulfate solution, 0.1 N, standardized. Commercially available, or prepare as in APPENDIX.
13. Sodium iodide solution, 20% (w/v). Dissolve 20 g sodium iodide in 100 mL methanol.
14. Sodium bisulfite.
15. Nochromix.
16. Dichlorodimethylsilane, 5% (w/v), in toluene (Sylon CT, or equivalent).

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: glass midget impinger, 25-mL, silanized.\*
2. Personal sampling pump, 0.5 to 2 L/min, with

**SPECIAL PRECAUTIONS:** MEKP is shock and heat sensitive. Store below 25 °C. MEKP solutions are extremely irritating and corrosive to the skin and eyes and may cause permanent eye injury. Use safety goggles. Dispose of waste MEKP solutions as follows:

- a. Prepare 250 mL saturated aqueous sodium bisulfite in a 1-L beaker.
- b. Store in a hood. Add all waste solutions containing MEKP to this beaker.
- c. Allow to stand one week before disposing of the two-phase mixture.

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Pipet 15 mL dimethyl phthalate into the impinger. Mark the level. Wrap with aluminum foil.
3. Sample at an accurately known flow rate between 0.5 and 2 L/min for a total sample size of 52 to 520 L.
4. Check liquid level in impinger and add dimethyl phthalate if necessary to bring level to 15.0 mL. Quantitatively transfer the contents of each impinger to a silanized, Al foil-wrapped vial and seal tightly. Quickly place in a cold chest.
5. Whenever possible, hand-deliver the samples packed in dry ice. Otherwise, ship samples in container with dry ice. Mark "FRAGILE" on the container.
6. Upon receipt in the laboratory, store vials in the freezer. Complete analysis as soon as possible.

**SAMPLE PREPARATION:**

7. Adjust sample volume to 15.0 mL if necessary. Transfer in duplicate exactly 5.0 mL (1/3) of each sample or field blank to silanized test tubes.

8. Pipet 5.0 mL color reagent into the test tubes. Stopper and invert several times to mix.
9. Loosen the stoppers and heat the test tubes in a waterbath at  $85 \pm 5$  °C for 15 min.
10. Cool in a waterbath at  $25 \pm 5$  °C for exactly 5 min.

**CALIBRATION AND QUALITY CONTROL:**

11. Calibrate daily with at least six working standards in duplicate.
  - a. Pipet, e.g., 1.0, 2.0, 5.0, and 10.0 mL calibration stock solution to 25-mL silanized volumetric flasks, fitted with glass stoppers. Dilute to the mark with DMP. These working standards contain ca. 5, 10, 25, and 50 mg MEKP/mL (25, 50, 125, and 250 µg MEKP per 5-mL aliquot).
  - b. Process the working standards together with samples, field blanks, media blanks, and reagent blanks (steps 7 through 10 and 12 and 13) during the same time period using the same batch of reagents.
  - c. Prepare calibration graph (absorbance vs. µg MEKP). Extrapolate to zero concentration (y-intercept). Any sample whose absorbance is less than twice the "blank" should be reported as less than that level (about 25 µg MEKP per 5-mL aliquot). Perform a volumetric dilution to extend the range upward.

**MEASUREMENT:**

12. Set spectrophotometer according to manufacturer's instructions. Set zero with dimethyl phthalate vs. air.
13. Read sample absorbance at 565 nm vs. air when a stable value is obtained.  
NOTE: See SPECIAL PRECAUTIONS for procedure for disposal of waste MEKP solutions.

**CALCULATIONS:**

14. Determine the mass, µg, of MEKP in the 5-mL aliquot of sample, W, and the average media blank, B, from the calibration graph.
15. Calculate the concentration, C, of MEKP in the air volume sampled, V (L):

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

NOTE: Correct for the average media blank, B, only if it exceeds twice the reagent blank (y-intercept).

**EVALUATION OF METHOD:**

This method is based on P&CAM 331 which was issued on August 29, 1980 [1] and was studied using technical grade MEKP containing 58.7% MEKP [2].

A two-level factorial experiment was run to study the effect of three different parameters on the color produced in the reaction between MEKP and DPC. A reaction bath temperature of 85 °C and reaction time of 15 min were determined to be optimum. Samples containing 204 µg MEKP per 5 mL stored in the freezer for 21 days showed 10% loss of MEKP. MEKP standard solutions were tested for interference with acetone, methyl ethyl ketone, cyclohexanone, and 3-methyl-2-butanone. All these ketones, except acetone, exhibited positive interference. Stability of MEKP solutions was tested using various substances which could be likely co-contaminants. At freezer temperatures, samples containing styrene were stable for a week.

After 4 hrs at 1 L/min airflow through impingers containing MEKP standards in DMP, less than 10% of the MEKP carried over from the front to the backup bubbler.

The RSD of slopes of the calibration line determined from three levels approximately to 100, 170, and 210 µg/10 mL sample obtained over a six-month period was 9.8%. When the standards and samples were run on the same day, the RSD was 5.2%.

**REFERENCES:**

- [1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, P&CAM 331, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-125 (1980).
- [2] Okenfuss, J. R. and J. C. Posner. Investigation of an Air Sampling and Analytical Method for Methyl Ethyl Ketone Peroxide, available as Order No. PB 81-167868 from NTIS, Springfield, VA 22161 (1980).

**METHOD REVISED BY:**

Judd C. Posner, Ph.D., NIOSH/DPSE and Julie R. Okenfuss.

## APPENDIX:

## 1. STANDARDIZATION OF 60% MEKP STOCK SOLUTION

- a. Weigh to nearest mg, 1 g 60% MEKP in a 100-mL volumetric flask. Dilute to the mark with isopropyl alcohol and cover flask with foil.
- b. Place ca. 25 mL isopropyl alcohol in a 250-mL iodine flask. Add 5 mL glacial acetic acid then add 10 mL 20% sodium iodide solution to the flask.
- c. Pipet exactly 10.0 mL MEKP-isopropyl alcohol solution (from step 1.a above) into the flask, cover and let stand in the dark for 15 min.
- d. Add 10 mL distilled water to the flask immediately before titrating.
- e. Titrate with 0.1 N sodium thiosulfate from a yellow to colorless end point. Record the volume in mL used. Titrate a blank containing all reagents except MEKP in exactly the same way.
- f. Calculate the weight % MEKP:

$$C_s = \frac{(V_s - V_b) 4.405}{W}$$

where:  $C_s$  = percent MEKP as the cyclic dimer

$V_s$  = volume of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  used to titrate the sample (mL)

$V_b$  = volume of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  used to titrate the blank (mL)

$W$  = weight of commercial MEKP used (g)

4.405 = constant containing the milliequivalent weight of MEKP (as the cyclic dimer) and various dilution factors.

2. STANDARDIZATION OF SODIUM THIOSULFATE, 0.1 N (or use commercially available standard)

- a. Prepare the following solutions:
  - (1) Potassium dichromate, 0.1000 N. Dissolve 4.904 g anhydrous  $\text{K}_2\text{Cr}_2\text{O}_7$ , primary standard grade, in distilled water; dilute to 1 L.
  - (2) Starch indicator. Prepare a thin paste of 1 g soluble starch in a few mL distilled water. Bring 200 mL distilled water to a boil, remove from heat and stir in the starch paste. Prepare fresh before use.
  - (3) Sodium thiosulfate solution. Dissolve 25 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in freshly boiled, cooled distilled water; dilute to 1 L. Add 5 mL  $\text{CHCl}_3$  as preservative. Age 2 weeks before standardizing.
- b. Place 80 mL distilled, deionized water in 150-mL beaker, stirred with magnetic stirrer. Add 1 mL conc.  $\text{H}_2\text{SO}_4$ , 10.0 mL 0.1000 N  $\text{K}_2\text{Cr}_2\text{O}_7$  and ca. 1 g KI. Allow to stand in dark for 6 min. Titrate with sodium thiosulfate solution. Upon approaching end point (brown changing to yellowish green), add 1 mL starch indicator solution and continue titrating to the end point (blue to light green). Calculate the normality, N, of the sodium thiosulfate solution:

$$N = \frac{1}{\text{mL Na}_2\text{S}_2\text{O}_3 \text{ used}}$$