Phosphorus Pentasulfide

Method no.:	ID-128SG
Matrix:	Air
OSHA Standards:	1 mg/m³
Collection Procedure:	Collected on 37-mm PVC filter (FWS-B or equivalent)
Recommended Air Volume:	120 L
Recommended Sampling Rate:	1-2 L/min
Analytical Procedure:	Extracted in sodium hydroxide and hydrogen peroxide and analyzed by ion chromatography as phosphate and sulfate.
Detection Limit:	0.025 mg/m³ for a 60-L air sample
Precision:	CV1 = 0.0055 - 0.058 for phosphate in the range of 24 to 34 µg/mL CV1 = 0.023 - 0.047 for sulfate in the range of 62 to 87 µg/mL
Method Classification:	Partially validated

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1. General Discussion:

1.1 Collection Procedure:

The sample is drawn through a cassette containing a FWSB filter for the collection of particulate phosphorus pentasulfide.

1.2 Analytical Procedure:

The collected phosphorus pentasulfide is extracted by the mixture of sodium hydroxide and hydrogen peroxide based on the following proposed reaction and analyzed by ion chromatography (IC) as phosphate and sulfate ions.

$$P_2S_5 + 20H_2O_2 + 160H^{-1} = 2PO_4^{-3} + 5SO_4^{-2} + 28H_2O$$

2. Range and Detection Limit:

2.1 The range is from 1.25 to 2,500 µg phosphate. This corresponds to either 1.5 to 3,000 µg phosphorus pentasulfide or 0.025 to 6.25 mg/m³ of phosphorus pentasulfide for a 60 to 480 L air volume at a flow rate of 1 Lpm, respectively.

2.2 The quantitative detection limit is 0.01 µg of phosphate per injection or 1.5 µg of phosphorus pentasulfide in a 25 mL sample volume for a 200 µL sample injection volume. This corresponds to 0.025 mg/m³ of phosphorus pentasulfide for a 60 L air volume at a flow rate of 1 Lpm for 60 minutes.

3. Precision and Accuracy:

The precision and accuracy have not been completely determined this time, but the preliminary study has shown that the coefficients of variation for analytical method in terms of phosphate were between 0.0055 and 0.058 in the range of 24 to 34 µg/mL and in terms of sulfate were between 0.023 and 0.047 in the range of 62 to 87 µg/mL.

4. Interferences:

4.1 If both phosphate and sulfate are present in the atmosphere, they would give a positive interference; otherwise, either one of them causes no serious interference.

4.2 Any ionic substance that would elute at the same retention time as phosphate and sulfate would be a positive interference.

4.3 When other substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Substances, such as phosphoric acid and all kinds of phosphorus compounds, etc, may interfere with the determination of phosphate.

4.4 It has been reported (11.1, 11.2) that phosphorus pentasulfide may decompose upon exposure to moist air or moisture to form phosphoric acid and hydrogen sulfide. This may result in the low recovery of phosphorus pentasulfide based on only the sulfate determination.

5. Advantage and Disadvantage:

5.1 With the proper selection of instrumental conditions and conductivity range, this method has adequate sensitivity for measuring workplace atmosphere concentrations of phosphorus pentasulfide.

5.2 Although it is not required, the method can be fully automated.

5.3 The amount of phosphorus pentasulfide may be simultaneously confirmed from both phosphate and sulfate ions formed during the sample determination.

5.4 One disadvantage is that no information is available so far for the sampling procedure due to the lack of aerosol generation system. However, this problem can be solved in the future.

6. Apparatus:

6.1 Ion chromatograph: Dionex 10 or equivalent.

6.2 Auto sampler: WISP Model 710A or equivalent.

6.3 WISP auto sampler containers, including 4 mL vials, caps and septums.

6.4 Recorder: Varian Model 9176 or equivalent.

6.5 Anion pre-column, anion separator column and anion suppressor column.

6.6 Timer: Universal timer or equivalent.

6.7 Vacuum filtration apparatus.

6.8 Membrane filters, 5.0 µm pore size, 37mm diameter (MSA FWSB or equivalent)

6.9 Miscellaneous assorted laboratory glassware: beakers, pipettes, volumetric flasks, etc. (Note: All glassware should be washed in "phosphate-free" detergent and rinsed thoroughly with deionized water and then air-dried prior to use.)

6.10 Hot plate.

7. Reagents:

All chemicals should be ACS reagent grade or equivalent

7.1 Sodium carbonate, anhydrous

7.2 Sodium bicarbonate

7.3 Strong eluent (0.003 M sodium bicarbonate/0.006 M sodium carbonate): Dissolve 1 g of sodium bicarbonate and 2.5 g of sodium carbonate and dilute to a 4 L volume with deionized water.

7.4 Sulfuric acid, concentrated (98%)

7.5 Anion regenerant solution, 1N sulfuric acid: Slowly dilute 111 mL of concentrated sulfuric acid to 4 L with deionized water.

7.6 Sodium sulfate, anhydrous

7.7 Sulfate stock standard (1,000 ppm sulfate): Dissolve and dilute 1.4792 g of sodium sulfate to 1 L with deionized water.

7.8 Potassium dihydrogen phosphate, anhydrous

7.9 Phosphate stock standard (1,000 ppm phosphate): Dissolve and dilute 1.389 g of anhydrous potassium dihydrogen phosphate to 1 L with deionized water.

7.10 Sodium hydroxide, 5 N: Dissolve 200 g of sodium hydroxide pellets in approximately 600 mL of deionized water and dilute to 1 L.

7.11 Hydrogen peroxide, 3%: Dilute 10 mL of 30% hydrogen peroxide to 100 mL with deionized water.

8. Proposed OSHA Collection Procedure:

8.1 Apparatus:

8.1.1 Personal sampling pump.

8.1.2 Filter cassettes: A 37 mm diameter FWSB filter contained in a 37-mm polystyrene two piece cassette filter holder.

8.2 Procedure:

8.2.1 Sampling is done in accordance with instructions contained in the IHFOM (or the Industrial Hygiene Technical Manual when available to the OSHA industrial hygienist).

8.2.2 Collect each sample with a 5.0 µm FWSB filter at a known flow rate of 1 L/min. A minimum air volume of 120 L is recommended.

9. Analytical Procedure:

9.1 Sample preparation:

9.1.1 Rinse all glassware with deionized water. Commercial detergents containing phosphate should not be used.

9.1.2 Remove the filter from the cassette and place in a clean 125-mL conical beaker.

9.1.3 Pipette 1 mL of 5 N NaOH into each conical beaker and let stand, with occasional vigorous shaking for 30 minutes.

9.1.4 Add 2 mL of 3% hydrogen peroxide into each sample and let stand for a while.

9.1.5 Add 5 mL of deionized water and cover with watch glass. Heat to boiling for 5 minutes.

9.1.6 Cool to room temperature and transfer each sample to 25 mL volumetric flask and dilute to the mark with deionized water.

9.1.7 Filter the sample solution by means of the vacuum filtration apparatus.

9.1.8 If an auto sampler is to be used in the analysis, transfer a portion of each sample filtrate to an auto sampler vial. A minimum volume of 1.5 mL is required in each auto sampler vial.

9.1.9 If manual injection is to be used in the analysis, quantitatively transfer each sample filtrate to a clean glass 20 mL vial.

9.1.10 Be sure to label each vial with the appropriate laboratory ID number.

9.2 Standard Preparation:

9.2.1 Prepare a series of mixtures of phosphate and sulfate standards in the ratio of 1:2, respectively, by making appropriate serial dilutions of the 1,000 ppm phosphate and sulfate stock solution with the strong eluent.

9.2.2 If an auto sampler is to be used in the analysis, fill the auto sampler vials with appropriate standard solutions.

9.3 Analysis:

9.3.1 Typical operating conditions are:

Eluent: 0.003 M sodium bicarbonate/0.006 M sodium carbonate

Pre-column: 3-mm × 50-mm anion

Separator column: 3-mm × 250-mm anion

Suppressor column: 6-mm × 100-mm anion

Column temperature: Ambient

Conductivity meter: 10 or 30 μMHO full scale

Pump setting: 20-25% of total capacity

Retention time: Approximately 9 minutes for phosphate and 19 minutes for sulfate.

9.3.2 Set up the dual pen recorder at two different full-scale ranges (typically 200 and 500 mv).

9.3.3 Equilibration: Allow the IC columns to equilibrate by pumping the eluent through the system for a least one hour before analysis or until a stable baseline is achieved.

9.3.4 Auto sampler:

9.3.4.1 If an auto sampler is used in the analysis, place the standard and sample auto sampler vials in the carriage. Use the Sample Identification Record Sheet to identify each standard and sample.

9.3.4.2 Check the operation manual to select the appropriate programming mode.

9.3.4.3 Set the timer for controlling the recorder and ion chromatograph. Start the auto sampler.

9.3.5 Manual injection: Inject the standard or sample into the 100 μL sample loop of the ion chromatograph with a 1mL syringe. It is advisable to inject a sample volume of at least three times the sample loop volume to ensure adequate rinsing of the loop from sample contamination and to prevent standard carryover. Rinse the syringe several times with deionized water between sample injections.

9.3.6 Observe the first few standard chromatograms to ensure proper operation. Periodically, check the zero offset between samples to detect and correct any baseline drift and ensure proper sensitivity.

9.3.7 Analyze the standards and samples under the same operation conditions and time period to monitor the performance of the analytical system. Check the retention times of the standards and samples to ensure uniformity as the analysis proceeds.

9.3.8 Analyze a series of standards in the range of interest at concentrations about 25% above and below the apparent sample concentrations.

9.3.9 Establish positive identity of the phosphate and sulfate peaks by adding known amounts of standard solutions if interfering substances are present.

9.3.10 Measure the peak heights of phosphate and sulfate of the samples and standards in millimeters.

9.3.11 Use the Auto Colorimetric or any available least square regression program to establish calibration curves of peak heights vs. the amount of phosphate and sulfate in the standards in units of µg or µg/mL.

10. Calculations:

10.1 Read the sample weight as phosphate and as sulfate in µg from the calibration curves (see Section 9.3.11).

10.2 Make a blank correction, if necessary, as follows:

$$W = (A - B) \times V \times G$$

Where: W = Corrected amount (µg) of phosphorus pentasulfide in the sample solution.
A = Amount (µg/mL) as phosphate or as sulfate found in the sample solution.
B = Amount (µg/mL) as phosphate or as sulfate found in the blank sample solution.
V = Sample volume (mL) = 25 mL
G = Gravimetric factors = 1.17 for phosphate and 0.463 for sulfate

10.3 The corrected amount of phosphorus pentasulfide (W) calculated from both phosphate and sulfate peaks should be in agreement within plus and minus 10%. Otherwise, the lower amount, W, should be used for calculating the concentration of phosphorus pentasulfide in air (see next section).

10.4 The concentration of phosphorus pentasulfide in the air sample is expressed in mg/m^3, which is numerically equal to µg/L. mg/m^3 = [W (from Sec.10.2 and 10.3),µg]/(Air sampled vol., L)

11. References:

11.1 The Condensed Chemical Dictionary, 8th Ed.,1971

11.2 The Merck Index, 9th Ed., Published by Merck and Co., Inc. Rahway, N.J.

Table 1

Purity of Phosphorus Pentasulfide(1)

Weight of Phosphorus Pentasulfide: 632.15 mg

Solution Volume: 500 mL

Theoretical Concentrations: 1080.8 µg/mL as Phosphate
2730.5 µg/mL as Sulfate

Sample No.	Phosphate Found, µg/mL	Sulfate Found, µg/mL
1	1030.3	2733.4
2	1030.3	2591.8
3	1020.5	2492.2
n =	3	3
mean =	1027.0	2605.8
SD =	5.7	121.2
CV1 =	0.0055	0.047
Purity =	95.0%	95.4%

(1) P1316, Eastman, Lot No. 671-1X, Practical

Table 2

Independent Method

IC vs. NIOSH Colorimetric for Phosphate

Sample No.	Wt. of P_2S_5, mg	P_2S_5 Found, mg		P_2S_5 Recovery, %	
		IC	Color.	IC	Color.
1	31.62	27.75	25.41	87.8	80.4
2	40.17	32.46	32.13	80.8	80.0
3	56.91	44.81	29.19(1)	78.6	51.2(1)
	n =	3		2	
	Mean =	82.4		80.2	
	SD =	4.8		0.28	
	CV1	0.058		0.0035	

(1) Sample lost during analysis, excluded from statistical analysis.

Reference: P and CAM 216 and No.S333 NIOSH Methods.