TUNGSTEN (soluble and insoluble) 7074

W MW: 183.85 CAS: 7440-33-7 RTECS: Y07175000

METHOD: 7074, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
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OSHA : no PEL
NIOSH: 1 mg/m^3 solubles; STEL 3 mg/m^3
5 mg/m^3 insolubles; STEL 10 mg/m^3
ACGIH: 1 mg/m^3 solubles, STEL 3 mg/m^3
5 mg/m^3 insolubles, STEL 10 mg/m^3

PROPERTIES: brittle metal; MP 3410 °C; valence 2,3,4,5,6

SYNONYMS: wolfram.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 200 L @ 1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 2 weeks @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.42 to 2.0 mg/m^3 (soluble) [1];
0.84 to 19.7 mg/m^3 (insoluble) [1]

BIAS: + 0.015

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 (soluble) [1];
0.056 (insoluble) [1]

ACCURACY: ± 12.5%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: tungsten

EXTRACTION: H_2O; 6 min, 25 °C (soluble)

ASHING: 1:1 HF:HNO_3, 10 mL; 6 h, 150 °C (insoluble)

FINAL SOLUTION: 0.05 M NaOH/2% Na_2SO_4; 25 mL

FLAME: nitrous oxide-acetylene, reducing

WAVELENGTH: 255.1 nm

BACKGROUND CORRECTION: none used

CALIBRATION: W in 0.05 M NaOH and 2% Na_2SO_4

RANGE: 0.1 to 0.5 mg per sample (soluble);
0.25 to 12 mg per sample (insoluble)

ESTIMATED LOD: 50 µg soluble W per sample;
125 µg insoluble W per sample [2]

PRECISION ($\hat{S}_r$): 0.029 [1]

APPLICABILITY: The working range of this method is 0.25 to 5 mg/m^3 (soluble) and 0.6 to 5 mg/m^3 (insoluble) for a 400-L air sample. This is an elemental analysis and not compound-specific. For cemented tungsten carbide samples, cobalt can be quantitatively determined from the HCl extract used to remove interferences.

INTERFERENCES: None known. Ni, Mo, V, Mn, Cr, Co and Fe do not interfere at concentrations up to 50 times the tungsten concentration [3].

OTHER METHODS: This revises P&CAM 271 [1,3]. Method 7300 (ICP-AES) is an alternate measurement method; however, the extraction and ashing procedures described in this method must be followed.

REAGENTS:

1. Nitric acid, conc.*
2. Hydrofluoric acid, conc.*
3. Hydrochloric acid, conc.*
4. Hydrochloric acid, 1% (v/v). Add 26.5 mL conc. HCl to 500 mL water; dilute to 1 L.
5. Sodium hydroxide, 0.5 M. Dissolve 20 g NaOH in 500 mL water; dilute to 1 L.
6. Sodium sulfate, 20% (w/v). Dissolve 20 g Na_2SO_4 in 80 mL water; dilute to 100 mL.
7. Calibration stock solution, 10 mg W/mL. Commercially available or dissolve 1.5985 g Na_2WO_4 (dried at 125 °C) in water; add 10 mL 0.5 M NaOH and dilute to 100 mL.
8. Water, distilled, deionized.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head.
4. Tungsten hollow cathode lamp.
5. Two-stage regulators for N_2O and acetylene.
6. Beakers, PTFE, 100-mL (with covers).*
7. Volumetric flasks, 10-, 25- and 100-mL.*
8. Assorted volumetric pipets, as needed, with pipet bulb.*
9. Hotplate for use at 150 °C.
10. Steam bath or 100 °C hotplate.
11. Filtering apparatus (funnel, clamp, frit, holder) with 47-mm, 0.45-µm pore size cellulose ester membrane filter and collection vessel.

* Clean all labware with conc. nitric acid and rinse thoroughly with distilled water before use.

SPECIAL PRECAUTIONS: Wear protective equipment (gloves, labcoats, and safety glasses) when working with HF. Do not use HF with glass labware. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open the cassette and transfer the filter to the filtering apparatus on top of a 47-mm filter.
4. Add 3 mL deionized water to the sample filter, allow it to stand 3 min, apply vacuum to transfer the extract to the holding vessel, and repeat with an additional 3 mL water.
5. Transfer the extracts to a 10-mL volumetric flask, add 1.0 mL 20% Na_2SO_4, dilute to volume, and analyze for soluble tungsten (steps 17 through 19).
6. Digest the filters and residue in a covered PTFE beaker with 5.0 mL conc. HNO_3 and 5.0 mL conc. HF at 150 °C.
7. Remove the beaker cover and reduce the volume to 2 mL (150 °C). Take to dryness at 100 °C.
8. Remove from heat, cool, add 10 mL 1% HCl, and agitate manually for 5 min.
9. Filter through an additional 47-mm filter (the filtrate may be analyzed for cobalt).
10. Digest the filter and residue in a PTFE beaker with 5.0 mL conc. HNO_3 and 5.0 mL conc. HF at 150 °C.
11. Remove the beaker cover and reduce the volume to 1 mL (150 °C). If filter residue (dark, charred material) is visible, add additional HNO_3 and HF (2 mL each).
12. Take to near-dryness at 100 °C.
13. Dissolve residue in beaker with 2.5 mL 0.5 M NaOH and 2.5 mL 20% Na_2SO_4 at 100 °C (15 min).
14. Transfer to a 25-mL volumetric flask and dilute to volume.

CALIBRATION AND QUALITY CONTROL:

15. Calibrate with at least six working standards over the range 0.05 to 12 mg W per sample.
    a. Add known amounts of calibration stock solution to 100-mL volumetric flasks containing 10 mL 0.5 M NaOH and 10 mL 20% Na_2SO_4; dilute to volume with distilled, deionized water.
    b. Analyze together with samples and blanks (steps 17 through 19).
    c. Prepare calibration graph (absorbance vs. solution concentration, µg/mL).
16. Analyze three quality control blind spikes and three analyst spikes to ensure that the recovery and calibration graph are in control (steps 6 through 14 and 17 through 19).

MEASUREMENT:

17. Set spectrophotometer to conditions on page 7074-1.
18. Aspirate standards and samples. Record absorbance readings.
19. If the absorbance values for the samples are outside of the range of the standards, dilute the solutions with 0.05 M NaOH/2% Na_2SO_4 solution, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

20. Determine the solution concentrations of tungsten in the sample, C_s (µg/mL), and average media blank, C_b (µg/mL), from the calibration graph.
21. Using the solution volumes, mL of the sample (V_s) and media blank (V_b), calculate the concentration of tungsten, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method is based on P&CAM 271 [3,4] and was further evaluated and ruggedized under contract [1]. Laboratory testing with spiked samples over the ranges of 0.17 to 0.8 mg per sample (soluble) and 0.34 to 7.9 mg per sample (insoluble) gave precisions ($\bar{S}_r$) of 0.079 (soluble) and 0.076 (insoluble) [1]. Both soluble and insoluble tungsten species collected on filters were stable for two weeks [1].

REFERENCES:

[1] Carlin, L. M., G. Colovos, D. Garland, M. Jamin, M. Klenck, T. Long, and C. Nelson. Analytical Methods Evaluation and Validation: Arsenic, Nickel, Tungsten, Vanadium, Talc and Wood Dust, NIOSH Contract No. 210-79-0060 (1981), available as Order No. PB 83-155325 from NTIS, Springfield, VA 22161.
[2] User check, UBTL, Inc., NIOSH Sequence #4213-M (unpublished, May 23, 1984).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 271, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Hull, R. D. Analysis of Tungsten by Atomic Absorption Spectrophotometry: A Feasibility Study, NIOSH, DPSE, MRB, IMDS Technical Report (unpublished, December, 1977).

METHOD WRITTEN BY:

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