



# VOLATILE ACIDS by Ion Chromatography

7907

(Hydrogen Chloride, Hydrogen Bromide, Nitric Acid)

Formulae: 1. HCl;  
2. HBr;  
3. HNO<sub>3</sub>

MW: Table 1

CAS: Table 1

RTECS: Table 1

**METHOD:** 7907, Issue 1

**EVALUATION:** FULL

**Issue 1:** 20 May 2014

**OSHA:** Table 2  
**NIOSH:** Table 2  
**Other OELs:** [1,2]

**PROPERTIES:** Table 3

**SYNONYMS:** 1) HCl: Hydrochloric acid, salt acid, muriatic acid; 2) HBr: Hydrobromic acid; 3) HNO<sub>3</sub>: azotic acid

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	Two (2) FILTERS in series separated with a chemically inert spacer: (1) pre-filter: 37-mm diameter quartz fiber filter; (2) sampling filter: 37-mm diameter quartz fiber filter impregnated with 500 µl Na <sub>2</sub> CO <sub>3</sub> solution (1 M)	<b>TECHNIQUE:</b>	ION CHROMATOGRAPHY (IC) with conductivity detection
<b>FLOW RATE:</b>	2 L/min	<b>ANALYTES:</b>	Chloride (Cl <sup>-</sup> ), bromide (Br <sup>-</sup> ) and nitrate (NO <sub>3</sub> <sup>-</sup> ) ion
<b>VOL-MIN:</b>	30 L	<b>EXTRACTION:</b>	Aqueous solution of sodium carbonate / sodium hydrogen carbonate
<b>-MAX:</b>	600 L	<b>INJECTION VOLUME:</b>	25 µL
<b>SHIPMENT:</b>	Routine	<b>ELUENT:</b>	3.1 mM Na <sub>2</sub> CO <sub>3</sub> / 0.35 mM NaHCO <sub>3</sub> , flow rate 1.5 mL/min
<b>SAMPLE STABILITY:</b>	Stable for 1 week @ 20 °C and 4 °C thereafter to at least 28 days [3]	<b>COLUMNS:</b>	Pre-column, anion-exchange column and suppressor column
<b>BLANKS:</b>	3 blanks minimum per set	<b>CALIBRATION RANGE:</b>	Chloride, bromide and nitrate at 0.4 mg/mL to 4 mg/mL
<b>ACCURACY*</b>		<b>ESTIMATED LOD:</b>	0.003 mg/sample for all three acids; or 0.0012 mg/m <sup>3</sup> for a 240 L air volume [4]
<b>RANGE STUDIED:</b>	HCl: 0.04 to 1.6 mg/sample; HBr: 0.03 to 2.3 mg/sample; HNO <sub>3</sub> : 0.04 to 1.5 mg/sample	<b>PRECISION ( <math>\bar{S}_r</math> ):</b>	0.01 for all three acids [3]
<b>BIAS*:</b>	Negligible [4]		
<b>OVERALL PRECISION ( <math>\hat{S}_{r,T}</math> )*:</b>	HCl, 0.06; HBr, 0.06; HNO <sub>3</sub> , 0.07 [4]		
<b>EXPANDED UNCERTAINTY*:</b>	Less than 12% for HCl and HBr; less than 14 % for HNO <sub>3</sub> [3,5]		
*Accuracy calculations were determined using ISO Guide 98 [5] rather than the traditional NIOSH accuracy criterion.			

**APPLICABILITY:** The working range is (at least) 0.01 to 2.0 mg/sample for a 240 Liter air sample [3,4].

**INTERFERENCES:** Inorganic acids can react with co-sampled particulate matter on the pre-filter, leading to low results. One such example is in the galvanizing industry, where the presence of zinc oxide can be a major confounding factor in the measurement of HCl. Potentially interfering particulate chlorides and nitrates removed by the pre-filter can react with the sampled acids and liberate HCl and HNO<sub>3</sub> that is subsequently collected on the sampling filter, leading to high results [6].

**OTHER METHODS:** This procedure, which is consistent with ISO 21438-2 [4], replaces NIOSH 7903 [7] for the determination of HCl, HBr and HNO<sub>3</sub> in workplace air samples by IC. The main advantage of this method is that it provides for lower limits of detection and quantitation for volatile acids due to higher sampling flow rates.

**REAGENTS:**

1. Water, deionized (DI),  $\geq 18$  M $\Omega$ -cm resistivity
2. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), anhydrous, American Chemical Society (ACS) analytical grade
3. Sodium hydrogen carbonate (NaHCO<sub>3</sub>), ACS analytical grade
4. Extraction & eluent stock solution: 0.62 M Na<sub>2</sub>CO<sub>3</sub> / 0.069 M NaHCO<sub>3</sub>; Dissolve 13.14 g Na<sub>2</sub>CO<sub>3</sub> and 1.15 g NaHCO<sub>3</sub> in 50 mL of deionized water and swirl to mix. Then bring to 200 mL in a volumetric flask, stopper and mix thoroughly.
5. Extraction and eluent solution; 0.0031 M Na<sub>2</sub>CO<sub>3</sub> / 0.00035 M NaHCO<sub>3</sub>; transfer 10 mL 0.62 M Na<sub>2</sub>CO<sub>3</sub> / 0.069 M NaHCO<sub>3</sub> stock solution to a 2 liter volumetric flask, dilute to the mark with deionized water, stopper and mix thoroughly.
6. Chloride (Cl<sup>-</sup>), bromide (Br<sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) standard solutions, 1000 mg/L.
7. Calibration stock solution, 100  $\mu$ g/mL (as the anion): Transfer 10 mL aliquots of chloride, bromide and nitrate standard solution into a 100 mL volumetric flask, dilute to the mark with deionized water, stopper and mix thoroughly.
8. Sodium carbonate solution, for impregnation of 37 mm diameter quartz fiber filters, 1 mol/L: dissolve 10.6 g Na<sub>2</sub>CO<sub>3</sub> in deionized water, quantitatively transfer the solution into a 100 mL volumetric flask, dilute to the mark with deionized water, stopper and mix thoroughly.
9. Preparation of the sampling filter: Apply 500  $\mu$ L of the sodium carbonate solution, 1 mol/L, evenly on the 37 mm quartz fiber filter and allow to dry for 6 hours in a desiccator. (See NOTE 1, Step 1, p 7907-3.) Good for 14 days.

\*See Special Precautions

**EQUIPMENT:**

1. Sampler: filter, 37-mm diameter quartz fiber impregnated with 500  $\mu$ L 1 M Na<sub>2</sub>CO<sub>3</sub>; and pre-filter, 37-mm diameter quartz fiber filter separated by a spacer in a chemically inert cassette filter holder
2. Spacers, of 37-mm diameter suitable for use with the samplers, manufactured from a chemically inert material, e.g. polypropylene sleeves
3. Personal sampling pump, 1 to 5 L/min, with flexible connecting tubing
4. Ion chromatograph (IC), with pre-column (50 mm by 4.0 mm), anion-exchange column (200 mm by 4.0 mm), suppressor column (4 mm) and conductivity detector; and connected to data processing unit
5. Ultrasonic bath
6. Vessels, 15-mL, plastic, with screw caps
7. Volumetric flasks, 10- to 2000 mL
8. Pipets, 10 to 5000  $\mu$ L
9. Beakers, 25 to 100 mL
10. Water purification system, to prepare  $\geq 18$  M $\Omega$ -cm resistivity deionized water
11. Bottles, polyethylene, 100 mL
12. Syringes, plastic, 5 mL
13. Syringe filter cartridges, with 0.45- $\mu$ m pore size polytetrafluoroethylene (PTFE) membrane filters
14. Micro-syringes, 50  $\mu$ L, with 60 mm x 0.6 mm needles
15. Auto-sampler vials, with slotted septum, 2 mL capacity
16. Analytical balance, with capability of weighing to nearest 0.01 mg

**SPECIAL PRECAUTIONS:** Wear gloves, lab coat, and safety glasses while handling acids. All work should be performed with adequate ventilation for personnel and equipment. It is imperative that acid be added to water in order to avoid a violent exothermic reaction. Avoid direct contact since acids are both corrosive and irritants to eyes, skin, and the respiratory system [8,9].

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**SAMPLING, SAMPLE TRANSPORT AND STORAGE:**

1. Prior to sampling, load each clean sampler, first with a sampling (impregnated) filter, then with a pre-filter, separating the filters with a spacer. Ensure that the configuration in which the filters are loaded leads to the sampled air passing first through the pre-filter and then through the sampling filter.  
Note 1: Three-piece polystyrene cassettes are appropriate, with the middle ring section of the cassette acting as the spacer. Impregnated filters that are stored in a desiccator can be prepared up to 14 days prior to their use for sampling.  
Note 2: Silica gel sorbent tubes [7] can be used in lieu of impregnated filters, but each sorbent tube must be preceded by a pre-filter.
2. Calibrate each personal sampling pump with a representative sampler in the line.
3. Sample accurately at 2 L/min for a total sample size of 30 to 500 L. Avoid sampler overloading [6].
4. Transport the samples to the laboratory in a manner that prevents contamination or damage to the filters.
5. Submit at least three blank impregnated filters as field blanks for each set of samples collected per day. Handle these in the same way as the field samples.
6. Ship all samples to the laboratory in accordance with established chain-of-custody procedures [10].
7. The samples can be stored at room temperature for one week; for longer storage, refrigerate the samples (4 °C).
8. Analyze samples between 4 days and 4 weeks of sample collection.

**SAMPLE PREPARATION:**

9. Prior to carrying out sample dissolution, store the sampling filter for at least four days (to avoid nitric acid losses).
10. Remove sample cassettes from storage and bring them to room temperature. Discard the pre-filters.  
NOTE: If desired, the pre-filters can be analyzed for determination of particulate chlorides, bromides and nitrates. If this analysis is carried out, it is recommended to rinse the inside surfaces of the sampler with a few mL of DI water so as to include wall deposits along with material collected on the prefilter.
11. Place the sampling filters (i.e., impregnated filter samples) in 15-mL plastic screw-cap vessels and add 10 mL of deionized water to each sample. Securely cap the vessels.
12. Sonicate the samples in an ultrasonic bath for at least 15 minutes, and allow to cool for approx. 30 minutes.
13. Using 5-mL syringes, filter 5-mL aliquots of each sample extract solution through a PTFE filter into clean auto-sampler vials.

**CALIBRATION AND QUALITY CONTROL:**

14. With dilution of the calibration stock solution in eluent solution, prepare calibration working standard solutions covering the range of approximately 0.4 to 4 mg/L of chloride, bromide and nitrate. Store working standards in tightly sealed polyethylene bottles. Prepare fresh working standards weekly.
15. Calibrate the ion chromatograph with at least six working standards covering the range of 0.4 to 4 mg/L of chloride, bromide and nitrate per sample by preparing a calibration graph of anion peak height (mm or  $\mu\text{S}$  [micro-siemens]) vs. concentration (mg/L).

16. Analyze working standards together with samples, reagent blanks and field blanks at a frequency of at least 1 per 20 samples (3 minimum of each).

#### MEASUREMENT:

17. Set the ion chromatograph to recommended eluent flow rate (e.g., 1.5 mL/min) and recommended pressure ( e.g.,  $1.1 \times 10^5$  kPa), and other conditions as specified by the instrument manufacturer.
18. Inject a sample aliquot, e.g., 25- $\mu$ L, into the chromatograph, and measure the peak heights of the chloride, bromide and nitrate peaks (at retention times of approx. 5 min, 9 min and 12 min, respectively). If the peak height exceeds the linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

#### CALCULATIONS:

19. Calculate the mass concentration of each anion, C (mg/m<sup>3</sup>), in the air volume sampled, V (L):

$$C = \left\{ \frac{(C_1 \cdot V_1 \cdot F_d) - (C_0 \cdot V_0)}{V} \right\} \cdot F_c$$

where:

$C_0$  = mean concentration, in mg/L, of anion in the field blank test solutions;

$C_1$  = concentration, in mg/L, of anion in the sample test solution;

V = volume, in liters, of the air sample;

$V_0$  = volume, in mL, of the field blank test solutions;

$V_1$  = volume, in mL, of the sample test solutions

$F_d$  = dilution factor for each sample test solution

$F_c$  = conversion factor to convert from anion to acid concentration ( $F_c = 1.0284$  for chloride, 1.0126 for bromide, and 1.0163 for nitrate)

#### EVALUATION OF METHOD:

On impregnated quartz fiber filters, greater than 95 % recovery of hydrochloric and nitric acid was found four weeks after sample collection, and no breakthrough was observed at sample loadings of up to 2.5 mg HCl or 5 mg HNO<sub>3</sub> [3,4,11]. Mean analytical recovery determined from the analysis of spiked filters has been found to be in the range of 97 to 100% for HBr, HCl and HNO<sub>3</sub> [3,11]. The component of the coefficient of variation of the method that arises from analytical variability, determined from the analysis of filters sampled at a dynamic test gas apparatus, was 0.8% to 1.3% for hydrogen chloride and 1.1% to 8.8% for nitric acid; and as determined from the analyses of spiked samples of hydrogen bromide, this value was 0.8% to 1.4% [3]. The method has been independently verified for all three acids, in accordance with applicable performance criteria [11,12]. An interlaboratory study with 5 participants found negligible biases and good agreement for hydrogen chloride and nitric acid at concentrations between 0.6 and 8 mg/m<sup>3</sup> for HCl and 0.8 and 10 mg/m<sup>3</sup> for HNO<sub>3</sub> [6]. The back-up data and user check reports are references 6 and 11, respectively.

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#### METHOD WRITTEN BY:

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**TABLE 1. General Information**

Acid	MW	CAS Number	RTECS Number
HCl	36.46	7647-01-0	MW4025000
HBr	80.91	10035-10-6	MW3850000
HNO <sub>3</sub>	63.01	7697-37-2	QU5775000

**TABLE 2. Occupational Exposure Limits**

Acid	OSHA	NIOSH
HCl	C <sup>a</sup> 5 ppm, 7 mg/m <sup>3</sup>	C <sup>a</sup> 5 ppm, 7 mg/m <sup>3</sup>
HBr	8 hr TWA <sup>b</sup> 3 ppm 10 mg/m <sup>3</sup>	C <sup>a</sup> 3 ppm, 10 mg/m <sup>3</sup>
HNO <sub>3</sub>	8 hr TWA <sup>b</sup> 2 ppm 5 mg/m <sup>3</sup>	TWA <sup>c</sup> 2 ppm 5 mg/m <sup>3</sup> STEL <sup>d</sup> 4 ppm 10 mg/m <sup>3</sup>

- a Ceiling Limit  
b Time-Weighted Average  
c Up to 10 hr TWA in a 40 hr work week  
d Short Term Exposure Limit

**TABLE 3. Properties**

Acid	Physical State	MP (°C)	BP (°C)	Vapor Pressure (VP)
HCl	gas	-114	-84.9	(38%) 28.3 kPa
	liquid	--	110	(azeotropic, 20.2%)
HBr	gas	-86.9	-66.8	2026.4 kPa
HNO <sub>3</sub>	liquid	-42	--	(68% Nitric) 101.3 kPa