Method no.:	ID-174-SG
Matrix:	Air
Collection Procedure:	A known volume of air is drawn through a silica gel tube. Particulates are collected on the glass fiber plug while HCl is collected on the silica gel sorbent.
Recommended Air Volume:	7.5 liters
Recommended sampling rate:	0.5 liters per minute
Analytical Procedure:	The silica gel tube is desorbed with standard eluent and is analyzed by Ion Chromatography (IC).
Detection Limit:	See section 2.2
Precision and Accuracy:	$(CV_A) = 0.225$ for HCl
Method Classification:	P

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1. Introduction

This method describes the collection and analysis of airborne hydrogen chloride using Ion Chromatography. Other acids which can be collected and analyzed simultaneously are HBr, H_3PO_4, HNO_3, and H_2SO_4.

1.1 History (9.1, 9.2)

Prior to the use of this method, HCl was collected using 0.1 N NaOH in an impinger and analyzed by specific ion electrode, or by adding $AgNO_3$ and measuring the turbidity of the AgCl formed.

1.2 Uses (9.3)

Hydrogen chloride is used in the manufacture of pharmaceutical hydrochlorides, making vinyl chloride from acetylene, alkyl chlorides from olefins, and arsenious chloride from arsenious oxide. Hydrogen chloride is also used in the chlorination of rubber and in organic reactions involving isomerization, polymerization, and alkylation. HCl is also used to make chlorine, when it is economical.

1.3 Physical and Chemical Properties (9.4, 9.5)

Specific Gravity: 1.268
Melting Point: -114.8 °C
Boiling Point: -84.9 °C
Molecular Weight: 36.46

2. Working Range and Detection Limit

2.1 The working range for a 7.5-liter air sample is 0.01 to 1.0 ppm for Cl^- for a 10-mL sample volume. This corresponds to 0.10 to 10.0 µg of chloride. The upper range can be extended by sample dilution.

2.2 The qualitative detection limits for Cl^- were calculated using the Student's T-Test. The detection limit for Cl^- is 0.10 µg at a confidence level of 95%. This detection limit was calculated based on a sample volume of 10 mL and an injection volume of 100 µL. 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. Stability, Collection Efficiency, and Coefficient of Variation.

3.1 The storage stability of HCl on silica gel tubes was found to be acceptable. Aqueous HCl was spiked onto 9 silica gel tubes at a level corresponding to 1.0 × PEL. Air with 80% humidity and 25 °C was pumped through the tubes at 0.5 Lpm for 15 minutes. Three tubes were analyzed on that day (Day 0). Three tubes each were analyzed 7 and 14 days later. There were no significant losses of HCl.

SAMPLE	DAY	PPM	AVE	STD. DEV.
1STA	0	6.12		
2STA	0	7.31	6.60	0.511
3STA	0	6.38		
4STA	7	6.06		
5STA	7	6.40	6.13	0.192
6STA	7	5.94		
7STA	14	5.46		
			6.07	0.482

8STA	14	6.10
9STA	14	6.64

All samples were re-analyzed on day 14, and it was found that there were no losses. This suggests that once the tubes were desorbed the HCl is not lost for at least 2 weeks.

3.2 Aqueous HCl was spiked onto 9 silica gel tubes at a level corresponding to 1.0 × PEL. Air with 80% humidity and 25 °C was pumped through the tubes at 0.5 Lpm for 15 minutes. Part B of the sample were analyzed and no breakthrough was found. This is in accordance with a NIOSH study (9.6) which found that the collection efficiency of silica gel tubes in generated HCl test atmospheres was 100%.

3.3 The coefficient of variation (CV_A) for the analytical method in the range of 35 to 114 µg Cl^- was 0.225 (9.7).

4. Interferences

Large quantities of fluoride will cause some masking of the chloride peak.

5. Advantage and Disadvantages

5.1 The method can be automated and is quick and accurate.

5.2 This procedure uses silica gel tubes instead of impingers which are used in other sampling methods for HCl. This eliminates the inherent problems of using impingers.

5.3 Unlike previous methods, particulates are not an interference in this method, since they can be captured on the glass fiber filter in the tube 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 ±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 a flow rate of 0.5 liters per minute, 7.5 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 to list as interferences any particulate acids or salts known to be present in the workplace atmosphere.

7. Analytical Procedure

7.1 Apparatus - Ion exchange chromatograph, equipped with electrical conductivity detector and recorder, or integrator, 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, 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 water with a specific conductance of 10 µmho/cm or less for preparation of eluents and other solutions which will be used in the analysis.

7.2.2 Chloride Stock Standard (1000 µg/mL Cl^-) - Dissolve 1.648 g NaCl and dilute to 1 liter with deionized water. Chloride working standards are made by diluting the stock solution with standard eluent.

7.2.3 Standard Eluent (0.003 M $CO_3^=$/0.0024 M HCO_3^-) Dissolve 5 g Na_2HCO_3 and 5 g $NaHCO_3$ in 20-liter carboy with deionized water.

7.2.4 Regenerant Solution (1 N H_2SO_4). Carefully add 111 mL of concentrated H_2SO_4 to 2 liters of deionized water and dilute to 4 liters.

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 not 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 in order 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 µg/mL to 50 µg/mL from dilutions of the 1000 µg/mL stock solution. These standard solutions should be prepared fresh weekly.

7.4.2 If an auto sampler capable of variable volume injections is used, a 3 µg/mL Cl^- 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 collects any particulate. The second part is a silica gel backup section (section A) which collects the acid mists. The third part is a silica gel section (section B) which collects any acid mists not collected by section A. The second and third parts are separated by a foam plug, which is discarded.

7.5.2 Score the sample tube with a file in front of the primary sorbent section (section A) and break the tube 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 HCl, 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.

7.5.3 Place silica gel section B in a separate clean 20-mL vial.

7.5.4 If the air volume is greater than or equal to 1 liter, pipette about 5 mL of eluent
(0.003 M $CO_3^=$/0.0024 M HCO_3^-) into each sample vial and cap tightly. If the air volume is less than 1 liter,

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 1 liter, dilute to 5 mL in a volumetric flask). When particulate acids are listed as interferences, the glass fiber plug should be discarded. 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

7.6.1 For general instrument set up refer to Section 7 of the Ion Chromatography Standard Operating Procedure (9.8)

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
Run Time: Approximately 20 minutes, depending upon analytical conditions.

7.6.3 With the instrument set up and stabilized, place the auto sampling vial 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 (9.8)

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.

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 height or 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:

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

GF^* = Gravimetric Factor = 1.03 for HCl

7.7.4 HCl is reported in ppm rather than in mg/m^3. To convert the mg/m^3 values to ppm, the mg/m^3 value must be multiplied by the conversion factor 0.671.

8. Reporting Results for Compounds Determined by Ion Chromatography

8.1 Results are reported on the OSHA Form 91 in ppm for HCl, 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 91s are given to the supervisor.

9. References

9.1 Hydrogen Chloride in Workplace Atmospheres, OSHA Method # ID-173SG.

9.2 Hydrogen Chloride, OSHA Method # VI-5, last revised on January, 1978.

9.3 *Merck Index*, 10th Edition, pg. 696, 1983.

9.4 *CRC Handbook of Chemistry & Physics*, 62nd Edition, 1981-1982.

9.5 *The Condensed Chemical Dictionary*, 10th Edition, pg. 544, 1981.

9.6 *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.

9.7 OSHA Laboratory Quality Control Data, Cl^- by IC to September 6, 1979.

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

9.9 NIOSH Manual of Analytical Methods, Second Edition, Volume 7, Method Number P&CAM 339 (revised), Issued on 2/15/84.