ZINC OXIDE

7502

ZnO   MW: 81.38   CAS: 1314-13-2   RTECS: ZH4810000

METHOD: 7502, Issue 2	**EVALUATION: FULL**	**Issue 1: 15 February 1984**
		Issue 2: 15 August 1994

OSHA : 5 mg/m^3 (fume); 15 mg/m^3 (dust)
NIOSH: 5 mg/m^3; C 15 mg/m^3/15 min (dust);
      5 mg/m^3; STEL 10 mg/m^3 (fume)
ACGIH: 5 mg/m^3; STEL 10 mg/m^3 (fume)
      10 mg/m^3 (dust)

PROPERTIES: solid; d 5.61 g/cm^3 @ 25 °C; MP 1975 °C

SYNONYMS: China white; zinc white; zincite.

SAMPLING	MEASUREMENT
SAMPLER: FILTER (0.8-µm PVC membrane, 25-mm diameter, in open-face cassette)	**TECHNIQUE:** X-RAY POWDER DIFFRACTION
FLOW RATE: 1 to 3 L/min	**ANALYTE:** crystalline zinc oxide; direct analysis on filter
VOL-MIN: 10 L **-MAX:** 400 L	**XRD:** Cu target X-ray tube. Optimize for intensity; 1° slit, Graphite monochromator; scintillation detector. Slow step scan, 0.02°/10 sec, Integrated intensity with background subtraction
SHIPMENT: routine	
SAMPLE STABILITY: stable	**CALIBRATION:** suspensions of ZnO in 2-propanol
BLANKS: 2 to 10 field blanks per set	**RANGE:** 50 to 2000 µg per sample
	ESTIMATED LOD: 5 µg per sample
BULK SAMPLE: high-volume air sample required	**PRECISION ($\bar{S}_r$):** 0.15 @ 1 mg/m^3; 0.05 for greater than 2 mg/m^3

ACCURACY	
RANGE STUDIED:	0.1 to 11 mg/m^3 [1,2] (180-L samples)
BIAS:	2.7% [2,3,4]
OVERALL PRECISION ($\hat{S}_{rT}$): 0.09 [2]	
ACCURACY:	± 21.6%

APPLICABILITY: The working range is 0.25 to 10 mg/m^3 for a 200-L air sample. The method does not distinguish zinc oxide fume from zinc oxide dust.

INTERFERENCES: Major interferences include Fe$_2$O$_3$, Zn, Zn(NH$_3$)$_2$Cl$_2$, (NH$_4$)$_3$ZnCl$_5$, (NH$_4$)$_2$ZnCl$_4$ and (NH$_4$)$_2$Zn(SO$_4$)$_2$·6H$_2$O; these are resolved by using alternate analyte peaks. Particle size affects intensity measurements.

OTHER METHODS: This method combines and replaces Methods P&CAM 222 [1] and S316 [5]. The criteria document contains an elemental analysis for zinc [6].

REAGENTS:

1. Zinc oxide, ACS reagent grade. Average particle size between 0.5 µm and 10 µm.
2. 2-Propanol.
3. Desiccant.
4. Glue or tape for securing filters to XRD holders.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) or PVC-acrylonitrile membrane filters, 25-mm diameter, 0.8-µm pore size; three-piece filter cassette.
   NOTE: An extension cowl on the filter cassette is desirable to produce a more uniform deposit and to prevent contamination of the open-face filter during sampling.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High-volume sampling pump, 10 L/min.
4. X-ray powder diffractometer equipped with copper target X-ray tube and scintillation detector.
5. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
6. Filtration apparatus and side arm vacuum flask with 25-mm filter holders.
7. Analytical balance (0.01 mg); magnetic stirrer; ultrasonic bath or probe; volumetric pipettes and flasks; desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.

SPECIAL PRECAUTIONS: none.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample open-face at 1 to 3 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Take a high-volume (4000 L) air sample using a clean sampler and high-volume sampling pump in the same area as the personal sample(s) for qualitative identification.

SAMPLE PREPARATION:

4. Mount field samples and blanks on XRD sample holders using appropriate methods for securing the sample to the XRD holder.

CALIBRATION AND QUALITY CONTROL:

5. Prepare two suspensions of ZnO in 2-propanol by weighing 10 mg and 50 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer to a 1-L glass-stoppered bottle using 1 L 2-propanol.
6. Suspend the powder in 2-propanol by using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Cool the solution to room temperature before withdrawing aliquots.

7. Prepare a series of standard filters using the 10 and 50 mg/L suspensions. Using appropriate pipets, prepare a sufficient number of standards in triplicate to cover the analytical range (or sample range if known). Standards at 20, 30, 50 100, 200 and 500 µg are usually sufficient.

8. Mount a filter on the filtration apparatus. Place several mL 2-propanol on the filter surface. Turn off the stirrer and shake vigorously by hand. Within a few seconds of setting the bottle down, remove the lid and withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet. Transfer the aliquot from the pipet to the filter funnel, keeping the tip of the pipet near the surface of the liquid but not submerged.

9. Rinse the pipet with several mL of 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.

10. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place to avoid disturbing it. Transfer the filter to the XRD sample mount.

11. Perform step scans on the standards using the same diffraction peaks and instrumental conditions as for samples (step 16). The resulting intensities for standards, I_x^o, are normalized in the following procedure.

12. Determine the net count, I_r, of the reference specimen before or after each unknown, standard or blank is scanned. Use a diffraction peak of high intensity that can be measured rapidly but reproducibly (less than 1% S_r). Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak. This factor never changes and should be used for all measurements made on a particular diffractometer.

    Calculate and record the normalized intensity, $\hat{I}_x^o$, for the analyte or silver peaks on each sample, field blank, media blank and standard:

$$\hat{I}_x^o = \frac{I_x^o}{I_r} \cdot N.$$

    NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently. In this case, the net intensities of the analyte, I_x, should be normalized to the most recently measured reference intensity.

13. Prepare a calibration graph ($\hat{I}_x^o$ vs. µg analyte).
    NOTE: Poor reproducibility at any given level indicates problems in the sample preparation technique and new standards should be made. The data should lie along a straight line. A weighted least squares (1/σ^2 weighting) is preferable. Curvature can be eliminated with absorption corrections based on the mass absorption coefficient of the analyte [7,8,9].

14. Determine the initial slope, m, of the linear portion of the calibration graph in counts/µg. The intercept, b, of the line with the $\hat{I}_x^o$ axis should be approximately zero.
    NOTE: A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.

MEASUREMENT:

15. Obtain a qualitative X-ray diffraction scan (broad 2-theta range) of the high-volume respirable sample to determine the presence of ZnO and any matrix interference. The expected diffraction peaks are as follows:

ZnO Peak (2-Theta Degrees)		
Primary	Secondary	Tertiary
36.26	31.75	34.44

16.   Analyze the sample filters by step-scanning the most intense interference-free diffraction peak of zinc oxide and determine the integrated intensity. Measure the background on each side of the peak for one half the time used for peak scanning and add the counts from each side for a total (average) background. Determine the 2-theta position of the background for each sample. The net count or intensity, I_x, is the difference between the peak integrated count and the total background count. The net intensity is normalized as in step 12 to obtain $\hat{I}_x$.

17.   Scan each field blank over the same 2-theta range used for the analyte. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent.

CALCULATIONS:

18.   The concentration of ZnO in the air sample is:

$$C = \frac{(\hat{I}_x - b)}{m \cdot V}, \text{ mg/m}^3.$$

where: $\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration curve (I_x^o vs. W)
m = initial slope of calibration graph (counts/µg)
V = air volume sampled (L).

In heavily-loaded samples, particularly those rich in heavy elements, X-ray absorption may cause reduced intensities and underestimation of ZnO. If this is suspected, an absorption correction can be made [8]. The collection filters and blanks are mounted on a smooth metal plate (substrate) for XRD quantitation. The substrate should have a non-interfering diffraction peak which is measured at the same time as the ZnO peak. By measuring the substrate peak on both samples and blanks, an absorption correction like that in the silica method (Method 7500) can be made. The absorption correction factor must be calculated for each sample from the formula in Method 7500 which takes into account the diffraction angles for the particular substrate chosen. Altree-Williams used a silver filter under the collection filter [7].

EVALUATION OF METHOD:

In a comparison of this method with atomic absorption spectrophotometry [3,4], zinc was determined on 15 Gelman DM-800 filters containing added zinc oxide in the range 250 to 1000 µg. The average percent difference for the 15 pairs was 2.7%. Method S316 was validated with generated samples in the range of 2.4 to 9.9 mg/m^3 [2,5,10]. A pooled $\hat{S}_{rT}$ of 0.088 was found for 18 samples of 180 L collected from the aerosol.

REFERENCES:

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