Method no.:	ID 111
Matrix:	Air
OSHA Standards:	1.0 mg/m³
Collection Procedure:	A known volume of air is drawn through a mixed cellulose ester membrane filter.
Recommended Air Volume:	960 liters
Recommended Sampling Rate:	2 liters per minute
Analytical Procedure:	Filters are desorbed and the sample is analyzed by ion chromatography.
Detection Limit:	0.5 µg/mL of solution
Precision:	(CV_T) = 0.067
Method Classification:	P

1. Introduction

This method describes the collection and analysis of airborne phosphoric acid using ion chromatography.

1.1 History

Prior to the use of this method, samples were analyzed calorimetrically using vanadate-molybdate color reagent. However, the analysis was not specific for H_3PO_4 and an acid titration was needed for all samples above the PEL.

1.2 Uses (8.1)

Most phosphoric acid is used as ammonium phosphate for fertilizer and in the manufacture of superphosphates. Phosphoric acid is also used in rustproofing, electro polishing, engraving, lithographic work, coagulation of rubber latex, as an additive in glass manufacture, and as a catalyst in the manufacture of some pharmaceuticals.

1.3 Physical Properties (8.2 and 8.3)

Phosphoric acid is a dense, colorless liquid which is toxic and is a strong irritant to tissue.

Physical Constants:

Specific Gravity:	1.0028
Melting Point:	42.35 °C
Boiling Point:	213 °C
Molecular Weight:	98.00

2. Working Range and Detection Limit

2.1 The working range for a 960 liter air sample is 0.01 to 1.0 mg/m^3 PO_4^{-3}. This corresponds to 10 to 1000 µg of phosphate.

2.2 The sensitivity at 30 µmho full scale is 5 µg of analyte (PO_4^{-3} per sample per mm chart deflection).

2.3 The detection limit is approximately 0.5 µg PO_4^{-3}/mL of solution injected, corresponding to 5 µg of analyte per 10 mL of sample. The detection limit may be improved by using scale expansion of the read-out, by using a larger injection volume (for auto sampler only), or by using a smaller volume than 10 mL to desorb the sample.

3. Precision and Accuracy (8.4)

3.1 The coefficient of variation (CVT) = 0.067. This value was calculated from tabulated Quality Control samples in the range of 60 to 200 µg of PO_4^{-3} (N = 27). These samples were analyzed from June 1977 to September 1978.

4. Interferences (8.5)

4.1 Due to the method of collection (cellulose ester filters) and analysis (IC for PO_4^{-3}) any particulate phosphate will cause a positive error.

4.2 Large quantities of nitrate will cause some masking of the phosphate peak.

5. Advantages and Disadvantages

5.1 Interferences may not easily be identified if identification is based on retention time.

5.2 This method can be automated and is quick and accurate compared to the previous method.

5.3 In this sampling procedure, filters are used instead of impingers, which are used in other sampling methods for acid mist. This sampling procedure eliminates the inherent problems of using impingers.

6. Sampling Procedure

6.1 Apparatus – 37-mm diameter polystyrene 2 or 3 piece cassette filter holders. Mixed cellulose ester membrane filters with 0.8 micrometer pore size and a 37-mm diameter, supported by cellulose backup pads. Personal sampling pump with calibrated flow in line with a loaded filter holder to an accuracy of ±10% at the 95% confidence limit at the recommended flow rate, stopwatch, tweezers, screwcaps, and 20-mL scintillation vials.

6.2 A mixed cellulose ester membrane filter, with a 0.8 micrometer pore size and a 37 millimeter diameter is placed in a two or three piece cassette, supported by a cellulose backup pad.

6.3 The cassette is then attached to a personal sampling pump that has been calibrated in line with a loaded filter holder to an accuracy of ±10% at the 95% confidence limit at the recommended flow rate (2 liters/minute).

6.4 The cassette is placed in the sampling area or worker's breathing zone and approximately 960 liters of air are drawn through the cassette using a calibrated sampling pump.

6.5 After sampling, the cellulose ester membrane filter is removed from the cassette and placed in a clean 20-mL scintillation vial to avoid low recovery of phosphoric acid. The filter is handled with tweezers to avoid contamination. The vial is sealed, identified with OSHA Form 21 and shipped to the Laboratory for analysis.

6.6 With each batch of up to 20 samples, an appropriate blank filter is submitted for analysis.

6.7 When particulate phosphates are believed to be present in the workplace atmosphere they should be listed as interferences.

7. Analytical Procedure

7.1 Apparatus - An Ion exchange chromatograph equipped with an electrical conductivity detector, a recorder or integrator, an auto sampler, 10-mL pipettes, a 1-mL plastic syringe with male luer fitting, an Anion Separator Column 3 × 250-mm with Concentrator Column, an Anion Suppressor Column 10 × 100-mm, and appropriate volumetric glassware for dilutions and standard preparation.

7.2 Reagents - All reagents used should be ACS analyzed reagent grade or better.

7.2.1 Deionized, filtered conductivity grade water with a specific conductance of 10 umho/cm or less for preparation of eluents and other solutions which will be used in the ion chromatograph.

7.2.2 Sodium carbonate, Na_2CO_3.

7.2.3 Sodium bicarbonate, $NaHCO_3$.

7.2.4 Phosphate Stock Standard (1000 µg/mL PO_4^{-3}) - Dissolve 1.495 g of Na_2HPO_4 and dilute to 1 liter with deionized water. Phosphate working standards are made by diluting the stock solution with eluent.

7.2.5 Standard Eluent (0.003 M $CO3^{=}$ /0.0024 M $HCO3^{-}$) - Dissolve 5 g Na_2CO_3 and 5 g $NaHCO_3$ in deionized water and dilute to volume in a 20 liter carboy.

7.2.6 Regenerant Solution (1 N H_2SO_4). Dilute 111 mL of concentrated H_2SO_4 to 4 liters with deionized water.

7.3 Safety Precautions

7.3.1 When using the ion chromatograph, the column door should be kept closed during the analysis in case the columns burst. To avoid this danger the pressure should be checked at the beginning of the analysis and periodically during the analysis. The pressure should never exceed 500 psi.

7.3.2 Care should be used when handling the reagents, especially the reagents solution (1 N H_2SO_4), to avoid chemical burns.

7.3.3 Care should be exercised when using laboratory glassware. Chipped pipettes, volumetric flasks, beakers, or any glassware with sharp edges exposed should not be used to avoid the possibility of cuts, abrasions, and lost samples.

7.3.4 Pipetting should never be done by mouth - a bulb should always be used.

7.4 Standard Preparation

7.4.1 A 1000 µg/mL stock standard solution is prepared by dissolving 1.495 g of Na_2HPO_4 and diluted to one liter with deionized water.

7.4.2 Working standards are prepared in the analytical range of 0.5 µg/mL to 50 µg/mL PO_4^{-3} by dilution of the 1000 µg/mL stock solution. These standard solutions should be prepared fresh weekly.

7.4.3 If an auto sampler capable of variable injections is used, only a 50 µg/mL PO_4^{-3} standard is necessary. This intermediate working standard should be prepared fresh monthly.

7.5 Sample Preparation

7.5.1 If the filter is not in a 20-mL scintillation vial, remove the filter from the cassette and place in a clean 20-mL vial.

7.5.2 If the air volume is adequate (greater than or equal to 960 liters) pipette 10 mL of eluent (0.003 M $CO_3^{=}$/0.0024 M $HCO3^{-}$) into each sample vial and cap. Let stand, with occasional vigorous shaking, for 30 minutes. When particulate phosphates are listed as interferences, the filter should be extracted with appropriate amounts of eluent to allow the determination of total acid content by titration. Sample solutions which are not clear should be filtered before analysis.

7.5.3 If using an auto sampler, transfer some of the sample into an appropriate sampling vial. The vial should be at least half full. Label each vial with the appropriate laboratory identification number.

7.5.4 For hand injection, use 1 mL of the eluent to flush the 0.1-mL injection loop thoroughly.

7.6 Analysis (9.6)

7.6.1 For general instrument set-up refer to Section 7 of the Ion Chromatography Standard Operating Procedure.

7.6.2 The normal instrument parameters are:

Sensitivity:	30 µmho full scale
Eluent:	0.003 M Na_2CO_3 and 0.0024 M $NaHCO_3$
Flow Rate:	138 mL/hr approximately 30% on vernier
Concentrator Column:	3 mm I.D. × 50 mm
Anion Separator Column:	3 mm I.D. × 250 mm
Suppressor Column:	10 mm I.D. × 100 mm
Retention Time:	Approximately 5 minutes, depending upon the analytical conditions

7.6.3 With the instrument set up and stabilized, place the auto sampling vials into the sampling tray using tray positions one through five for standards, and place a standard following every 5 samples thereafter.

7.6.4 Enter the proper parameters into the auto sampler (See Section 4 of the Ion Chromatography Standard Operating Procedure).

7.6.5 Start the auto sampler and observe the first few chromatograms to ensure proper operation. Periodically check the zero offset between samples to correct any baseline drift and to ensure proper sensitivity and retention time of the analyte (PO_4^{-3}).

7.6.6 Use the timer to stop the run if the auto sampler is to be left unattended.

7.6.7 For hand injection, a 1 mL aliquot is taken up in a syringe from the 20-mL vial and injected into the injection port with the toggle switch in the load position. After the sample is loaded, switch the toggle to the inject position and start the integrator or push the PIP button if a strip chart recorder is being used.

7.6.8 For both hand and auto sample injections, record the sample number onto the chromatogram. A record of the sample identity and instrument conditions should be kept.

7.6.9 As the analysis proceeds, check the retention times of standards vs. samples to ensure uniformity.

7.6.10 If interfering substances are present, establish positive identity of the phosphate peak by spiking with known amounts of standard solutions and obtain better separation by changing the eluent concentration, or by reducing the flow rate.

7.7 Calculations

7.7.1 Peak areas or heights of the standards are used to construct a standard curve using the Auto Colorimetric Program. The sample results are obtained from a plot of peak height or peak area vs. PO_4^{-3} concentration. The blank corrected sample values are then calculated using the Auto Colorimetric Program.

7.7.2 Sample numbers and volumes are entered into the calculator in the following way:

Sample Number, Peak Area or Heights, L Air Volume, mL Solution Volume, Aliquot Volume.

7.7.3 Air concentration values are calculated by the following equation:

$$mg/m^3 = \frac{(\mu g \text{ calculated})(mL \text{ sample vol})(1\text{-}03^*)(\text{dil factor})}{(\text{liters of Air})(mL \text{ Aliquot})}$$

*Gravimetric Factor for H_3PO_4.

8. References

8.1 Encyclopedia of Chemical Technology, Second Edition, Volume 15, 1968, page 269.

8.2 CRC Handbook of Chemistry & Physics, 56th Edition, 1975-1976, page D-239.

8.3 Merck Index, Ninth Edition, 1976, page 1193.

8.4 Tabulated data from Occupational Safety & Health Administration Quality Control Division.

8.5 OSHA Ion Chromatography Standard Operating Procedure, Prepared by the Ion Chromatograph Committee, Occupational Safety & Health Administration Analytical Laboratory Inorganic Division.

8.6 NIOSH Manual of Analytical Methods, Second Edition, Volume 5, Method Number P&CAM 268.