LEAD SULFIDE 7505

PbS MW: 239.25 CAS: 1314-87-0 RTECS: OG4550000

METHOD: 7505, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
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OSHA : 0.05 mg (Pb)/m^3
NIOSH: <0.1 mg (Pb)/m^3; blood Pb ≤ 60 µg/100 g
ACGIH: 0.15 mg (Pb)/m^3

PROPERTIES: solid; d 7.5 g/mL; MP 1114 °C

SYNONYMS: galena (mineral)

SAMPLING

SAMPLER: CYCLONE + FILTER
(10-mm nylon or Higgins-Dewell (HD) cyclone + 5-µm PVC membrane)

FLOW RATE: HD cyclone: 2.2 L/min
nylon cyclone: 1.7 L/min

VOL-MIN: 600 L @ 0.05 mg (Pb)/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: 4% degradation in 45 days; protect samples from light

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; area respirable or settled dust

ACCURACY

RANGE STUDIED: 12 to 37 µg/m^3 [1]

BIAS: not significant when samples and standards have equivalent particle size

OVERALL PRECISION ($\hat{S}_{rT}$): 0.103 [1]

ACCURACY: ca. ± 22%

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: lead sulfide

DISSOLVE: filter in tetrahydrofuran

SUSPEND: dust in tetrahydrofuran

REDEPOSIT: 0.45-µm Ag membrane filter

XRD: Cu target X-ray tube
Optimize for intensity; 1° receiving slit
Graphite monochromator; scintillation detector
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: suspensions of PbS in 2-propanol

RANGE 30 to 2000 µg per sample

ESTIMATED LOD: 5 µg per sample

PRECISION ($\hat{S}_r$): 0.081 (40 to 260 µg per sample [1]

APPLICABILITY: The working range is 0.06 to 4 mg/m^3 for a 500-L air sample. The method is specific for lead sulfide among other mine dusts.

INTERFERENCES: Lead oxide (PbO, Pb_3O_4), lead sulfate (anglesite), copper iron sulfide (chalcopyrite); also see APPENDIX.

OTHER METHODS: This method was originally designated P&CAM 350, which it replaces [2].

REAGENTS:

1. Lead sulfide, ACS grade, <10-µm particle size.*
   NOTE: Perform a qualitative analysis (step 10) to determine the purity of the lead sulfide. The material also must be ultrasonically wet-sieved with a 10-µm pore size sieve to approximate respirable dust. Evaporate the alcohol. Dry the sieved material in an oven at 110 °C for 1 h, cool and store in a desiccator.
2. 2-Propanol.
3. Tetrahydrofuran (THF).*

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-µm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Bulk sampler: PVC membrane filter, 37-mm, 5-µm pore size in two-piece filter cassette. Sample closed face at 2 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size (Selas Flotronics, Millipore Corp., or equivalent).
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
7. Filtration apparatus and side arm vacuum flask with 25- and 37-µm filter holders.
8. Sieve, 10-µm, for wet sieving.
9. Analytical balance (0.01 mg); magnetic stirrer; ultrasonic bath or probe; volumetric pipettes and flasks; centrifuge tubes (wide mouth), 40-mL, and test tube rack; desiccator; reagent bottles, 1-L, with ground glass stoppers; drying oven; polyethylene wash bottle; Pyrex beakers, 50-mL, and matching watchglasses; and glue or tape for securing Ag filters to XRD holder.

SPECIAL PRECAUTIONS: THF is extremely flammable and should be used in a fume hood.

Avoid inhaling lead sulfide dust [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with a nylon cyclone or 2.2 L/min with an HD cyclone for a total sample size of 600 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

3. Take a high-volume bulk dust sample (e.g., 1 m^3 @ 3 L/min).
   NOTE: Protect the filters from exposure to intense light during storage.

SAMPLE PREPARATION:

4. Using forceps, place filters in 40-mL wide-mouth centrifuge tubes. Add 10 mL THF to each tube. Place the centrifuge tubes on the test tube rack in the ultrasonic bath for 10 min.
5. Place a silver filter in the filtration apparatus and attach the funnel. Pour the suspensions from the centrifuge tube into the funnel.
6. Wash the empty centrifuge tube with 5 mL THF and shake tube by hand or by vortex mixer for a few seconds. Transfer the THF to the filtration funnel. Repeat with two more 5-mL portions of THF.
7. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add THF to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sampler holder.

CALIBRATION AND QUALITY CONTROL:

8. Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to correct for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}$, for each media blank (step 11). Average the values for the six media blanks.
9. Prepare and analyze working standard filters.
   a. Prepare two suspensions by weighing 10 and 100 mg of the dry, sieved lead sulfide to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L 2-propanol.
   b. Suspend the powder in the 2-propanol 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. Cool to room temperature before use.
   c. Mount a silver filter on the filtration apparatus. Place 2 to 4 mL 2-propanol on the filter. Turn off the stirrer and shake the suspension vigorously by hand. Immediately 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 and take a new aliquot. Transfer the aliquot from the pipet to the filter keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
   e. 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 since this will rearrange the material on the filter. Transfer the filter to the XRD sample mount. Prepare working standard filters in triplicate by this technique at, e.g., 5, 10, 30, 50, 100, 200, 500, 1000, and 2000 µg lead sulfide.
   f. Analyze by XRD (step 11). Use the same diffraction peaks and instrumental conditions as for samples. Designate the net and normalized XRD intensities for the working standard filters as I^o_x (step 11.d) and $\hat{I}^o_x$ (step 11.e), respectively. Correct $\hat{I}^o_x$ for matrix absorption for standards containing more than 200 µg PbS (steps 11.f and 12).
   g. Prepare a calibration graph by plotting $\hat{I}^o_x$ vs. mass PbS (µg). A weighted least squares (I/σ^2) fit is preferable.
   h. Determine the slope, m (counts/µg), of the calibration graph. The intercept of the line should be zero ±5 µg.

MEASUREMENT:

10. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80° 2 Θ) of the settled dust sample or high-volume respirable sample to determine the presence of lead sulfide and any matrix interference (see APPENDIX). If quantitative analysis is to be performed on the field sample (percent PbS), wet-sieve it through a 10-µm sieve in order to match the particle size of the standards. The expected diffraction peaks are:

	Peak (2Θ Degrees)	
	Primary	Secondary
Lead Sulfide	30.10°	25.98°
Silver	38.12°	44.28°

11. Mount the filter (sample, standard or blank) in the XRD instrument and:
    a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak and use this value of N for all analyses.
    b. Measure the diffraction peak area of the most intense interference-free diffraction peak of PbS. Scan times must be long, e.g., 15 min.
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. Add the counts from each side to obtain a total (average) background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x (the difference between the peak integrated count and the total background count).
    e. Calculate the normalized intensity, $\hat{I}_x$, for the sample peak on each sample, field blank and standard:

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

    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 and the net intensities should be normalized to the most recently measured reference intensity.
    f. Determine the net count, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Scan each field blank over the same 2- Θ range used for PbS and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

12. Calculate the concentration of lead sulfide, C (mg/m ^{3}), in the air volume sampled, V (L):

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

where: $\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration curve ($\hat{I}^{o}_{x}$ vs. W)
m = initial slope of calibration curve, counts/µg

$$f(T) = \frac{-R \ln T}{1 - T^R} = \text{absorption correction factor (Table 1)}$$

R = sin (Θ_{Ag})/sin (Θ_x)
T = $\hat{I}_{Ag}$/(average $\hat{I}_{Ag}$ = transmittance of sample
$\hat{I}_{Ag}$ = normalized silver peak intensity from sample
average $\hat{I}_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: For a more detailed discussion of the absorption correction procedure, see references [4] and [5].

EVALUATION OF METHOD:

The measurement precision, $\bar{S}_r$, initially determined with 30 samples in the range 30 to 2000 µg PbS per filter was 0.0047 [6]. The same 30 samples plus five blank filters were analyzed by X-ray fluorescence for lead and sulfur and by ICP-AES for lead in order to verify the accuracy of the PbS filter depositions. A recovery study with 20 spiked samples in the range of 30 to 150 µg PbS per filter indicated a 102.6% average recovery and a 0.05 relative standard deviation.

Another recent study [1] involving 54 spiked samples in the range 40 to 250 µg PbS per filter indicated an 0.0081 precision and a 98% recovery. The overall method was also evaluated in the study using eight sets of samples collected in galena mills. A set consisted of six filters collected side by side. Average PbS in air concentrations for these sets ranged from 12 to 35 µg/m^3 and the pooled $\hat{S}_{rT}$ for seven of these averages was 0.103. The eighth set was an outlier [1].

Two stability studies [6] were performed: a short-term (47 days) and a long-term (6.5 months). In the short-term study, 15 PbS samples were exposed to various conditions from intense light to no light, from moist air to vacuum; all were analyzed at intervals. During analysis, they were all subjected to a total of over 2 h exposure to X-ray radiation at 1400 watts. Under continuous intense light, the PbS degradation was 14.4%. The smallest degradations were with no light (1.2 to 3.8%). In the long-term study, a PbS bulk sample exposed to ambient laboratory air and light conditions and a total of 36 h of X-ray radiation degraded 37.6%. A filter similarly exposed in the lab for 158 days and a total of 28 h of X-radiation degraded 12.2%. It is, therefore, recommended that the samples be protected from light.

REFERENCES:

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[4] Leroux, J. and C. Powers. Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters, Occup. Health Rev., 21, 26 (1970).
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APPENDIX:

INTERFERENCES

If interferences are present, use a different lead sulfide peak. Lead oxide (PbO yellow-form), lead sulfate (anglesite) and copper iron sulfide ($CuFeS_2$ chalcopyrite) interfere with the primary lead sulfide peak, using copper K_α X-ray radiation. Lead oxide (Pb_3O_4 orange-form) and lead sulfate (anglesite) also interfere with the secondary lead sulfide peak. The oxides of lead do not occur naturally in appreciable amounts in galena mining but are formed when lead sulfide is heated at high temperatures (i.e., in smelting and roasting operations) [7]. Dolomite, zinc sulfide (ZnS sphalerite) and chalcopyrite that are normally found in galena mining do not interfere with the secondary lead sulfide peak; for this reason the secondary lead sulfide peak was chosen as the analytical peak. The tertiary lead sulfide peak interferes with the secondary silver peak.

When peak overlaps are not severe, a smaller receiving slit or chromium X-radiation may be used; however, a new calibration curve will be necessary.

The presence of some elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to increased background intensity. This can be minimized by a diffracted beam monochromator.

The interfering effects of X-ray absorption by the sample result in attenuation of the diffracted beam and correction must be made (step 12 and Table 1).

Table 1. Matrix absorption correction factors for lead sulfide/silver peaks, degrees 2 Θ.

Lead Sulfide		30.10	25.98		30.10	25.98
Silver		38.12	38.12		38.12	38.12
	T	f(T)	(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2013	1.2346
	0.99	1.0063	1.0073	0.73	1.2109	1.2460
	0.98	1.0128	1.0147	0.72	1.2208	1.2575
	0.97	1.0193	1.0223	0.71	1.2308	1.2693
	0.96	1.0259	1.0299	0.70	1.2410	1.2814
	0.95	1.0326	1.0377	0.69	1.2514	1.2936
	0.94	1.0394	1.0456	0.68	1.2620	1.3062
	0.93	1.0463	1.0536	0.67	1.2729	1.3190
	0.92	1.0533	1.0618	0.66	1.2839	1.3320
	0.91	1.0605	1.0701	0.65	1.2952	1.3453
	0.90	1.0677	1.0785	0.64	1.3067	1.3590
	0.89	1.0751	1.0870	0.63	1.3185	1.3729
	0.88	1.0825	1.0957	0.62	1.3305	1.3871
	0.87	1.0901	1.1046	0.61	1.3428	1.4017
	0.86	1.0978	1.1136	0.60	1.3554	1.4165
	0.85	1.1057	1.1227	0.59	1.3682	1.4318
	0.84	1.1136	1.1320	0.58	1.3813	1.4473
	0.83	1.1217	1.1414	0.57	1.3948	1.4633
	0.82	1.1300	1.1511	0.56	1.4085	1.4796
	0.81	1.1383	1.1609	0.55	1.4226	1.4963
	0.80	1.1469	1.1708	0.54	1.4370	1.5135
	0.79	1.1555	1.1810	0.53	1.4518	1.5311
	0.78	1.1644	1.1913	0.52	1.4669	1.5491
	0.77	1.1733	1.2018	0.51	1.4825	1.5676
	0.76	1.1825	1.2126	0.50	1.4984	1.5866
	0.75	1.1918	1.2235	0.49	1.5148	1.6061

T = sample transmittance (step 12).
f(T) = sample correction factor (step 12).