ZINC STEARATE AS A CONTAMINANT IN THE COAL TAR PITCH VOLATILES ANALYSIS, BENZENE SOLUBLE FRACTION

Method Number:	ID-220SG
Matrix:	Air
OSHA Standard:	The OSHA standard which applies is the coal tar pitch volatiles standard of 0.2 mg/m^3
Collection Procedure:	Same as for OSHA Method 58, Coal Tar Pitch Volatiles analysis for air samples.
Recommended air volume and sampling rate:	960 L at 2.0 L/min
Status of method:	Stop-gap
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Date:	August 20, 2015

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ZINC STEARATE AS A CONTAMINANT IN THE COAL TAR PITCH VOLATILES ANALYSIS, BENZENE SOLUBLES FRACTION

1. Introduction

The purpose of this method is to make a correction for zinc stearate in the coal tar pitch volatiles analysis as it relates to the carbon and graphite products industry (SIC code 3624). There are concerns that OSHA is reporting coal tar pitch volatiles (CTPV) values that are too high due to zinc stearate and sulfur interferences and if the values for the sulfur and zinc stearate are subtracted, the CTPV values would be below the standard of 0.2 mg/m^3.

This method would be used based on the following rationale: (1) the coal tar pitch volatiles analysis results must be greater than 0.2 mg/m^3 and (2) the benzene soluble fraction must be positive for PAHs and be confirmed by mass spectrometry. Then zinc stearate and/or sulfur, as requested, would be analyzed to identify potential false high CTPV analytical results.

2. Sampling

2.1. Equipment

2.1.1. Calibrated personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 2.0 L/min are used.

2.1.2. A two piece cassette containing a glass fiber filter is the sampling device.

2.1.3. Other equipment relevant to the initial sample collection is shown in the method for coal tar pitch volatiles, OSHA Method 58, Coal Tar Pitch Volatiles (Ref. 1).

2.2. Reagents

No sampling reagents are required. CTPV uses a glass fiber filter.

2.3. Sampling technique

Sampling information is provided as per OSHA Method 58, Coal Tar Pitch Volatiles (Ref.1) for the air samples.

2.4. Extraction efficiencies

The extraction efficiency of zinc stearate in benzene appears to be based on the solubility. The solubility is approximately 0.3% for the zinc stearate. While this is

a low solubility for zinc stearate, there may still be a significant zinc stearate contribution to the coal tar pitch volatiles mass.

3. Analysis

3.1. Safety Precautions

3.1.1. Observe laboratory safety regulations and practices.

3.1.2. Review any MSDSs provided with reagents and samples.

3.1.3. Review both organic and inorganic methods (OSHA Method 58 and ID-121), particularly that information relating to handling carcinogenic materials.

3.2. Equipment

3.2.1. Atomic absorption spectrophotometer (Perkin-Elmer Model 5000 or Model 603).

3.2.2. Hotplates for inorganic ashing.

3.2.3. Glassware assortment including Philips beakers, volumetric flasks, 10-ml glass syringes with 5 μm filters.

3.2.4. Vacuum oven

3.2.5. Laboratory hood with sufficient face velocity to accommodate working with carcinogens (approximately 125 lfpm).

3.3 Reagents

3.3.1. Benzene

3.3.2. Nitric Acid

3.4. Working Standards See Ref. 5.2.

3.5. Sample Preparation (note the two part prep - organic and inorganic)

3.5.1. Air samples for the zinc analysis are prepared by obtaining a known volume (approximately 0.25 to 1.0 mL) of the benzene soluble sample material left over from the CTPV analysis (OSHA Method 58) and placing that material into a 125 mL Philips beaker for evaporation.

3.5.2. The benzene is evaporated from the above air sample aliquot(s) by direct nitrogen purge. This is accomplished by passing a stream of nitrogen through an aspirator and into the Philips beaker. Note that extreme care must be taken to assure that all the benzene is evaporated before digesting the samples with nitric acid !

3.5.3. The residue from the above procedure is taken to a hotplate where the samples are digested using the inorganic ashing method for zinc, OSHA ID-121 (Ref. 2).

3.5.4. The digested samples are diluted to volume with deionized water. It is recommended that 10 ml volume be used for air samples. Dilutions are prepared with 4% HNO_3.

3.6. Analysis

3.6.1. Analyze samples, standards, and blanks according to the general metals procedure for zinc, OSHA ID-121 (Ref. 2).

3.6.2. Set up one of the atomic absorption spectrophotometers for flame analysis of zinc.

3.6.3. Typical operating parameters are listed below:

Model PE 5000	Element analyzed: Zinc
Flame: Air-acetylene	Lamp current: 15 ma
Oxidant Flow: 40	Burner Height: 7
Fuel Flow: 20	
Burner depth: 7	Response: ABS
Slit: H, 0.7	Integration Time: 3 sec.

3.7. Calculations

3.7.1. After the analysis is completed, retrieve the absorbances or concentrations. Obtain hard copies of raw data from a printer.

3.7.2. Prepare a concentration-response curve by plotting the absorbance or expanded scale response versus the concentration of the zinc standards in µg/mL.

3.7.3. Determine the total zinc concentration in the samples and blanks. Make a blank correction if necessary by subtracting the total µg for the whole blank sample from the total µg for the entire volume for each field sample.

3.7.4. Calculate the Zn stearate concentration from the zinc concentration using the gravimetric factor (GF) of 9.671. Then apply that concentration of zinc stearate to the air samples, in order to correct the CTPV analyses using:

$A_s = (\mu g/mL\ zinc)_s(V_1)_s(DF)(GF)$

$A_b = (\mu g/mL\ zinc)_b(V_1)_b(DF)(GF)$

$A = A_s - A_b$

Then calculate the air concentration of zinc stearate for each air sample using the following equation:

$$\mu g/m^3 \text{ zinc stearate} = \frac{A}{AV}$$

Where:

A_s is the total micrograms of zinc stearate in the sample.
A_b is the total micrograms of zinc stearate in the blank.
A is the µg zinc stearate after blank correction.
GF is the gravimetric factor for zinc stearate.
AV is the air volume of the sample in cubic meters.
V_1 is the inorganic sample dilution volume for either sample or blank, in mL.
DF is the dilution factor that converts the sample aliquot that was used to the original sample volume such that:

$$DF = \frac{\text{original benzene volume, typically 3-5 mL}}{\text{aliquot volume, typically 0.25-1.0 mL}}$$

At this point, the industrial hygienist will subtract any zinc stearate result from the CTPV result, assuming the latter was greater than 0.2 mg/m^3.

4. Backup Data

4.1. Solubility of Zinc Stearate

A solubility study of zinc stearate in benzene focused on conditions recommended in the General Methods Procedure for metals. It was soon apparent that zinc stearate was not very soluble in benzene.

4.1.1. Procedure: To test the solubility of zinc stearate in benzene, zinc stearate bulk reagent (ICN Pharmaceuticals, INC., Life Sciences Group, Plainview, New York, no lot number was listed, approximately 100% zinc stearate) was spiked directly into a 10 mL volumetric flask. Six samples were prepared by adding known amounts of zinc stearate and diluting to volume with benzene. At first, approximately 20 mg aliquots were added to 4 mL and 10 mL, but the resulting solutions appeared very cloudy, as if very little material actually went into

solution or as if an emulsion had formed. For this reason the smaller aliquot weights were used. At least under these lower weight conditions, the resulting solution/suspension would filter through the 5 µm syringe filters so a benzene soluble fraction could be obtained. At the higher weight aliquots, the suspensions filtered with difficulty.

Another solubility study was done by weighing approximately 20 mg of zinc stearate into 200 mL benzene. This solution was cloudy, so the whole volume was filtered into another 200 mL volumetric flask. Then, 20 mL aliquots were transferred to Philips beakers for drying. It is these results that are contained herein.

4.1.2. Results: Results of the zinc and zinc stearate solubility study are shown below. As shown, zinc stearate appears to be only slightly soluble in benzene (approximately 0.3%).

Aliquot	% Zinc Recovered	% Zinc Stearate Recovered
ZS1	0.0376	0.3638
ZS2	0.0337	0.3257
ZS3	0.0360	0.3485
ZS4	0.0423	0.4096
ZS5*	0.0117	0.1132
ZS6	0.0353	0.3409

	Zinc	Zinc Stearate
N	5	5
Mean Recovery	0.03698	0.3577
sd	0.00329	0.0321
CV	0.0889	0.0897

* ZS5 is considered to be an outlier and is not used in these calculations.

4.2. Detection Limit

The analytical detection limit for zinc is 0.01 µg/mL. This is the same as found in OSHA method ID-121 when the samples are ashed in nitric acid and diluted to volume so that the final matrix concentration is 4% HNO_3.

4.3. Zinc Oxide/Zinc Chloride Solubility Study

Procedure: Several aliquots of zinc oxide and zinc chloride were prepared in benzene to establish the solubility of these compounds.

Results: The results of the solubility studies are shown below.

Date	Aliquot Number	Spiked wt. of Zn material, mg	% Recovery as ZnO or $ZnCl_2$
7/25/95	ZNO	5.2	0.05
8/18/95	ZNO1	5.59	ND
8/18/95	ZNO2	5.59	ND
8/18/95	ZNO3	5.59	ND
8/24/95	ZNO1	6.36	ND
8/24/95	ZNO2	12.72	ND
8/24/95	ZNO3	19.08	0.0077
7/25/95	ZNCl2	10.6	ND
8/18/95	ZNCL21	11.41	ND
8/18/95	ZNCL22	11.41	ND
8/18/95	ZNCL23	11.41	ND
8/24/95	ZNCL21	15.76	ND
8/24/95	ZNCL22	31.52	ND
8/24/95	ZNCL23	47.28	0.0043

All of these results have been blank corrected. The preponderance of these results shows that neither the zinc oxide nor the zinc chloride are soluble in benzene. If there is a percentage indicated it may be attributed to a potential low level zinc contamination.

4.4. Other comments

1. Part of one old air sample was obtained from an organic chemistry division analyst. An aliquot of this sample was analyzed by both the benzene extraction and zinc ashing procedures. Approximately 6 µg zinc or 58 µg zinc stearate were recovered from this air sample.

5. References

5.1. Occupational Safety and Health Administration Salt Lake Technical Center, Coal Tar Pitch Volatiles Method No. 58. July, 1986.

5.2. Occupational Safety and Health Administration Salt Lake Technical Center, Metal and Metalloid Particulates in Workplace Atmospheres (Atomic Absorption), Method No. ID-121. 1985(1991).