Ag, Cd, Cr, Cu, Fe, Ni, Mn, Zn (metals and oxides) CAS: None RTECS: None

**METHOD: 7200, Issue 2** **EVALUATION: FULL** **Issue 1: 15 February 1984**
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**OSHA :** 5 mg/m$^3$
**NIOSH:** lowest feasible (suspect carcinogen)
**ACGIH:** 5 mg/m$^3$

**PROPERTIES:** solid, stable, non-volatile particles; very small diameter

**SYNONYMS:** none.

| SAMPLING | | MEASUREMENT | |
|---|---|---|---|
| **SAMPLER:** | FILTER (0.8-µm cellulose ester membrane) | **TECHNIQUE:** | X-RAY FLUORESCENCE |
| **FLOW RATE:** | 1 L/min | **ANALYTE:** | Ag, Cd, Cr, Cu, Fe, Ni, Mn, Zn |
| **VOL-MIN:** | 10 L | **INTENSITY RATIO:** | analyte to Co; or analyte to external standard containing analyte. |
| **-MAX:** | 400 L | | |
| **SHIPMENT:** | routine | **CALIBRATION:** | Cobalt-impregnated internal standard; laboratory-made fume standards, calibrated by atomic absorption spectrophotometry; optional external ratio standard |
| **SAMPLE STABILITY:** | stable at least 1 year @ 25 °C | **RANGE:** | 0.02 to 1 mg of each metal per sample [1,2] |
| **BLANKS:** | 2 to 10 field blanks per set | **ESTIMATED LOD:** | 2 µg of each metal per sample [1,2] |
| **ACCURACY** | | **PRECISION ($\bar{S}_r$):** | see EVALUATION OF METHOD |
| **RANGE STUDIED:** | see EVALUATION OF METHOD | | |
| **BIAS:** | see EVALUATION OF METHOD | | |
| **OVERALL PRECISION ($\hat{S}_{rT}$):** | see EVALUATION OF METHOD | | |
| **ACCURACY:** | see EVALUATION OF METHOD | | |

**APPLICABILITY:** The working range is 0.2 to 10 mg/m$^3$ for a 100-L air sample. The elemental composition of metal fumes from welding and brazing operations depends on the nature of the base metal, flux, and welding material used. Mild steel welding fume typically contains iron and manganese; stainless steel welding fumes may contain iron, nickel, chromium, and manganese; and brazing fumes usually contain cadmium, zinc, and copper [1].

**INTERFERENCES:** Interferences are easily controlled with wavelength-dispersive X-ray fluorescence, but are more severe with energy-dispersive systems. Also, the presence of cobalt in the fumes will require the use of a different ratio standard element.

**OTHER METHODS:** The method is based on P&CAM 345 [2]. Other methods applicable to welding fumes are 7300 (Elements), 70XX (atomic absorption methods for individual metals), and 7600 (Chromium, hexavalent).

**REAGENTS:**

1. Elemental standards, powdered, containing only elements of interest (Spex Industries); or sample of welding fume.
2. Isopropanol.
3. Deionized water.
4. Internal ratio standard. Ion exchange filter paper (e.g., Gelman Acropor SA-6404), and cobalt standard solution (1000 µg/mL).
5. External ratio standard. Organo-metallic compounds for the various analyte elements, e.g., Cr 2,4-pentanedionate; Mn(II) cyclohexanebutyrate; Bis[dicarbonyl (MeCyclopentane-dienyl)Iron]; Co(II)cyclohexane-butyrate; Bistriphenylphosphine $Ni(CO)_6$.
6. Polyester resin monomer, with hardener.

**EQUIPMENT:**

1. Sampler: filter unit consisting of a 37-mm cellulose ester membrane filter, 0.8-µm pore size, in a three-piece cassette filter holder.
2. Personal sampling pump, 1 L/min, with flexible connecting tubing.
3. X-ray fluorescence spectrometer, energy- or wavelength-dispersive.
4. Buchner funnel, filtering apparatus with 0.45 µm cellulose ester membrane filter, and vacuum source.
5. Freezer mill.
6. Ultrasonic bath.
7. Magnetic stirrer with stir bars.
8. Glassware*: 1-L volumetric flask, 50-mL and 100-mL beakers, various pipets, 0.1- to 5-mL.
9. For initial calibration of standards, Inductively coupled argon plasma-atomic emission spectrophotometer (ICP-AES) or Atomic absorption spectrophotometer (AAS) with deuterium background correction capability, and electrodeless discharge lamp or hollow cathode lamp for each element.

* Soak in 50% (v/v) nitric acid and rinse thoroughly with deionized water before use.

**SPECIAL PRECAUTIONS:** none.

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Secure the end of a length of PVC tubing to the inside of the welder's helmet and attach the other end to the inlet of the sampler.
3. Sample at 1 L/min for a total sample size of 10 to 400 L. Visually inspect the samples and terminate sampling in time to avoid heavy deposition on the filter.
   NOTE: Heavy deposits (>2 mg) will not adhere to the filter and may be lost. In addition, heavy deposition may necessitate a non-linear calibration graph because of XRF shadowing.

**SAMPLE PREPARATION:**

4. Transfer the sample filters to XRF sample holders with tweezers, using care not to disturb the deposit.
   NOTE: Place the sample filter on top of a cobalt ratio standard filter (step 7.a) if the internal ratio method is to be used.

**CALIBRATION AND QUALITY CONTROL:**

5. Obtain a qualitative scan of one of the filters to establish which elements are present in the samples. Set the XRF spectrometer parameters for the elements detected plus cobalt, according to the manufacturer's specifications.
6. Determine line overlap correction factors.
   Example: Cr Kβ emission interferes with the Mn K α analyte line. From the spectrum of pure Cr, a factor, F, is found which relates the intensity of the Cr Kß line (measured at the Mn Kα wavelength), to the intensity of the Cr K α line:

$$F = \frac{\text{Cr K}\beta \text{ (at Mn K}\alpha \text{ wavelength)}}{\text{Cr K}\alpha \text{ (at Cr K}\alpha \text{ wavelength)}}$$

   For the determination of the Mn K α emission intensity, measure Cr at Cr K α. Subtract the product of [Cr Kα emission] x F from the intensity measured at Mn K α. The result is a measure of the Mn Kα intensity without the contribution from the line overlap interference of Cr.
7. Prepare a set of at least six standard filters, in quadruplicate, covering the range 0.02 to 1 mg per filter for the elements of interest.
   a. Add approximately 0.2 g powdered elemental standard to 1 L isopropanol. Mix ultrasonically for 30 min. Add a PTFE-coated stirring bar and stir continuously during use.
   b. Place a 0.45-µm cellulose ester membrane filter in the Buchner filtration apparatus. Add 50 mL isopropanol.
   c. Turn off the stirrer, shake the standard suspension vigorously three times and immediately withdraw an aliquot with a pipet (0.1 to 5 mL). Add the contents of the pipet to the isopropanol above the filter. Stir the liquid carefully with the pipet tip. Rinse the inside and outside of the pipet with a few mL isopropanol. Turn on the stirrer.
   d. Apply vacuum slowly to draw the suspension through the filter.
   e. Remove the filter. Let it air dry.
   f. Wet-ash two standard filters at each deposition level, including blank. Analyze the ashed filters (e.g., by atomic absorption spectrophotometry (AAS) or ICP AES - Method 7300). Retain the two remaining standard filters at each deposition level for analysis by XRF.
8. Prepare one of the following ratio standards:
   a. Internal ratio standard. Place the ion-exchange paper on the Buchner filtration assembly. Pour approximately 50 mL deionized water onto the filter, apply a slight vacuum, and collect the water in a second 100-mL beaker. Add 200 µL of 1000 µg/mL cobalt standard solution to the collected water, pour into the Buchner filter device, and draw the liquid again through the filter with a slight vacuum. Collect the liquid with the first beaker and repeat, passing the liquid through the filter seven times. When completed, remove the filter to dry. Prepare identical cobalt-impregnated filters for every position in the sample changer of the spectrometer.
      NOTE 1: Prior to use, analyze the cobalt-impregnated filters for cobalt by XRF to determine their similarity. They should give the same XRF analyte-line intensity for cobalt within normal statistical variation (i.e., the analyte-line intensity of any filter should differ from any other by an amount equal to the square root of the intensity in counts/sec).
      NOTE 2: Alternate method. Thoroughly mix about 0.2 g organocobalt compound, accurately weighed, with about 30 mL of polyester resin monomer. Mix in a few drops of hardener and pour equal amounts into clean 50-mL beakers. Prepare identical standards for each position in the XRF sample carrousel. When resin is completely hardened, break away glass. Mill the resin blocks to fit the XRF sampler holder and to present a flat surface to the X-rays.
   b. External ratio standard. Thoroughly mix about 0.2 g of organometallic compounds of interest into about 10 mL of polyester resin monomer. Mix in a few drops of hardener and allow to harden. Break away the glass. Mill to fit the XRF standard holder and to present a flat surface to the X-ray beam.

**MEASUREMENT:**

9. Load the sample, standard filters, and blank filters into the XRF instrument.
10. Obtain intensities of analyte elements and internal ratio standard or external ratio standard for each filter.

**CALCULATIONS:**

11. Divide analyte element line intensity on samples, standard filters, and blank filters by the internal ratio standard intensity of Co or by the external ratio standard intensity of the analyte element to calculate intensity ratio, R.
12. Prepare a calibration graph (mass of element, µg, on the standard filters vs. R (corrected for blank)).
13. Calculate the concentration, C (mg/m $^3$), of analyte element in the air volume sampled, V (L):

$$C = \frac{K\,(I - B - X)}{V}$$

where: K = slope in µg/(R) of the standard calibration graph
I = XRF ratio intensity of the analyte line
B = corrections for XRF analyte-line background intensity and line overlap, if needed (ratio intensity)
X = XRF ratio intensity of the filter blank.

**EVALUATION OF METHOD:**

The method was developed using welding (shielded metal arc welding on stainless and mild steels) and brazing (StaFlo-45 brazing wire on copper) fume samples having loadings of 30-280 µg filter (as oxides). The method was validated for iron, nickel, chromium, and manganese [1,2,3], using the internal standard method. Copper, zinc, and cadmium were also evaluated but not validated. A 120-L sample will provide sufficient deposition to detect the above-mentioned elements at air concentrations of one-half the current PEL for the compounds.

| Element | Range[1] (mg/m$^3$) | Detection Limit[2] (µg) | ($S_r$) | Mean Bias[3] (%) | Accuracy (%) | PEL [5] (mg/m$^3$) | Sensitivity[4] (relative intensity/mµg) |
|---|---|---|---|---|---|---|---|
| Iron | 0.05-0.50 | 1.5 | 0.07 | 5.9 | ± 19.6 | 10 | 178.1 |
| Manganese | 0.04-0.29 | 2.7 | 0.067 | 4.6 | ± 17.7 | 1 | 168.1 |
| Chromium | 0.04-0.42 | 1.8 | 0.068 | 12.3 | ± 25.6 | 0.5[5] | 21.1 |
| Nickel | 0.02-0.14 | 1.5 | 0.071 | 6.8 | ± 20.7 | 1 | 47.2 |
| Copper[6] | 0.01-0.03 | - | 0.12 | - | - | 0.1 | - |
| Zinc | 0.05-0.06 | - | 0.043 | - | - | 5 | - |
| Cadmium | 0.3-5.0 | - | 0.063 | - | - | 0.1[7] | - |

[1]Based on a 120-L sample. Upper limit defined by highest validation sample; may be extended to approximately 2 mg/m $^3$ within the linear calibration curve.
[2]DL = 3A($I^{1/2}$)/120 L where I is the filter blank intensity, and A is the slope of the calibration graph [(AI) = concentration in µg], as defined in [4].
[3]Mean of (100 x [AAS - XFR]/AAS), where AAS is the amount of metal determined by atomic absorption spectroscopy, from the four deposition levels.
[4]Defined as [analyte line intensity/cobalt line intensity]/[AAS result, µg/filter].
[5]Chromium (VI) compounds have a PEL of C 0.1 [5].
[6]PTFE filter holder required.
[7]In process of 6(b) rulemaking.

**REFERENCES:**

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[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 345, U. S. Dept. of Health and Human Services Publ. (NIOSH) 82-100 (1982).
[3] Carsey, T. Standardization Techniques in X-ray Fluorescence, U.S. Department of Health and Human Services, (NIOSH) Internal Report (1981).
[4] Bertin, E. P. Principles and Practice of X-ray Spectrometric Analysis, 2nd ed., Plenum, NY (1975).
[5] Air Contaminants - Permissible Exposure Limits. (Title 2.9 Code of Federal Regulations Part 1910.1000). U.S. Department of Labor, Occupational Safety and Health Administration (1989).

**METHOD WRITTEN BY:**

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