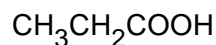


ETHYL FORMATE

1452



MW: 74.08

CAS: 109-94-4

RTECS: LQ8400000

METHOD: 1452, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 August 1994

OSHA : 100 ppm
 NIOSH: 100 ppm; Group I Pesticide
 ACGIH: 100 ppm
 (1 ppm = 3.03 mg/m³)

PROPERTIES: liquid; BP 54.5 °C; d 0.917 g/mL @ 20 °C;
 VP 26 kPa (194 mm Hg) @ 20 °C;
 vapor density (air = 1) 2.6; explosive range
 2.8 to 16% v/v

SYNONYMS: formic acid, ethyl ester; ethyl methanoate

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal; 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	ethyl formate
VOL-MIN:	0.3 L @ 100 ppm	EXTRACTION:	1 mL CS ₂ ; stand 30 min.
-MAX:	10 L	INJECTION VOLUME:	5 µL
SHIPMENT:	routine	TEMPERATURE-INJECTION:	225 °C
SAMPLE STABILITY:	unknown	-DETECTOR:	250 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	65 °C
ACCURACY		CARRIER GAS:	helium, 30 mL/min
RANGE STUDIED:	171-666 mg/m ³ (10-L samples) [1]	COLUMN:	stainless steel, 10% FFAP on 80/100 Chromosorb W AW-DMCS (20 ft. x 1/8 in.)
BIAS:	7.3%	CALIBRATION:	standard solutions of ethyl formate in carbon disulfide with n-nonane as internal standard.
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.0782 [1]	RANGE:	0.1 to 6 mg per sample [1]
ACCURACY:	± 21.1%	ESTIMATED LOD:	0.02 mg per sample
		PRECISION (\hat{S}_r):	0.019 @ 1.71 to 6.66 mg per sample [1]

APPLICABILITY: The working range is 3.3 to 210 ppm (10 to 630 mg/m³) for a 10-L air sample.

INTERFERENCES: Any compound having the same retention time as ethyl formate under the same analytical conditions is an interference. A different temperature program or column with a different phase may eliminate the problem.

OTHER METHODS: This revises Method S36 [2].

REAGENTS:

1. Ethyl formate, ACS reagent grade.
2. Eluent: carbon disulfide, chromatographic quality, with 0.1% v/v n-nonane, ACS reagent grade (optional internal standard).
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID flame-sealed ends with plastic caps, containing two sections of 20/40 mesh of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column.
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10- μ L and other convenient sizes for preparing standards.
6. Flasks, volumetric, 10-mL.
7. Pipet, 1-mL graduated in 0.1 mL increments with bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a sample size of 0.3 to 10 L.
4. Replace the caps on the sampling tube and pack securely for shipment.
5. Obtain a small quantity (5 mL) of the bulk material in a glass container with a Teflon-lined cap. Ship to the laboratory in a separate container from the charcoal tube samples.

SAMPLE PREPARATION:

6. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
7. Add 1.0 mL eluent to each vial. Attach cap to each vial.
8. Allow to stand for 30 min. with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range 0.01 to 6 mg/sample.
 - a. Add known amounts of ethyl formate to eluent in 10-mL volumetric flasks with a concentration equal to 70% of that of the highest standard.
 - b. Analyze together with the samples (steps 12 and 13).

- c. Prepare a calibration graph of the ratio of peak area of ethyl formate to that of n-nonane vs. mg of ethyl formate).
10. Determine the desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 9). Prepare three tubes at each of five levels and three media blanks.
 - a. Remove and discard the back sorbent section of a media blank sample.
 - b. Inject a known amount of ethyl formate or a standard solution directly onto the front sorbent section with a microliter syringe.
 - c. Cap the tubes. Allow to stand overnight.
 - d. Desorb (steps 6 through 8) and analyze together with the working standards (steps 12 and 12).
 - e. Prepare a graph of DE vs. mg ethyl formate recovered.
11. Analyze three quality control blind spikes and three analysts spikes to ensure that the results are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1452-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent reanalyze, and apply appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of ethyl formate 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.
15. Calculate concentration, C, of ethyl formate in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was validated over the range 171 to 666 mg/m³ at 23 °C and 766 mm Hg using 10-L samples. Overall sampling and measurement precision, \hat{S}_{rt} , was 0.0782, with average recovery of 104%. Desorption efficiency from charcoal was 82% in the range of 1.48 to 5.91 mg per sample. Break through volume was 14 L when sampling an atmosphere containing 666 mg/m³ at 0.190 L/min. This corresponds to a capacity of 9.5 mg of ethyl formate. Storage stability was not determined.

REFERENCES:

- [1] Backup Data Report for Ethyl Formate, prepared under NIOSH Contract No. CDC-99-74-45.
- [2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S36, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

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