

# NICKEL CARBONYL

6007

Ni(CO)<sub>4</sub>

MW: 170.73

CAS: 13463-39-3

RTECS: QR6300000

**METHOD:** 6007, Issue 2

**EVALUATION:** PARTIAL

**Issue 1:** 15 August 1987

**Issue 2:** 15 August 1994

**OSHA :** 0.001 ppm (as Ni)  
**NIOSH:** 0.001 ppm; carcinogen  
**ACGIH:** 0.05 ppm (as Ni)  
 (1 ppm = 6.98 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** liquid; d 1.318 g/mL @ 20 °C; BP 43 °C;  
 MP -25 °C; VP 43 kPa (321 mm Hg; 42%  
 v/v) @ 20 °C; lower explosive limit 2%  
 v/v in air

**SYNONYMS:** nickel tetracarbonyl

**APPLICABILITY:** The working range is 0.00036 to 0.007 ppm (0.0025 to 0.05 mg/m<sup>3</sup>) nickel carbonyl for a 20-L air sample.

**INTERFERENCES:** Particulate nickel compounds will give a positive interference unless a prefilter is used during sampling.

**OTHER METHODS:** This revises P&CAM 344 [2]. A colorimetric method has also been recommended [3].

**REAGENTS:**

1. Water, double-distilled (or deionized).
2. Nitric acid, 70% (w/v) HNO<sub>3</sub>, redistilled in glass.
3. Nitric acid, 3% (w/v) HNO<sub>3</sub>. Add 31 mL 70% HNO<sub>3</sub> to distilled water. Dilute to 1 L.
4. Nickel stock solution, 1000 µg Ni/mL. Dissolve 1.000 g pure Ni metal in minimum volume 70% HNO<sub>3</sub>. Dilute to 1 L with 3% HNO<sub>3</sub>. Commercially available.
5. Calibration stock solution, 50 µg Ni/mL. Dilute 0.500 mL nickel stock solution (1000 µg/mL) to 10 mL in a volumetric flask with 3% HNO<sub>3</sub>. Store in a polyethylene bottle. Prepare fresh weekly.
6. Argon, high-purity purge gas in cylinder with a two-stage regulator.  
NOTE: Nitrogen cannot be used as purge gas because of the formation of UV-absorbing cyanogen.
7. Charcoal, acid-washed, activated. Acid-wash a sufficient quantity of coconut-based charcoal having an initial blank value of less than 0.02 µg Ni/200 mg, by soaking overnight in 3% nitric acid. Rinse several times with distilled water. Pour off excess water, cover with a watchglass, and activate by heating at 600 °C for 1.5 hrs in still air.

**EQUIPMENT:**

1. Sampler:
  - a. Prefilter: 37-mm, 0.8-µm cellulose ester filter and cellulose backup pad in a plastic filter holder.
  - b. Glass tube, 8 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh acid-washed activated (600 °C) coconut shell charcoal (front = 120 mg; back = 60 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 at 1 L/min airflow must be less than 3.4 kPa.  
NOTE: The prefilter must be used when particulate nickel is present in the air to be sampled. Connect prefilter to sorbent tube with a short section of plastic tubing.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. File, triangular.
4. Atomic absorption spectrophotometer equipped with:
  - a. Heated graphite atomizing rod, tube or furnace (either non-pyrolitic or pyrolitic; better sensitivity with pyrolitic).  
NOTE: Reproducible control of times and temperatures during dry, char, and atomize cycles is essential; minimum atomization temperature 2700 °C.
  - b. Readout device (recorder or digital peak height or peak area analyzer).
  - c. Pipetting system (automatic or manual, 5- to 50-µL, as appropriate to atomizer size).
  - d. Background correction, e.g., D<sub>2</sub> or H<sub>2</sub> lamp or non-absorbing line (231.5 nm for the 232 nm Ni line).
  - e. Hollow cathode lamp for nickel.
5. Vials, 2-mL, with plastic-lined screw caps.\*
6. Pipet, TD, 1-mL.\*
7. Ultrasonic water bath.
8. Volumetric flasks, 10-mL and 1-L.\*
9. Bottles, polyethylene, 20-mL.
10. Syringe, 25-µL, readable to 0.1 µL.

\*Soak new glassware 1 h in hot, conc. nitric acid followed by thorough rinsing with distilled water. After each use, wash glassware with, in order, detergent solution, tap water, 3% nitric acid (soak ≥4 h) and distilled water.

**SPECIAL PRECAUTIONS:** None.

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**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach prefilter. Attach 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 a total sample size of 7 to 80 L.
4. Cap the samplers. Pack securely for shipment.

**SAMPLE PREPARATION:**

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs. Discard prefilter or analyze for particulate Ni.
6. Add 1.0 mL 3% HNO<sub>3</sub> to each vial. Cap each vial.
7. Allow to stand 30 min in an ultrasonic water bath.

**CALIBRATION AND QUALITY CONTROL:**

8. Calibrate daily with at least six working standards.
  - a. Add known amounts of calibration stock solution to 3% HNO<sub>3</sub> in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain Ni<sup>2+</sup> concentrations in the range 0.01 to 0.6 µg/mL. Store in polyethylene bottles and prepare fresh daily.
  - b. Analyze with samples and blanks (steps 11 through 13).
  - c. Prepare calibration graph (absorbance vs. µg Ni<sup>2+</sup>).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
  - a. Remove and discard back sorbent section of a media blank sampler.
  - b. Inject a known amount (2 to 20 µL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
  - c. Cap the tube. Allow to stand overnight.
  - d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 through 13).
  - e. Prepare a graph of DE vs. µg Ni<sup>2+</sup> recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

**MEASUREMENT:**

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations, conditions given on page 6007-1, and the following:
  - a. Inert gas flow: increased sensitivity if flow is interrupted during atomization.
  - b. Wavelength: either 232 nm (more sensitive) or 341.5 nm.
  - c. Dry cycle: 30 sec at 110 °C; longer time and ramp program may be needed for aliquots >20 µL.
  - d. Ash (char) cycle: 15 sec at 800 °C.
  - e. Atomize cycle: 10 sec at 2700 to 3000 °C; atomization is too slow for reproducible results below 2600 °C; "maximum power" feature will increase sensitivity.
12. Inject sample aliquot manually or with autosampler.
13. Measure peak height. Analyze a series of standards before and after each set of samples and analyze one mid-range standard after each ten samples. Analyze all solutions, including sorbent tube blanks and reagent blanks, in triplicate.

NOTE 1: Peak occurs about 3 sec after start of atomize cycle.

NOTE 2: If peak height is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with 3% HNO<sub>3</sub>, reanalyze and apply the appropriate dilution factor in calculations.

**CALCULATIONS:**

14. Determine the mass, µg (corrected for DE) of Ni found in the sample front (W<sub>f</sub>) and back (W<sub>b</sub>) sorbent sections, and in the average media blank front (B<sub>f</sub>) and back (B<sub>b</sub>) sorbent sections.  
NOTE: If W<sub>b</sub> > W<sub>f</sub>/10, report breakthrough and possible sample loss.
15. Calculate concentration, C, of nickel carbonyl in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2.91}{V}, \text{ mg/m}^3.$$

where: 2.91 = stoichiometric conversion factor from Ni to Ni(CO)<sub>4</sub>.

**EVALUATION OF METHOD:**

Method P&CAM 344 was issued on August 31, 1981 [2], and evaluated with generated atmospheres of Ni(CO)<sub>4</sub> containing 6 to 300 ppm added carbon monoxide. Mean recovery was 93% (24 samples) in the range 5 to 121 µg/m<sup>3</sup> (0.0007 to 0.017 ppm). Breakthrough (effluent = 5% of test concentration) did not occur after sampling for 240 min at 0.475 L/min from an atmosphere containing 34 µg/m<sup>3</sup> (0.005 ppm) Ni(CO)<sub>4</sub> in air at 22 °C and 19% RH. Desorption efficiency for eighteen samples containing 0.08 to 0.5 µg Ni (nickel nitrate standard solution added to 120 mg charcoal) averaged 0.934 with S<sub>r</sub> = 0.029. Nickel carbonyl was observed to pass quantitatively through 0.8-µm cellulose ester membrane filters in these experiments.

**REFERENCES:**

- [1] Eller, P. M. "Determination of Nickel Carbonyl by Charcoal Tube Collection and Furnace Atomic Absorption," *Appl. Ind. Hyg.* 1:115-118 (1986).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 344, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
- [3] Special Occupational Hazard Review and Control Recommendations for Nickel Carbonyl, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-184 (1977).

**METHOD WRITTEN BY:**

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