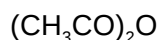


ACETIC ANHYDRIDE

3506



MW: 102.09

CAS: 108-24-7

RTECS: AK1925000

METHOD: 3506, Issue 2

EVALUATION: FULL

Issue 1: 5 May 1985

Issue 2: 15 August 1994

OSHA : 5 ppm
 NIOSH: C 5 ppm
 ACGIH: C 5 ppm
 (1 ppm = 4.17 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.080 g/mL @ 15 °C;
 BP 139 °C; MP -73 °C;
 VP 4 mm Hg @ 20 °C;
 explosive range 2.9 to 10.3% v/v in air

SYNONYMS: acetic acid anhydride; acetyl oxide

SAMPLING		MEASUREMENT	
SAMPLER:	LIQUID IN BUBBLER (mixed bubbler with 10 mL alkaline hydroxylamine)	TECHNIQUE:	VISIBLE ABSORPTION SPECTROPHOTOMETRY
FLOW RATE:	0.2 to 1.0 L/min	ANALYTE:	acetic anhydride-hydroxylamine-ferric chloride complex
VOL-MIN:	25 L	FINAL VOLUME:	50 mL
-MAX:	100 L	WAVELENGTH:	540 nm
SHIPMENT:	hand delivery or special bubbler cases	CALIBRATION:	complexed acetic anhydride standards
SAMPLE STABILITY:	≥ 4 days @ 25 °C [1]	RANGE:	0.5 to 4 mg acetic anhydride per sample [2]
BLANKS:	2 to 10 field blanks per set	ESTIMATED LOD:	0.05 mg acetic anhydride per sample
ACCURACY		PRECISION ($\hat{S}_p$):	0.021 @ 1 to 4 mg acetic anhydride per sample [1]
RANGE STUDIED:	9.35 to 37.4 mg/m ³ [1] (100-L samples)		
BIAS:	4.9%		
OVERALL PRECISION ($\hat{S}_{RT}$):	0.060 [1]		
ACCURACY:	± 15.3%		

APPLICABILITY: The working range is 1.2 to 10 ppm (5 to 40 mg/m³) for a 100-L air sample. The upper limit of the range may be extended by diluting the sample with the collection medium prior to color development. The method is sensitive enough for short-term (>5 min) determinations if a 5-cm or longer cuvette is used.

INTERFERENCES: Any substance containing a hydrolyzable carbonyl group, such as esters, acid chlorides, and aldehydes, is an interference. The most likely interference to coexist with acetic anhydride in air is ketene [2,3].

OTHER METHODS: This revises Method S170 [2].

REAGENTS:

1. Hydroxylamine hydrochloride solution. Dilute 200 g (NH₂OH)Cl to 1 L with distilled water in a volumetric flask. Refrigerate in a light-protected container. Discard after two weeks.
2. Sodium hydroxide solution. Dissolve 200 g in distilled water. Cool and bring to volume in a 1-L volumetric flask with distilled water. Store in a polyethylene bottle.
3. Absorbing solution (needed for sampler). Mix equal volumes of the hydroxylamine hydrochloride and sodium hydroxide solutions just prior to use. Do not use after 2 h.
4. HCl:water, 1:1 (v/v). Mix equal volumes of conc. HCl and distilled water.
5. Ferric chloride solution. Dissolve 100 g FeCl₃·6H₂O in a 1-L volumetric flask with 1:1 (v/v) HCl:water. Dilute to volume with this mixture.
6. Acetone.
7. Acetic anhydride calibration stock solution. Pipet 10 mL acetic anhydride* into a 100-mL volumetric flask. Make to volume with acetone. The solution must be used within 2 h of preparation.

* See Special Precautions

EQUIPMENT:

1. Sampler: bubbler, standard midget glass, stem containing fritted end with porosity ca. 170 to 220 mm maximum pore diameter with hard, non-reactive stopper (PTFE or glass).
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Splashover tube: glass tube, 5 cm long, 8-mm OD, 6-mm ID, loosely packed with glass wool.
4. Spectrophotometer reading at 540 nm with 5-cm matched cuvettes.
5. Flasks, volumetric, 1-L and 50- and 100-mL.
6. Pipets, graduated, 1-, 5- and 10-mL.
7. Micropipets, 10- to 100-μL.
8. Ice bath.

SPECIAL PRECAUTIONS: Acetic anhydride is readily combustible (flash point = 54 °C) and both the liquid and vapor produce irritation and necrosis of tissues. It may produce allergic sensitization of the skin [4].

SAMPLING:

1. Calibrate the personal sampling pump with a representative sampler in line.
2. Connect a splashover tube between the bubbler and the sampling pump with short pieces of flexible tubing. Do not allow the air being sampled to pass through any tubing or other equipment before entering the bubbler.
3. Pour 10 mL of absorbing solution into bubbler.
NOTE: Absorbing solution must be prepared just prior to use (see REAGENTS, 3).
4. Sample at an accurately known flow rate between 0.2 and 1 L/min for a sample size of 25 to 100 L. Change sampler every 2 hrs so that the absorbing solution is fresh.
5. After sampling, remove the bubbler stem and tap gently against the inside of the bubbler tube. Wash the stem with 1 to 2 mL absorbing solution and add the wash to the bubbler.
6. Seal the bubbler tightly with a hard, non-reactive stopper and transport the samples by hand. Alternatively, transfer contents of each bubbler to a glass vial, rinsing bubbler with 1 to 2 mL absorbing solution. Cap the vial securely for shipment.

SAMPLE PREPARATION:

7. Transfer sample solution to a 50-mL volumetric flask.
8. Rinse bubbler twice with 1 mL distilled water. Add rinses to the flask.
NOTE: For samples containing > 4 mg acetic anhydride, dilute an aliquot of the bubbler solution to 50 mL at this step. Apply the appropriate dilution factor in calculations.
9. Pipet 5 mL ferric chloride solution into the flask.
10. In an ice bath, mix equal volumes of sodium hydroxide solution, hydroxylamine hydrochloride solution and ferric chloride solution. Add this solution to bring the solution in the 50-mL volumetric flask to the mark. The purple complex is formed rapidly.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards over the range 0.05 to 4 mg acetic anhydride per sample.
 - a. Pipet 10 mL absorbing solution into each of six 50-mL volumetric flasks.
 - b. Transfer 0 (reagent blank), 10, 20, 40, 80 and 100 µL acetic anhydride calibration stock solution into the flasks.
 - c. Add reagents (steps 9 and 10).
 - d. Analyze with samples and blanks (steps 12 through 14).
 - e. Construct calibration graph (absorbance vs. mg acetic anhydride).

MEASUREMENT:

12. Set spectrophotometer to read at 540 nm.
13. Adjust the baseline to zero with distilled water in both cells.
14. Read absorbance of the sample vs. reagent blank in the reference cell.

CALCULATIONS:

15. Determine the mass, mg, of acetic anhydride in the bubbler, W, and in the average media blank, B, from the calibration graph.
16. Calculate the concentration, C (mg/m³), of acetic anhydride in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S170 was issued on August 1, 1975 [2], and validated using 100-L air samples over the range 9.35 to 37.4 mg/m³ at 22 °C and 761 mm Hg [1]. Overall precision, $\hat{S}_{IT}$, was 0.060, with a collection efficiency of 1.00 ± 0.01 . The average of concentrations obtained at 20 mg/m³ for the overall sampling and measurement technique was 2.5% higher than the true concentrations representing a non-significant bias for a limited number of experiments [1]. Sample atmospheres were generated using the apparatus and procedure for epichlorohydrin [5] and a total hydrocarbon analyzer was used to monitor the generated vapor concentrations [1].

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S170, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
- [2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S170, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [3] Diggle, W. M. and J. C. Gage. The Determination of Ketene and Acetic Anhydride in the Atmosphere, Analyst, 78, 473 (1953).
- [4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
- [5] Documentation of the NIOSH Validation Tests, op. cit., S118.

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE.