TUNGSTEN (soluble and insoluble)  7074

|-----------------------|------------------|---------------------------|------------------------|

**OSHA**: no PEL  
**NIOSH**: 1 mg/m³ soluble; STEL 3 mg/m³  
5 mg/m³ insoluble; STEL 10 mg/m³  
**ACGIH**: 1 mg/m³ soluble, STEL 3 mg/m³  
5 mg/m³ insoluble, STEL 10 mg/m³

**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/m³  
-MAX: 1000 L | SHIPMENT: routine |
| SAMPLE STABILITY: stable at least 2 weeks @ 25 °C  
BLANKS: 2 to 10 field blanks per set |

### Measurement

| TECHNIQUE: ATOMIC ABSORPTION, FLAME  
ANALYTE: tungsten  
EXTRACTION: H₂O: 6 min, 25 °C (soluble)  
ASHING: 1.1 HF:HNO₃, 10 mL; 6 h, 150 °C (insoluble)  
FLAME: nitrous oxide-acetylene, reducing  
WAVELENGTH: 255.1 nm  
BACKGROUND CORRECTION: none used  
CALIBRATION: W in 0.05 M NaOH and 2% Na₂SO₄ |
| FINAL SOLUTION: 0.05 M NaOH/2% Na₂SO₄; 25 mL  
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 (S): 0.029 [1] |

**ACCURACY**: The working range of this method is 0.25 to 5 mg/m³ (soluble) and 0.6 to 5 mg/m³ (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% Na₂SO₄; 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% Na₂SO₄ solution, reanalyze, and use the appropriate dilution
    factor in calculations.

CALCULATIONS:

20. Determine the solution concentrations of tungsten in the sample, Cₛ (µg/mL), and average media
    blank, Cₖ (µg/mL), from the calibration graph.
21. Using the solution volumes, mL of the sample (Vₛ) and media blank (Vₖ), calculate the
    concentration of tungsten, C (mg/m³), in the air volume sampled, V (L):

    \[ C = \frac{(CₛVₛ - CₖVₖ)}{V}, \text{ mg/m}^3. \]

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 (Sₚ) 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:

    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.

METHOD WRITTEN BY:

R. DeLon Hull, Ph.D., NIOSH/DBBS; additional data obtained under NIOSH Contract 210-79-0060.