**FORMIC ACID**

HCOOH  CAS: 64-18-6  RTECS: LQ4900000

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**OSHA:** 5 ppm  
**NIOSH:** 5 ppm  
**ACGIH:** 5 ppm  
(1 ppm = 1.882 mg/m³ @ NTP)

**PROPERTIES:** liquid; BP 107 °C; d 1.22 g/mL (90% solution) @ 20 °C; VP 4.7 kPa (33 mm Hg); vapor density (air = 1) 1.6; colorless; pungent odor

**SYNONYMS:** hydrogen carboxylic acid; methanoic acid

### SAMPLING

| SAMPLER: FILTER + SOLID SORBENT TUBE  
| FLOW RATE: 0.05 to 0.2 L/min  
| VOL-MIN: 1 L @ 5 ppm  
| VOL-MAX: 24 L  
| SHIPMENT: routine  
| SAMPLE STABILITY: 1 week @ 25 °C  
| BLANKS: 2 to 10 field blanks per set |

### MEASUREMENT

| TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION  
| ANALYTE: formate ion  
| DESORPTION: 10 mL deionized water; stand 5 minutes  
| INJECTION VOLUME: 50 µL  
| ELUENT: 2.5 mM Na₂B₄O₇·10 H₂O, 2.0 mL/min  
| COLUMN: Dionex HPIC-AG4 guard, HPIC-AS4 anion separator, anion micromembrane suppressor  
| DETECTOR: conductivity, 10 µS full scale  
| CALIBRATION: standard solutions of formate spiked onto sample media  
| RANGE: 6 to 100 µg formate per sample [1]  
| ESTIMATED LOD: 2 µg formate per sample [2,3]  
| ACCURACY: not studied  
| BIAS: not determined  
| OVERALL PRECISION (SD): not determined  
| PRECISION (SD): 0.026 @ 106 to 426 µg per sample [2]  
| 0.097 @ 10 to 80 µg per sample [3] |

**APPLICABILITY:** The working range is 0.13 to 12 ppm (0.25 to 22 mg/m³) for a 24-L air sample.

**INTERFERENCES:** None identified.

**OTHER METHODS:** This is a modification of Method 7903 (Acids, inorganic) and revises Method S173 [1,3].
REAGENTS:

1. Acetone, ACS reagent grade.
2. Water, deionized.
3. Eluent: 2.5 mM Na₂B₄O₇·10H₂O. Dissolve 3.82 g Na₂B₄O₇·10H₂O in 4 liters high purity water. Filter if necessary to remove any particulate matter.
4. Suppressor regenerant, 25 mM NH₄HSO₄.*
5. Calibration stock solution, 1 mg formate anion per mL. Dissolve 0.1511 g sodium formate (dried @ 110 °C for 4 h, stored in desiccator) in 100 mL deionized water.
6. Formic acid, 88% or 95% (Optional; see Appendix A).
7. Dioxane (Optional; see Appendix A).
8. 0.1 M Na₂B₄O₇·10H₂O. Dissolve 145 g Na₂B₄O₇·10H₂O in 4 liters deionized water. Filter if necessary to remove particles > 1 µm.

*SPECIAL PRECAUTIONS: Users of this method should be acquainted with the degree of hazard of each chemical and take the proper precautions. Handle all hazardous chemicals in a fume hood.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 7-mm OD, 4-mm ID, flamed-sealed ends with plastic 20/40 caps, containing 20/40 mesh washed silica gel (front = 400 mg, back = 200 mg) separated by a 4-mm urethane foam plug. A thick glass fiber filter plug precedes the front section and a 5-mm urethane foam plug follows the back section. Tubes are commercially available (ORBO-53, Supelco, or equivalent) or prepare according to APPENDIX B. Prefilter, PTFE, 25-mm, with porous plastic support pad. Pressure drop across the sampler at 1 L/min airflow must be less than 3.4 kPa.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible polyethylene or PTFE tubing.
3. Ion chromatograph, with a conductivity detector, chart recorder, integrator, and column.
4. Vials, polyethylene, 20-mL, with plastic caps.
5. Micropipettes, with disposable plastic tips.
6. Volumetric flasks, 100-mL.
7. Pipet, 10-mL, graduated in 0.1-mL intervals.
8. Pipet, volumetric, 20-mL.
9. Syringes, 10-mL, plastic, with luer tip.
10. Filters, luer tip, with membrane filter, 13-mm, 0.45-µm pore size.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach a sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for total volume of 1 to 24 L.
4. Cap the tubes with plastic (not rubber) caps, plug filter cassettes, and pack securely for shipment.

NOTE: Prefilters may be analyzed for particulate formates, or may be discarded.

SAMPLE PREPARATION:

5. Place the front with glass fiber filter plug and back sorbent sections of the sampler tube (and prefilter, optional) in separate 20-mL plastic vials. A glass rod may be used to push the contents out of the tube. Discard the foam plugs.
6. Add 10 mL deionized water to each plastic vial. Loosely cap.
7. Heat in boiling water for 10 min, cool, and analyze the same day the formic acid is desorbed.
8. Transfer a portion of sample to a syringe fitted with an inline membrane filter, for direct injection or for transfer to autosampler vials.
CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range of 2 to 100 µg formate per sample.
   a. Spike appropriate amounts of calibration stock solution or a dilution thereof, onto sorbent tubes.
   b. Desorb in the same manner as field samples.
   c. Analyze working standards together with samples and blanks (steps 12 through 14).
   d. Prepare a calibration graph of peak height vs. amount (µg) of formic acid per 10 mL of sample.
      NOTE: Apply the conversion 1 µg formate = 1.022 µg formic acid.

10. (Optional) Determine recovery for each lot of silica gel used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus three media blanks.
   a. Add a known amount of DE stock solution, or a dilution thereof, onto sorbent tube (see Appendix A).
   b. Analyze in the same manner as field samples.
   c. Prepare graph of recovery vs. µg formic acid.

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

MEASUREMENT:

12. Set ion chromatograph to conditions given on page 2011-1.
13. Inject 50-µL sample aliquot. For manual operation inject 2 to 3 mL of sample from the syringe (through inline filter) to ensure complete rinse of sample loop.
   NOTE: flushing the column between injections with 0.1 M Na₂B₄O₇·10 H₂O for one minute removes the later eluting ions quickly.
14. Measure peak height.
   NOTE: If peak height exceeds the linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

15. Read mass, µg of formic acid found on the front (Wₐ) and back (Wₜ) sections and the average media blank front (Bₐ) and (Bₜ) sections from the calibration graph.
   NOTE: If Wₜ > Wₐ/10, report breakthrough and possible sample loss.
16. Calculate concentration C of formic acid (mg/m³) in the actual air volume, V (L):

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C = \frac{(Wₐ + Wₜ - Bₐ - Bₜ)}{V}, \text{ mg/m}³.
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EVALUATION OF METHOD:

This method was validated over the range 4.4 to 21.6 mg/m³ at 23 °C and pressure of 759 mm Hg using 24-L samples [1]. Overall sampling and measurement precision, S_T is 0.073, with average recovery of 96% in the range 4 to 22 mg/m³ per sample [1]. Sample stability during storage was evaluated at 11 mg/m³ per sample. Samples showed 91.5% recovery after one week of storage at ambient conditions compared to one-day old samples [1]. Breakthrough did not occur when a 25 mg/m³ test atmosphere (85% relative humidity) was sampled at 0.18 liter/minute for 300 minutes. This modification of NMAM 7903, which uses 2.5 M Na₂B₄O₇·10 H₂O eluent, resulted in a LOD of 2 µg/sample and a range 7 to 100 µg per sample. Samples were collected on silica gel, desorbed in 10 mL eluent, heated 10 minutes in boiling water, then analyzed.[3]
REFERENCES:


METHOD REVISED BY:

George Y. Williamson, MRSB, DPSE.

APPENDIX A: DESORPTION EFFICIENCY STOCK SOLUTION, 51.5 mg FORMIC ACID/mL

Pipet 6 mL of 88% formic acid into a 125-mL volumetric flask. Make to volume with dioxane. For standardization, appropriate aliquots are withdrawn, diluted with deionized water, and analyzed as in steps 9 through 15.

NOTE: The solution must be prepared fresh daily. Loss of formic acid was observed after 24 h. Pipetting below the liquid level of the standard will minimize loss of formic acid from evaporation.

APPENDIX B: SAMPLING TUBE PREPARATION

Silica gel cleaning procedure: Add 500 to 600 mL deionized water, slowly and with stirring, to ca. 200 mL volume of silica gel in 1-L beaker. When exothermal reaction has subsided, heat in boiling waterbath for ca. 30 min with occasional stirring. Decant and rinse four to five times with deionized water. Repeat cleaning procedure and dry overnight in 100 °C oven until free flowing. If blank of silica gel shows impurities, repeat cleaning procedure.

Silica gel tubes: Pack glass tubes, 7-mm OD, 4.8-mm ID, 11 cm long, with 400 mg of 20/40 mesh washed silica gel in front section and 200 mg backup section. Use urethane foam plugs between sorbent sections and at back end. Hold front section in place with 6-mm diameter, 1-mm thick glass fiber filter plug (Gelman 66088).