



Acid Mist

Method number: ID-165SG

Version: 1.0

Matrix: Air

OSHA Standard: 3.0 ppm Hydrogen Bromide, HBr
2.0 ppm Nitric Acid, HNO₃
1.0 mg/m³ Phosphoric Acid, H₃PO₄
1.0 mg/m³ Sulfuric Acid, H₂SO₄

Collection Procedure: A known volume of air is drawn through a silica gel tube. H₂SO₄, H₃PO₄ and other particulates are collected on the glass fiber plug while HBr and HNO₃ are collected on the silica gel sorbent.

Recommended Air Volume: 96 liters

Recommended Sampling Rate: 0.2 liters per minute

Analytical Procedure: The glass fiber plug and the silica gel tubes are desorbed with standard eluent and analyzed by Ion Chromatography (IC).

Detection Limit: See Section 2.3.

Precision and Accuracy: (CVA) = 0.035 for HBr
0.037 for HNO₃
0.066 for H₃PO₄
0.079 for H₂SO₄

Method Classification: Partially Validated Method

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Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

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1. Introduction

This method describes the collection and analysis of airborne acids using Ion Chromatography. The method measures the total concentration of four airborne anions. The corresponding acids may be collected on a single sampler and determined simultaneously. Acids which can be collected and analyzed this way are HBr, H₃PO₄, HNO₃, and H₂SO₄.

1.1. History (Ref. 9.6., Ref. 9.7., and Ref. 9.8.)

Prior to the use of this method, HBr was collected in 0.01 N NaOH, HNO₃ was collected in deionized (DI) water, H₂SO₄ and H₃PO₄ were collected on 0.8-micron MCEF filters, and all were analyzed by IC.

1.2. Uses (Ref. 9.1.)

Hydrogen bromide is used in the manufacture of organic and inorganic bromides and hydrobromic acid, as a reducing agent, and as a catalyst in controlled oxidations. HBr is also used in the alkylation of aromatic compounds, and in the isomerization of conjugated diolefins.

Most nitric acid is used in fertilizer as ammonium nitrate and in the manufacture of explosives. Nitric acid is also used in the synthesis of a large number of industrial organic compounds. Relatively small quantities of this acid are used for stainless steel pickling and metal etching, and to make rocket propellants.

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

Sulfuric acid is used in the fertilizer industry for the production of superphosphates and ammonium sulfate. The chemical industry consumes sulfuric acid in the manufacture of phosphoric acid by the wet process. Sulfuric acid is used in the manufacture of paper and aluminum sulfate, and is used extensively for water purification. The petroleum industry uses sulfuric acid in the alkylation process and in the refining of petroleum distillates for removal of sulfur and gum-forming compounds. Other important industrial applications consuming large amounts of sulfuric acid include steel pickling and the manufacture of titanium pigments, rayon, dyes, intermediates, and detergents.

1.3. Physical Properties (Ref. 9.2. and Ref. 9.3.)

Hydrogen bromide is a colorless, corrosive, nonflammable gas with an acrid odor. HBr fumes in moist air forming clouds, which have a sour taste. Commercial grades are approximately 48% pure.

Nitric acid is a colorless liquid (depending upon purity and freshness). The acid produces fumes in moist air and has a strong choking odor. Long exposure to light causes nitric acid to become discolored (brownish). Commercial grades are approximately 70 - 71% pure.

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

Sulfuric acid is a dense oily liquid, colorless to dark brown (depending on purity). Commercial grades are approximately 96% pure. Sulfuric acid is a strong oxidant, which is toxic, a strong irritant to tissue, very corrosive, and has a great affinity for water.

Physical Constants:	HBr	HNO ₃	H ₃ PO ₄	H ₂ SO ₄
Specific Gravity:	2.71	1.50	1.003	1.84
Melting Point:	-86.9	-42.0	42.35	10.4°C
Boiling Point:	-66.8	83.0	213.	315 - 338°C
Molecular Weight:	80.92	63.02	98.00	98.08

2. Working Range and Detection Limit (Ref. 9.6., Ref. 9.7., and Ref. 9.8.)

- 2.1. The working range for a 100 liter air sample is 0.08 to 3.0 ppm for Br⁻, 0.10 to 3.9 ppm for NO₃⁻, and 0.25 to 10.0 mg/m³ for PO₄³⁻, and SO₄²⁻. This corresponds to 2.5 to 50 µg of bromide, nitrate, phosphate, and sulfate. The upper range can be extended by sample dilution.
- 2.2. The sensitivity at 30 µmho full scale is 5 µg of analyte (Br⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻) per sample per mm chart deflection (based on a 10 mL sample volume).
- 2.3. The qualitative detection limits for Br⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻ were calculated using the Student's T-Test. The detection limits are as follows at a confidence level of 95%:

PO ₄ ³⁻	= 0.25 µg
Br ⁻	= 0.20 µg
NO ₃ ⁻	= 0.125 µg
SO ₄ ²⁻	= 0.25 µg

These detection limits were calculated based on a sample volume of 10 mL and an injection volume of 100 µL. The detection limits for each analyte were calculated in the presence of the other three analytes. The detection limit may be improved 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

- 3.1. The average coefficient of variation (CVA) is: 0.035 for HBr, 0.037 for HNO₃, 0.079 for H₂SO₄, and 0.066 for H₃PO₄.

4. Interferences (Ref. 9.6., Ref. 9.7., and Ref. 9.8.)

- 4.1. Large quantities of any one analyte will cause some masking of some of the other peaks.

5. Advantages and Disadvantages

- 5.1. The method can be automated and is quick and accurate compared to previous methods, which involved titrations with nebulous endpoints.
- 5.2. The sampling procedure employed uses silica gel tubes as opposed to impingers, which are used in other sampling methods for acid mist. Such a sampling procedure eliminates the inherent problems of using impingers.
- 5.3. Unlike previous methods, nitrate and bromide particulates are not an interference in this method since particulates can be captured on the glass fiber filter in the tubes and analyzed separately if necessary.

6. Sampling Procedure

- 6.1. Apparatus - Silica gel sorbent tubes, Supelco, Inc. ORBO-53 (or equivalent silica gel tubes which have been demonstrated to show low levels of the anions of interest), personal sampling pump with calibrated flow in line with a silica gel tube to an accuracy of $\pm 10\%$ at the 95% confidence limit at the recommended flow rate.
- 6.2. The silica gel tube is attached to a calibrated personal sampling pump and the sampling tube is placed in the sampling area or worker's breathing zone. At least 10 liters of air are drawn through the sampling tube.
- 6.3. After sampling, the silica gel tube is removed from the tubing, sealed and identified with OSHA Form-21, and shipped to the Laboratory for analysis.
- 6.4. With each batch of up to 20 samples, a blank tube, which has had no air drawn through it, is submitted for analysis. The blank tube should be from the same lot of tubes used for sampling.
- 6.5. It is very important that when particulate acids or salts of an anion are known to be present in the workplace atmosphere they should be listed as interferences.

7. Analytical Procedure

7.1. Apparatus –

Ion exchange chromatograph, equipped with electrical conductivity detector and recorder, or integrator (an auto sampler helps automate the analysis),
10 mL pipette,
1 mL plastic syringe with male Luer fitting,
Anion Separator Column 3 × 250 mm with Concentrator Column,
Anion Suppressor Column 10 × 100 mm,
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 water with a specific conductance of 10 $\mu\text{mho/cm}$ 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. Bromide Stock Standard (1000 $\mu\text{g/mL Br}^-$). Dissolve 1.489 g KBr and dilute to 1 liter with deionized water. Bromide working standards are made by diluting the stock solution with eluent.

- 7.2.5. Nitrate Stock Standard (1000 $\mu\text{g}/\text{mL}$ NO_3^-). Dissolve 1.3708 g NaNO_3 and dilute to 1 liter with deionized water. Nitrate working standards are made by diluting the stock solution with eluent.
- 7.2.6. Phosphate Stock Standard (1000 $\mu\text{g}/\text{mL}$ PO_4^{3-}). Dissolve 1.495 g Na_2HPO_4 and dilute to 1 liter with deionized water. Phosphate working standards are made by diluting the stock solution with eluent.
- 7.2.7. Sulfate Stock Standard (1000 $\mu\text{g}/\text{mL}$ SO_4^{2-}). Dissolve 1.479 g of Na_2SO_4 into 1 liter of deionized water. Sulfate working standards are made by diluting the stock solution with eluent.
- 7.2.8. Standard Eluent (0.003 M CO_3^{2-} =/0.0024 M HCO_3^-). Dissolve 5 g Na_2CO_3 and 5 g NaHCO_3 in 20 liter carboy with deionized water.
- 7.2.9. Regenerant Solution (1 N H_2SO_4). Dilute 111 mL of concentrated H_2SO_4 to 4 liters in 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 reagents, especially the regenerant 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. Working standards are prepared in the analytical range of 0.2 $\mu\text{g}/\text{mL}$ to 50 $\mu\text{g}/\text{mL}$ from dilutions of the 1000 $\mu\text{g}/\text{mL}$ stock solutions. These standard solutions should be prepared fresh weekly.
- 7.4.2. If an auto sampler capable of variable volume injections is used, a combination 50 $\mu\text{g}/\text{mL}$ PO_4^{3-} , 10 $\mu\text{g}/\text{mL}$ Br^- , 25 $\mu\text{g}/\text{mL}$ NO_3^- , and 50 $\mu\text{g}/\text{mL}$ SO_4^{2-} standard is used. This intermediate working standard should be prepared fresh monthly.

7.5. Sample Preparation

- 7.5.1. The sample tube used with this analysis can be separated into 3 parts. The first part is the glass fiber filter plug, which will collect any particulate. The second part is a 150 mg silica gel section (section A) which collects the acid mists. The third part is a 75 mg silica gel section (section B) which is the backup section and will collect any acid mists which are not collected by section A. The second and third parts are separated by a foam plug which is to be discarded.
- 7.5.2. Score the sampler with a file in front of the primary sorbent section (section A), then break the sampler at the score line. Transfer the glass fiber filter plug and section A to a clean 20 mL vial. If the analysis is to be done only for HNO_3 and/or HBr , the glass fiber filter plug can be discarded. If sulfuric and/or phosphoric acids are requested, the glass fiber filter plug

must be analyzed separately. The glass fiber filter plug should be analyzed separately if sulfate and/or phosphate is requested and nitric and/or hydrobromic acids are also requested.

- 7.5.3. Place silica gel section B in a separate clean 20 mL vial. Discard the urethane plug.
- 7.5.4. If the air volume is greater than or equal to 20 liters pipette about 5 mL of eluent (0.003 M CO_3^{2-} /0.0024 M HCO_3^-) into each sample vial and cap tightly. If the air volume is less than 20 liters, a smaller volume of eluent is used.
- 7.5.5. Place the vial in a large beaker with DI water and boil for 10 minutes. Let cool and dilute to 10.0 mL with eluent in a volumetric flask (if the air volume is less than 20 liters, dilute to 5 mL in a volumetric flask). When particulate acids are listed as interferences for HNO_3 and/or HBr , the glass fiber plug should be desorbed separately with about 2 mL of eluent, which is then diluted to 10 mL with standard eluent. Sample solutions, which are not clear should be filtered before analysis.
- 7.5.6. 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.
- 7.5.7. For hand injection, use 1 mL of the eluent to flush the 0.1 mL injection loop thoroughly. When using automatic injection try to use about a 100- μL injection volume. The autosampler is less accurate below 100 μL .

7.6. Analysis (Ref. 9.4.)

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. \times 50 mm

Anion Separator Column: 3 mm I.D. \times 250 mm

Suppressor Column: 10 mm I.D. \times 100 mm

Run Time: Approximately 30 minutes, depending upon 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.
- 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 analytes.
- 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. A typical chromatograph of a mixed standard of Br⁻, NO₃⁻, PO₄⁻³, and SO₄⁼, is shown in Figure 1.

7.6.10. If interfering substances are present, establish positive identity of the peaks by spiking known amounts of standard solution or try to 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 OSHA Auto Colorimetric Program. The samples results are obtained from a plot of peak area vs. concentration.

The blank corrected sample values are then calculated using the Auto Colorimetric Program.

7.7.2. When using the OSHA Auto Colorimetric Program, sample numbers and volumes are entered into the calculator in the following manner:

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

7.7.3. Air Concentration values are calculated by the following equation:

$$\text{mg/m}^3 = \frac{(\mu\text{g calculated})(\text{mL sample vol})(\text{GF}^*)(\text{dilution factor})}{(\text{liters of air})(\text{mL aliquot})}$$

GF* = Gravimetric Factor = 1.013 for HBr
1.016 for HNO₃
1.021 for H₂SO₄
1.032 for H₃PO₄

7.7.4. HNO₃ and HBr are reported in ppm rather than in mg/m³. To convert the mg/m³ values to ppm, the mg/m³ value must be multiplied by the appropriate conversion factor.

<u>Acid</u>	<u>Conversion Factor</u>
HBr	0.302
HNO ₃	0.388

8. Reporting Results for Compounds Determined by Ion Chromatography

8.1. Results are reported on the OSHA Form 91 in milligram per cubic meter for H₂SO₄ and H₃PO₄ and in ppm for HBr and HNO₃, using two significant figures.

8.2. The estimated detection limit calculated by the Auto Colorimetric Program is reported on the OSHA Form 91 when no analyte is detected.

8.3. The presence of significant unidentifiable peaks is noted on the OSHA Form 91.

8.4. All data processor printouts and chart recorded chromatograms are filed in a central file according to laboratory sample identification.

8.5. Calculations are checked by a fellow chemist before the completed OSHA Form 91's are given to the supervisor.

9. References

- 9.1. Encyclopedia of Chemical Technology, Third Edition, 1981.
- 9.2. CRC Handbook of Chemistry & Physics, 62nd Edition, 1981-1982.
- 9.3. Merck Index, Tenth Edition, 1983.
- 9.4. OSHA Ion Chromatography Standard Operating Procedure, Prepared by the Ion Chromatography Committee, Occupational Safety & Health Administration Analytical Laboratory, Inorganic Division.
- 9.5. NIOSH Manual of Analytical Methods, Second Edition, Volume 7, Method Number P&CAM 339 (revised), Issued on 2/15/84.
- 9.6. Nitric Acid in Workplace Atmospheres, Method No. ID-127, OSHA Laboratory, Salt Lake City, UT.
- 9.7. Phosphoric Acid in Workplace Atmospheres, Method No. ID-111, OSHA Laboratory, Salt Lake City, UT.
- 9.8. Sulfuric Acid in Workplace Atmospheres, Method No. ID-113, OSHA Laboratory, Salt Lake City, UT.
- 9.9. Monitoring for Airborne Inorganic Acids, M.E. Cassinelli and D.G; Taylor, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH, 45226.

Full Scale 30 u MHO, Standard Eluent (0.003 M NaHCO₃ & 0.0024 M Na₂CO₃)
Ret. Time 30 min., Inj. Vol. 100 uL, Chart Speed 0.2 cm/min.

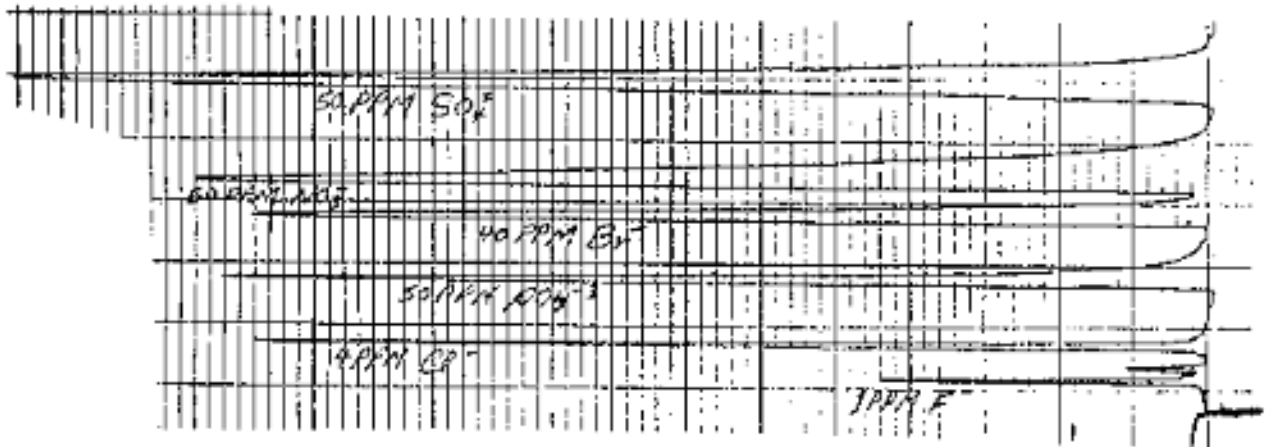


Figure 1