

ZINC OXIDE IN WORKPLACE ATMOSPHERES

Method Number: ID-143

Matrix: Air

OSHA Permissible Exposure Limits

Zinc Oxide Fume (Final Rule Limit): 5 mg/m³ Time Weighted Average (TWA)
10 mg/m³ Short-Term Exposure Limit (STEL)

Zinc Oxide Dust (Final Rule Limit)

Respirable Fraction: 5 mg/m³ TWA
Total Dust: 10 mg/m³ TWA

Zinc Oxide Fume (Transitional Limit): 5 mg/m³ TWA

Zinc Oxide Dust (Transitional Limit)

Respirable Fraction: 5 mg/m³ TWA
Total Dust: 15 mg/m³ TWA

Collection Device: A tared, 5- μ m, 37-mm polyvinyl chloride filter is used with a personal sampling pump

Recommended Sampling Rate: 2 L/min

Recommended Air Volume: 30 L (STEL), 960 L (TWA)

Analytical Procedure: A suspension of the sample particulate in tetrahydrofuran (THF) is created by dissolving the sample filter in THF and then sonicating. The sample particulate is then deposited onto a silver membrane filter and analyzed by X-ray diffraction.

Detection Limits

Qualitative: 30 μ g zinc oxide

Quantitative: 50 μ g zinc oxide

Precision and Accuracy

Validation Range: 2.5 to 10 mg/m³ (200-L air sample)

CV₁ 0.05

Method Classification: Validated Method

Date (Date Revised): 1985 (March, 1989)

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Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

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1. Introduction

This method describes the collection of airborne zinc oxide (ZnO) in the breathing zone of personnel and the subsequent analysis by X-ray diffraction (XRD).

1.1. History

1.1.1. There have been several methods used to analyze for ZnO. These include atomic absorption (AA), colorimetry, gravimetry, titrimetry, and XRD. The XRD determination of three or more lines is considered the preferred method, because ZnO can be distinguished from other compounds of zinc (Zn) or metallic Zn. Also, the diffraction method is less tedious than most alternative methods.

1.1.2. The previous analytical method (8.1.) used by the OSHA Salt Lake City Technical Center (OSHA-SLTC) was an AA method. Zinc oxide was collected on a cellulose membrane filter, digested, and analyzed according to reference 8.1. The AA method was not specific for ZnO since only Zn is analyzed.

1.2. Principle

A sample is collected by drawing air at approximately 2 L/min through a pre-weighed polyvinyl chloride (PVC) filter. The filter is post-weighed before submission to the lab for analysis. At the laboratory, the filter is dissolved in tetrahydrofuran (THF), the sample particulate is suspended in the THF, and then deposited on a silver membrane. The membrane is analyzed by XRD. The X-ray technique is based on the Bragg equation:

$$n\lambda = 2d \sin \theta$$

Where:

- n = order of diffracted beam
- λ = wavelength of X-ray beam
- d = distance between diffracting planes (in angstroms)
- θ = angle between incident X-rays and the diffracting planes (in degrees)

Note: Most X-ray spectrometers are designed to scan using degrees 2θ

1.3. Advantages and Disadvantages

1.3.1. This method is specific for ZnO; XRD can distinguish

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crystal structure based on the Bragg equation. The method does not distinguish between dust or fume forms of ZnO.

- 1.3.2. Zinc oxide can be identified and quantified on three or more different angles of diffraction.
- 1.3.3. Interferences can be minimized by using alternate angles of diffraction, computer-assisted methods of integration, or wide angle scans and subsequent line matching with diffraction pattern libraries.
- 1.3.4. This method is accurate and offers better sensitivity compared to previous methods of analysis.
- 1.3.5. Sample preparation is simple and analysis can be computer-controlled and automated. Also, sample preparation and analysis involves a non-destructive technique. Samples can be reanalyzed at a later date.
- 1.3.6. A disadvantage is the high cost of instrumentation, especially if equipped with computer hardware.
- 1.3.7. Another disadvantage is the sophisticated maintenance required for the instrumentation.

1.4. Physical and Chemical Properties of ZnO (8.2.)

CAS No.:	1314-13-2
Chemical Symbol:	ZnO
Synonyms:	china white, zinc white, zincite
Formula Weight:	81.37
Crystalline Form:	hexagonal
Specific Gravity:	5.606
Melting Point:	1975 °C
Solubility*:	0.00016 g/100 mL water at 29 °C; soluble in mineral acids, dilute acetic acid and ammonium chloride
Color:	white

*Tests conducted at the OSHA lab indicated the solubility of ZnO in suspending media such as 2-propanol or THF was insignificant. Zinc oxide is slightly soluble in water.

1.5. Uses

Occupations with potential exposures to Zn and Zn compounds are listed (8.3.):

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Alloy and electric fuse makers
Printing plate makers
Roofing makers
Metal cutters
Shipyards workers
Arc welders
Electric metallizers, galvanizers and electroplaters
Zinc, brass and bronze foundry workers
Metal sprayers
Braziers
Paint manufacturers
Smelters
Junk metal refiners

2. Analytical Working Range

2.1. Qualitative detection limits when using typical instrumental conditions are:

<u>Diffraction Peak</u>	<u>Peak ° 2θ</u>	<u>Integration Time (sec)</u>	<u>Detection Limit (µg)</u>
Primary (1')	36.30	1	30
Tertiary (3')	34.46	1	30
Quaternary (4')	56.62	1	30
Quinternary (5')	62.88	1	30

Note: 2θ peaks are more informative than absolute. Peak values may vary slightly.

2.2. The quantitative detection limit for the analytical method was 50 µg. The determination was performed using the primary or most sensitive ZnO diffraction line.

2.3. The range for samples containing mixtures and impurities is dependent upon the amount of interfering substances and X-ray absorbing substances present. A total sample weight in the range of 0.1 to 3 mg is recommended. Samples with weights in excess of 3 mg can be analyzed by deposition onto multiple silver membranes.

3. Method Performance

3.1. The overall coefficient of variation (CV) for ZnO fume was reported to be 0.088 (8.4%).

3.2. The analytical method was tested at the OSHA lab in the range of 2.5 to 10 mg/m³. The CV for the analytical method was 0.05. This value was determined from known samples in the range of 500 to

2,000 µg (N=18) for the primary ZnO diffraction line. The mean recovery was 99.98% (8.5.).

4. Interferences

According to data listed in a computer search of the Joint Committee on Powder Diffraction Studies (JCPDS) powder diffraction file (8.9.), several compounds have diffraction peaks that can potentially interfere with ZnO. Many of these compounds are listed in Appendix A.

- 4.1. The secondary ZnO line is normally not scanned. The possibility of silver chloride formation on the surface of silver membranes used in sample analyses has limited the use of this line. Silver chloride has a diffraction peak in close proximity to the secondary ZnO line.
- 4.2. Some elements (iron, in particular) can cause appreciable X-ray fluorescence which will result in high background intensity. This situation can be circumvented by using a diffracted beam monochromator.
- 4.3. If a severe interference is present on the primary ZnO line, analytical results are reported using another diffraction line.
- 4.4. The presence of interference can be verified and usually identified by XRD analysis. Interfering peaks are usually resolved at the OSHA-SLTC using custom in-house software (8.7.). Similar software developed by the instrument manufacturers or in-house can also be used.
- 4.5. Wide-angle scans are also performed to help identify interferences or assist in identification of ZnO. These scans are usually performed with line profile libraries where the diffraction lines of the sample are compared to lines of known compounds contained in the libraries.

5. Sampling

5.1. Sampling Equipment

5.1.1. Sample assembly:

Filter holder consisting of a two- or three-piece cassette, 37-mm diameter.

Backup pad, 37-mm, cellulose.

Low ash PVC membrane filter, 37-mm, 5-µm pore size [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA

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or cat. no. P-503700, Omega Specialty Instrument Co.,
Chelmsford, MA].

Note: During preparation for analysis, the sample is dissolved in tetrahydrofuran (THF). Certain acrylic copolymers added to PVC filters are insoluble in THF. If the membrane filter composition is unknown, a laboratory test should be conducted with THF to determine suitability before use.

- 5.1.2. For respirable samples only, a cyclone is also used. Cyclone: Nylon, 10-mm (BDX-99R, part no. 7010048-1, Sensidyne Inc., Largo, FL, or part no. 456243, MSA, Pittsburgh, PA).
- 5.1.3. Pump calibration system: Stop watch and bubble tube or electronic meter.
- 5.1.4. Sampling pump: For fume or nonrespirable dust samples, calibrate the personal sampling pump to approximately 2 L/min. Each pump must be calibrated with a representative sampler in-line to minimize errors associated with uncertainties in the volume sampled. For respirable samples, calibrate the pump with a cyclone in-line and use a flow rate of approximately 1.7 L/min.
- 5.1.5. Assorted flexible tubing.
- 5.1.6. Analytical balance (0.01 mg).
- 5.2. Sampling Procedure
 - 5.2.1. Desiccate and then weigh the PVC filter before sampling.
 - 5.2.2. Place the pre-weighed PVC filter and a cellulose backup pad in a two- or three-piece cassette.
 - 5.2.3. Attach the cassette to a calibrated personal sampling pump using flexible tubing. For respirable samples, attach a cyclone to the cassette.
 - 5.2.4. Place the sampling assembly in the breathing zone of the worker or sampling area and place the pump in an appropriate position. For fume or nonrespirable dust samples, take up to 960 L of air through the filter cassette at approximately 2 L/min. For respirable

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samples, take up to 816 L at approximately 1.7 L/min. Do not allow the cyclone to be inverted during or after sampling.

- 5.2.5. Check the pump and sampling assembly periodically to verify performance and to assure that the filter is not overloaded. If the filter becomes overloaded during the sampling interval, replace it with another filter.
- 5.2.6. Terminate sampling at the predetermined time and record the pump flow rate and collection time. Remove the filter, being careful not to lose any particulate. Desiccate and then weigh the filter. Replace the filter, and then firmly seal the cassette with plastic plugs in both the inlet and outlet ports. Calculate the net weight gain and the weight/air volume ratio of the filter. If this ratio is less than the Permissible Exposure Limit, do not submit the sample for ZnO analysis. Respirable dust samples are also not submitted to the lab; these samples are gravimetrically compared to the PEL of 5 mg/m³ for respirable particulates.
- 5.2.7. Record on the OSHA 91 form all pertinent sample data and any potential interferences. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the samples.
- 5.2.8. With each batch of up to 20 samples, submit an appropriate blank filter for analysis.
- 5.2.9. Seal the filter cassette and identify it with an OSHA Form 21. Mail samples to the laboratory in a suitable container designed to prevent damage.

~~5.3. Bulk samples~~

In order of laboratory preference, bulk samples may be one of the following:

- 1) a high-volume filter sample
- 2) a representative settled dust (rafter) sample
- 3) a sample of the bulk material in the workplace which is considered to be ZnO.

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The type of bulk sample should be stated on the OSHA 91 and cross-referenced to the appropriate air sample(s).

6. Analysis

6.1. Safety Precautions

- 6.1.1. Tetrahydrofuran (THF) has a low flash point, $-14\text{ }^{\circ}\text{C}$ ($6\text{ }^{\circ}\text{F}$), and is extremely flammable. Always use THF in a hood. THF is an ether which can form explosive peroxides upon exposure to air; therefore, it should be stored in closed containers. Always use latex gloves, a labcoat, and safety glasses when handling THF.
- 6.1.2. Parlodion and isopentyl acetate are flammable.
- 6.1.3. Always use a hood when working with dry ZnO.
- 6.1.4. Most X-ray diffractometers have built-in devices to prevent X-ray exposure. These devices should not be adjusted, removed, or overridden by unauthorized personnel for any reason.
- 6.1.5. A bench top warning light (yellow) is recommended. When lit, the warning light indicates the X-ray generator is powered up.
- 6.1.6. Most X-ray spectrometers have shutter devices which allow or prevent X-rays from entering the sample chamber. These devices should not be adjusted, removed, or overridden by unauthorized personnel for any reason. Instrument operators should familiarize themselves with correct operation of the shutters. Sample chamber access should only be allowable when X-rays from the source are completely blocked. These shutters should be routinely checked for proper operation.
- 6.1.7. An additional Geiger type alarm monitor to measure the general work area is recommended. The monitor can be interfaced to the X-ray generator to provide an additional safety interlock.
- 6.1.8. Avoid inserting fingers into the sample compartment. Use forceps to change samples.
- 6.1.9. Radiation monitors are worn by all X-ray operators. These monitors consist of film badges and finger rings which are

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periodically analyzed to detect exposure to low-level radiation.

6.2. Analytical Equipment

- 6.2.1. X-ray diffractometer system consisting of:
Automated Powder Diffractometer (APD).
X-ray Generator.
Long, fine-focus copper target X-ray tube.
Scintillation counter detector.
X-ray accessories include: pulse-height analyzer, graphite monochromator, 2θ compensating slit, 1° receiving slit, and sample spinner.
Recirculating cooling system for the X-ray tube.
- 6.2.2. Computer system consisting of:
Hardware and software for data reduction and graphic presentations.
Interface: Between the computer and the automated powder diffractometer an optical isolator and a mechanically operated switch have been used at OSHA-SLTC. Newer X-ray systems are usually equipped with computers already interfaced.
Line profile library (JCPDS-International Center for Diffraction Data Powder Diffraction File, JCPDS, Swarthmore, PA).
- 6.2.3. Standard and sample preparation:
Centrifuge tubes: Round bottom 40-mL (Pyrex 8260).
Drying oven.
Explosion-proof hot plate (Model HP-11515B, Sybron/Thermolyne, Dubuque, IA).
Filtration apparatus, 25 mm, (Filter Holder Hydrosol Manifold, cat. no. XX25 047 00, filtering clamps, cat. no. XX10 025 03, fritted glass bases with stoppers, cat. no. XX10 025 02, and glass funnels, cat. no. XX10 025 11, Millipore Corp., Bedford, MA).
Forceps.
Latex gloves (Cat. no. 8852, American Pharmaseal Lab., Glendale, CA).
Liquid nitrogen cold-trap system for suspending media collection (dewar, polypropylene vacuum flask, liquid nitrogen, etc.).
Micro-analytical balance (0.01 mg).
Plastic petri dishes (Product no. 7242, Gelman Sciences, Ann Arbor, MI).
Silver membrane filters: Diameter 25-mm, 0.45- μ m pore size (Cat. no. FM25-0.45, Osmonics, Inc., Minnetonka, MN).
Teflon sheet, 0.3 to 1 mm thick.
Vacuum system.
Volumetric pipettes, eyedropper, volumetric flasks and graduated cylinders.
Ultrasonic bath.

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- 6.2.4. Bulk sample preparation for membrane deposition:
 Freezer mill (Model no. 6700, Spex Industries, Edison, NJ).
 Mortar and pestle.
 Sieve or sonic sifter: Sieve, 325 mesh (or Model ATML3P Sonic Sifter with 325 mesh sieve, ATM Corporation, Milwaukee, WI).
- 6.3. Reagents - All chemicals should be reagent grade or better.
- 6.3.1. Tetrahydrofuran (THF).
- 6.3.2. Parlodion (Pyroxylin).
- 6.3.3. Isopentyl (Isoamyl) acetate.
- 6.3.4. Parlodion in isopentyl acetate, 1.5% (w/v): Dissolve 1.5 g of parlodion in isopentyl acetate and dilute to 100 mL with isopentyl acetate.
- 6.3.5. Zinc oxide standard, \leq 325 mesh.
- 6.3.6. 2-propanol.
- 6.4. Standard Preparation
- 6.4.1. Preparation of ZnO stock standards:
 Dry the ZnO standard for 2 h at 110 °C. This material is used for stock and working standards.
- 1) Prepare three suspensions of ZnO standard in 2-propanol by weighing 10, 50, and 500 mg of the ZnO to the nearest 0.01 mg. Quantitatively transfer each to a 1-L volumetric flask using 2-propanol, and bring each to half volume.
 - 2) Disperse the ZnO in the 2-propanol by using an ultrasonic bath for 10 min. Remove from the bath and allow to cool to room temperature for 15 min. Dilute each flask to the mark with 2-propanol.
- 6.4.2. Preparation of ZnO working standards:
- 1) Prepare a series of working standards on silver membranes from 10-, 50-, and 500- μ g/mL stock ZnO suspensions by pipetting appropriate aliquots using the procedure outlined in steps 3 through 5. Prepare three sets of the standards listed below. These will be used to construct the calibration curve.

Stock Standards (μ g/mL)	Aliquot (mL)	Working Standards (μ g)
500	2, 4, 6	1,000, 2,000, 3,000
50	2, 5, 10	100, 250, 500
10	3, 5	30, 50

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- 2) Assemble the filtering apparatus and liquid nitrogen cold trap. Connect the cold trap to the filtering apparatus to collect the waste suspending media (2-propanol or THF). The waste vapors should not enter the vacuum pump.
- 3) Center a silver membrane on a fritted-glass base of the filtering apparatus. Also center the glass chimney on top of the base and secure it with a clamp.
- 4) Add a stirring bar to the stock standard suspension and withdraw aliquots using the following technique:
 - 1a) Place the flask on a magnetic stirrer and turn the stirrer on until a uniform suspension is achieved.
 - 2a) Turn off the stirrer, remove and invert the flask, allowing the stirring bar to slide into the neck.
 - 3a) Shake the flask vigorously to ensure an even suspension.
 - 4a) Cautiously revert the flask and return it to the stirrer.
 - 5a) Turn on the stirrer and immediately withdraw an aliquot from the center of the stirred solution using an appropriate volumetric pipette (care should be taken not to withdraw solution above the volume mark of the pipette).
- 5) With the vacuum off, place 2 mL of 2-propanol in the chimney of the previously assembled vacuum filtering apparatus. Transfer the pipetted aliquot to the chimney. After the transfer, bring the total volume in the chimney to 20 mL with 2-propanol.
- 6) Apply vacuum to the filtering apparatus, drawing the 2-propanol through it. This should result in a thin, even layered deposition of ZnO onto the silver membrane. Do not rinse the chimney after the ZnO has been deposited on the membrane. Rinsing can disturb the thin layer deposition just created. Vacuum should be applied for sufficient time to dry the membrane.
- 7) Carefully disassemble the chimney and clamp. Remove the silver membrane from the fritted-glass base using forceps. Place 2 drops of 1.5% parlodion solution on a glass slide. Fix the standard to the membrane by placing the bottom side

of the membrane in the parlodion solution. By capillary action, the membrane draws the parlodion solution to the ZnO surface. Place a Teflon sheet on top of an explosion-proof hot plate which is set at the lowest setting. Then place the membrane on top of this heated Teflon sheet. When dry, place the fixed ZnO standard in a labeled Petri dish.

- 8) Inspect the deposition for uniformity; clumping indicates that insufficient sonication was used. The standard will have to be remade if a significant amount of clumping occurs.

6.5. Sample Preparation

6.5.1. When sample weights are greater than 3 mg, aliquots are taken to achieve depositions within the working range.

6.5.2. Examine the filter and backup pad to determine if any breakthrough to the backup pad has occurred. If there is significant breakthrough, the sample is either not analyzed or results are reported with a disclaimer (see Section 7.2.3. for reporting results).

6.5.3. Full-shift samples having calculated weight/volume ratios less than the PEL are normally not analyzed.

6.5.4. Filters:

Carefully transfer the air sample (PVC filter) from the cassette to a round-bottom 40-mL centrifuge tube. Add 10 mL THF to dissolve the filter and suspend the sample. Sonicate the sample suspension for 5 to 10 min. Quantitatively transfer the suspension with rinses of THF to a glass chimney of the vacuum filtering apparatus (described in Section 6.4.2., step 2). The total volume in the chimney should not exceed 20 mL. Apply a vacuum to achieve a thin, even deposition of sample on the membrane. Do not rinse the chimney after the vacuum has been applied. Remove the membrane and fix the deposition to the membrane in the same manner as for a standard (Section 6.4.2., step 7).

6.5.5. Bulks:

To prevent the possibility of contamination, a separate filtering apparatus should be used for bulk preparation.

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- 1) Bulk samples approximating respirable particle size:
Weigh an aliquot of 1 to 2 mg on a PVC filter, and place in a round bottom centrifuge tube.
- 2) Non-respirable bulks:
Grind the sample to a fine powder using either a mortar and pestle or a freezer mill. Then size the sample, using a 325-mesh sieve or sonic sifter. This results in a sample particle size of less than 45 μm . An aliquot of the sized sample is weighed on a PVC filter and placed in a round bottom centrifuge tube.

Add THF and deposit the weighed sample onto a silver membrane in the same fashion as an air sample. Care must be taken when transferring the membrane before fixing. Fix the sample as described in Section 6.4.2., step 7.

6.6. Analytical Procedure

Refer to the Standard Operating Procedure (8.8.) or instrument manuals for system startup and initialization procedures.

6.6.1. The X-ray generator is operated at 40 kV and 40 mA. Using forceps, transfer a standard from the Petri dish to a sample spindle or sample holder. If using a sample spindle, secure the standard to the spindle using Vaseline or a retaining ring. Place the spindle or holder into the sample chamber. Turn on the sample spinner.

6.6.2. Enter the following information into the controlling unit:

1. 2θ limits for each analytical line
2. 2θ scanning increment ($0.02^\circ 2\theta$)
3. Integration and background counting times (1 s)
4. Calibration using the secondary silver line ($44.33^\circ 2\theta$)
5. Present 2θ location of the X-ray instrument

Normal analytical parameters are:

<----- 2θ Values ----->			
<u>Zinc Oxide</u>	<u>Scanning Range</u>	<u>Peak Location</u>	<u>Peak Range</u>
1'	35.50 to 36.80	36.30	36.25 to 36.35
3'	33.80 to 35.10	34.46	34.41 to 34.51
4'	55.90 to 57.20	56.62	56.57 to 56.67
5'	62.10 to 63.40	62.88	62.83 to 62.93

Note: The peak locations listed are more informational than absolute. The actual peak is dependent on instrument and sample conditions and may vary slightly.

- 6.6.3. Confirm the presence of ZnO by analyzing at least three of the lines listed above. The secondary ZnO line is not listed because the primary diffraction line for silver chloride is in the general proximity and could cause a positive interference.
- 6.6.4. A custom analytical computer program is used by OSHA-SLTC to analyze samples by XRD. Directions for use and documentation of this system can be found in the X-ray documentation manual (8.7.) and in Appendix B. Other programs can be designed or obtained from X-ray system manufacturers.
- 6.6.5. Instrument considerations:
- 1) Perform a silver line angle calibration ($44.33^\circ 2\theta$) before each standard or sample is analyzed.
 - 2) Scan the standard or sample over the selected 2θ range in 0.02-degree increments (1 s each).
 - 3) A standard is analyzed after every fourth or fifth sample to assure correct instrumental operation.

For each sample or standard, the peak location of the secondary silver diffraction calibration line is used as an initial reference point. If the silver line intensity of a sample is much less than a standard, self-absorption of X-rays has occurred. This is most likely due to the sample matrix and can be remedied by:

- 1) Releasing the sample from the silver membrane
- 2) Dividing the sample into aliquots
- 3) Depositing each aliquot onto a membrane

7. Calculations

Prepare a linear regression concentration-response curve by plotting the concentration of the standards in μg versus counts. Blank correct the samples and then calculate the exposure as:

$$\text{mg/m}^3 \text{ ZnO} = \frac{\mu\text{g found}}{\text{Air Vol (L)}}$$

Note: If aliquots of a sample were taken and analyzed, calculations are adjusted according to the size and number of aliquots. Results from each aliquot are combined if the sample was split into a series of aliquots. If only one aliquot was taken, the result (Analyte mg/m³) is multiplied by:

$$\frac{\text{total suspension volume}}{\text{aliquot volume taken}}$$

7.1. Zinc oxide PEL

The PELs for ZnO (8.9.) are listed on the cover page of this document.

7.2. Reporting Results

7.2.1. Air sample results are reported to the industrial hygienist as mg/m³ ZnO. When peak limits are within acceptable ranges and ZnO amounts are in agreement on at least two, preferably three lines, the reported ZnO value is taken from the most sensitive, interference-free (or interference resolved) line. If interferences are present, the analyst should use available reintegration programs to resolve the interferences or report results on a less sensitive line.

7.2.2. For bulk samples, the results are reported as approximate % ZnO.

7.2.3. Particulate present on the backup pad constitutes some sample loss. Occasionally this may be seen and can be due to a poor cassette seal on the filter, improper positioning of the filter, or poor quality control of the filter and/or cassette. A note indicating that some of the sampled material was found on the backup pad and the reported value may be lower than actual is relayed to the compliance officer.

8. References

- 8.1. **Occupational Safety and Health Administration Analytical Laboratory: OSHA Manual of Analytical Methods** (OSHA-SLCAL Method No. I-1). Salt Lake City, UT. 1977.
- 8.2. **Weast, R.C., ed.: Handbook of Chemistry and Physics**, 57th ed., Boca Raton, FL: Chemical Rubber Company Press, 1976, pp B176 - B177.
- 8.3. **National Institute for Occupational Safety and Health: Criteria for a Recommended Standard ... Occupational Exposure to Zinc Oxide** (DHEW/NIOSH Publ. No. 76-104), Cincinnati, OH, 1975, p 79.
- 8.4. **National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods**, 3rd ed. (Method 7502) edited by P.M. Eller (DHHS/NIOSH Pub. 84-100), Washington, D.C.: Government Printing Office, 1984.
- 8.5. **Occupational Safety and Health Administration Analytical Laboratory: OSHA Laboratory Quality Control Division Data** by R.G. Adler. Salt Lake City, UT. 1981 (unpublished).
- 8.6. **Joint Committee on Powder Diffraction Standards (JCPDS): Powder Diffraction File 1988**, Swarthmore, PA: International Center for Diffraction Data, 1988.
- 8.7. **Occupational Safety and Health Administration Analytical Laboratory: X-ray Documentation Manual** by E.V. Thomas and M.C. Rose. Salt Lake City, UT. 1983 (unpublished).
- 8.8. **Occupational Safety and Health Administration Analytical Laboratory: Standard Operating Procedure--X-Ray Diffraction**. Salt Lake City, UT. In progress (unpublished).
- 8.9. "Air Contaminants; Final Rule": Federal Register 54:12 (19 Jan. 1989). pp. 2521-2523.

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Appendix A

Potential Interferences (Also see note below)

<u>Interferent Name, Formula</u>	<u>Primary ZnO Line</u>	<u>PDF No.*</u>
Aluminum Chloride, AlCl_3		22-10, 1-1133
Ammonium Zinc Chloride, $(\text{NH}_4)_3\text{ZnCl}_5$		30-69
Ammonium Zinc Sulfate, $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		35-767
Calcium Aluminum Silicate, $\text{CaAl}_2\text{SiO}_6$		31-249
Chaoite, C		22-1069
Ferric Oxide, $\epsilon\text{-Fe}_2\text{O}_3$, Fe_2O_3		16-653, 25-1402
Ferrous Silicate, Fe_2SiO_4		12-284, 29-720, 34-178
Lead Carbonate, PbCO_3		5-417
Magnesium Silicate, Mg_2SiO_4		13-230, 34-189, 34-556
Manganese Oxide, MnO		4-326
Nickel Chloride, NiCl_2		22-765, 1-1134
Tridymite, SiO_2		14-260, 18-1170
Silver Chloride, AgCl		22-1326
Talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$		19-770
Titanium Dioxide, TiO_2		21-1236, 35-88, 29-1360, 21-1276, 23-1446
Zinc, Zn		4-831

Secondary ZnO Line**

<u>Interferent Name, Formula</u>	<u>PDF No.*</u>
Silver Chloride, AgCl	22-1326, 31-1238

Tertiary ZnO Line

<u>Interferent Name, Formula</u>	<u>PDF No.*</u>
Ammonium Zinc Chloride, $(\text{NH}_4)_2\text{ZnCl}_4$	2-155
Ammonium Zinc Chloride, $(\text{NH}_4)_3\text{ZnCl}_5$	30-69
Ferrous Silicate, FeSiO_4	34-178
Magnesium Silicate, Mg_2SiO_4	34-556
Manganese Oxide, MnO	7-730
Manganese Sulfide, MnS	6-518
Montmorillonite, 18A or 21A	12-219, 29-1499
Potassium Aluminum Silicate, KAlSiO_4	31-965, 33-989, 33-988, 11-313
Talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	19-770, 13-558, 29-1493
Tridymite, SiO_2	14-260

ZINC OXIDE IN WORKPLACE ATMOSPHERES

Appendix A (Cont.)

Potential Interferences (Also see note below)

<u>Quaternary ZnO Line</u>	
<u>Interferent Name, Formula</u>	<u>PDF No.*</u>
Ferric Oxide, $\gamma\text{-Fe}_2\text{O}_3$	24-81
Ferrous Silicate, Fe_2SiO_4	34-178
Magnesium Silicate, Mg_2SiO_4	34-189, 34-556
Manganese Oxide, MnO	4-326
Silicon Dioxide, SiO_2	34-717
Titanium Dioxide, TiO_2	29-1360, 21-1276

<u>Quinternary ZnO Line</u>	
<u>Interferent Name, Formula</u>	<u>PDF No.*</u>
Aluminum Chloride, AlCl_3	1-1133
Ferric Oxide, $\epsilon\text{-Fe}_2\text{O}_3$, Fe_2O_3 , $\gamma\text{-Fe}_2\text{O}_3$, Fe_2O_3	16-653, 33-664, 24-81, 25-1402
Magnesium Silicate, Mg_2SiO_4	34-189
Titanium Dioxide, TiO_2	21-1236

*PDF No. = JCPDS Powder Diffraction File Number

**Only the most significant interference is listed for the secondary ZnO line.

Note: The majority of the analytes listed above will most likely not be present when sampling industrial operations which produce ZnO exposures. This list is presented as line-matches found in literature and not as definitive interferences. Some of these interferences may occur only when a large amount of interferent is present or at a temperature other than normal laboratory conditions. A substance is listed as a potential interference if one or more sensitive lines of that substance has a peak within $\pm 0.65^\circ 2\theta$ of the ZnO line.

Appendix B

Graphics and Calculations - Custom OSHA-SLTC Program

A custom OSHA-SLTC program reads and stores diffraction count data and evaluates or presents output data in the following ways:

1. Uses a symmetric five-point digital filter (weights = 0.6, 0.8, 1.0, 0.8, 0.6) to smooth the spectral count data.
2. Identifies peaks by maximum counts.
3. Determines upper and lower 2θ integration limits.
4. Chooses the integration method (either valley-to-valley or perpendicular drop) by observation of background and signal counts.
5. Integrates the peak by summing counts over the selected integration range.
6. Calculates the concentration of analyte in total μg and mg/m^3 .
7. Generates a hard copy report. An example of a report used at OSHA-SLTC is shown in Figure 1.

This program also allows the analyst to modify the computer selection of integration limits and method for each diffraction peak. A graphic representation of the scan can be displayed and an example of a 500 μg ZnO standard is shown in Figure 1. Areas of integration are shaded and outlying areas are non-shaded. The abbreviation "NORM CNTS" contained within the Figure stands for normalized counts (total counts/counting time). Other in-house or commercially available software programs can be used to minimize interferences and clarify results.

ZINC OXIDE IN WORKPLACE ATMOSPHERES

Zinc Oxide Diffraction Pattern - 500 µg ZnO Standard

500ZNO

500ZNO

AIR VOL. = 1.00
SAMPLE WT. = 500.

L - STANDARD -
UG

NG CAL. 19484 COUNTS AT 44.28 DEG.

PRI	ZNO	TERT	ZNO	4TH	ZNO	5TH	ZNO
PEAK =	36.30	PEAK =	34.46	PEAK =	56.60	PEAK =	62.86
LOW LIMIT =	35.58	LOW LIMIT =	33.92	LOW LIMIT =	55.98	LOW LIMIT =	62.16
UP LIMIT =	36.76	UP LIMIT =	35.00	UP LIMIT =	57.16	UP LIMIT =	63.26
INT TIME =	2	INT TIME =	2	INT TIME =	2	INT TIME =	2
NORM CNTS =	74905	NORM CNTS =	31411	NORM CNTS =	24324	NORM CNTS =	18186
EST UG =		EST UG =		EST UG =		EST UG =	
	(%)		(%)		(%)		(%)

12690
COUNTS

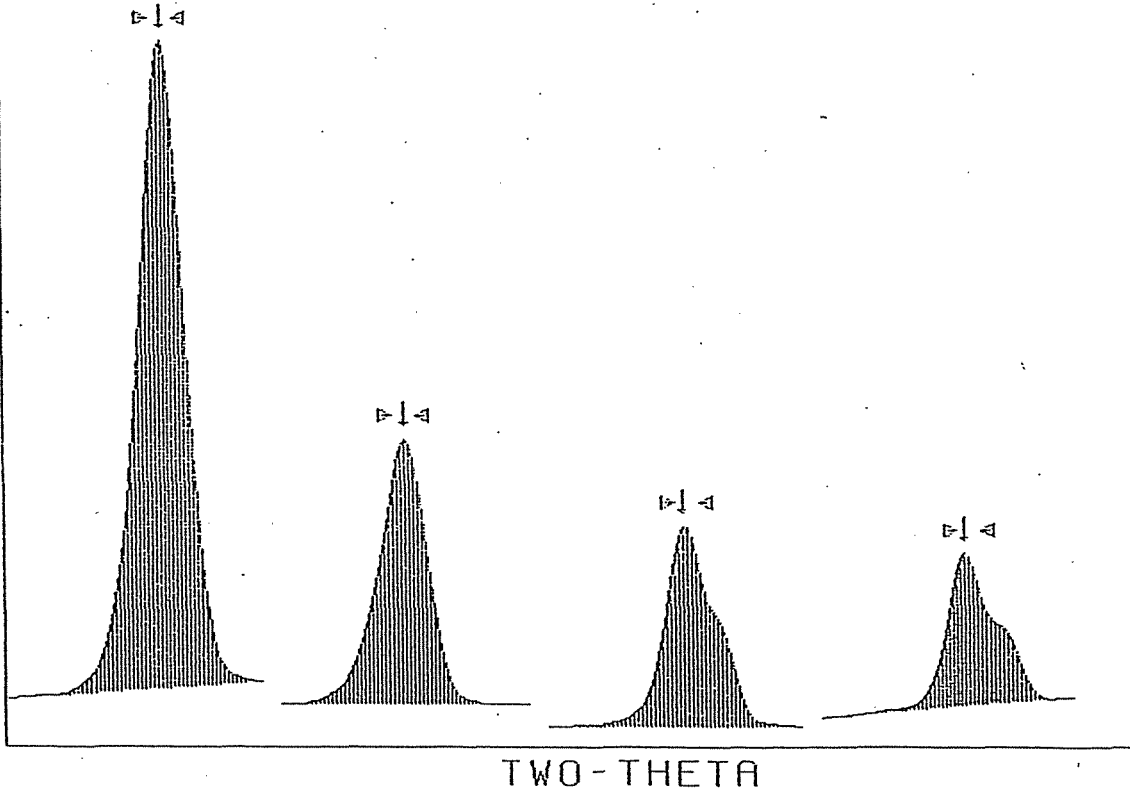


Figure 1

