

## NON-VOLATILE ACIDS (Sulfuric Acid and Phosphoric Acid) 7908

Formulae: H <sub>2</sub> SO <sub>4</sub>	MW: 98.08	CAS: 7664-93-9	RTECS: WS5600000
H <sub>3</sub> PO <sub>4</sub>	MW: 98.0	CAS: 7664-38-2	RTECS: TB6300000

**METHOD:** 7908, Issue 1

**EVALUATION:** FULL

**Issue 1:** 10 May 2014

*U.S. OELs*

**OSHA:** 1 mg/m<sup>3</sup> (H<sub>2</sub>SO<sub>4</sub> & H<sub>3</sub>PO<sub>4</sub>)

**NIOSH:** 1 mg/m<sup>3</sup> (H<sub>2</sub>SO<sub>4</sub> & H<sub>3</sub>PO<sub>4</sub>); STEL: 3 mg/m<sup>3</sup> (H<sub>3</sub>PO<sub>4</sub>)

*Other*

**OELs:** [1,2]

**PROPERTIES:**

**H<sub>2</sub>SO<sub>4</sub>:** Liquid, mp = 3.0 °C (98%); 10 °C (100%); bp = 338 °C (98%); 330 °C (100%); VP = < 0.0001 kPa @ 20 °C

**H<sub>3</sub>PO<sub>4</sub>:** Solid (often used in an aqueous solution), mp = 42.4 °C; bp = 158 °C; vp = 0.0038 kPa @ 20 °C

**SYNONYMS:** H<sub>2</sub>SO<sub>4</sub>: hydrogen sulfate, oil of vitriol;

H<sub>3</sub>PO<sub>4</sub>: ortho-phosphoric acid

SAMPLING	MEASUREMENT
<p><b>SAMPLER:</b> FILTER, 37-mm diameter quartz fiber; or polytetrafluoroethylene (PTFE), 0.45 µm pore size</p> <p><b>FLOW RATE:</b> 1 to 5 L/min</p> <p><b>VOL-MIN:</b> 15 L <b>-MAX:</b> 2000 L</p> <p><b>SHIPMENT:</b> 4 °C</p> <p><b>SAMPLE STABILITY:</b> Stable for 1 week at about 20 °C and at 4 °C thereafter to 28 days [3]</p> <p><b>BLANKS:</b> 3 field blanks minimum per set</p>	<p><b>TECHNIQUE:</b> ION CHROMATOGRAPHY (IC) with conductivity detection</p> <p><b>ANALYTES:</b> Sulfate (SO<sub>4</sub><sup>2-</sup>) ion, phosphate (PO<sub>4</sub><sup>3-</sup>) ion</p> <p><b>EXTRACTION:</b> Aqueous solution of sodium carbonate / sodium hydrogen carbonate</p> <p><b>INJECTION VOLUME:</b> 50 µL</p> <p><b>ELUENT:</b> 2.7 mM Na<sub>2</sub>CO<sub>3</sub>/0.3 mM NaHCO<sub>3</sub>, flow rate 1.5 mL/min</p> <p><b>COLUMNS:</b> Pre-column, anion-exchange column and suppressor column</p>
<b>ACCURACY*</b>	<p><b>CALIBRATION RANGE:</b> H<sub>2</sub>SO<sub>4</sub>: 0.2 mg/L to 8 mg/L; H<sub>3</sub>PO<sub>4</sub>: 0.8 mg/L to 8 mg/L [6]</p> <p><b>ESTIMATED LOD:</b> H<sub>2</sub>SO<sub>4</sub> = 0.002 mg/m<sup>3</sup>; H<sub>3</sub>PO<sub>4</sub> = 0.003 mg/m<sup>3</sup> (1 m<sup>3</sup> air volume)[6]</p> <p><b>PRECISION (<math>\bar{S}_r</math>):</b> H<sub>2</sub>SO<sub>4</sub> = 0.043; H<sub>3</sub>PO<sub>4</sub> = 0.032 [3,7]</p>
<p><b>RANGE STUDIED:</b> 0.005 to 2.0 mg/sample</p> <p><b>BIAS*:</b> Negligible [3]</p> <p><b>OVERALL PRECISION (<math>\hat{S}_{rT}</math>):</b> H<sub>2</sub>SO<sub>4</sub> = 0.086; H<sub>3</sub>PO<sub>4</sub> = 0.106</p> <p><b>EXPANDED UNCERTAINTY*:</b> less than 23% for both H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> [6]</p> <p>* Accuracy calculations were determined using references 5 and 6 rather than the traditional NIOSH accuracy criteria.</p>	

**APPLICABILITY:** The working range for H<sub>2</sub>SO<sub>4</sub> is (at least) 0.002 to 1.0 mg/sample, for H<sub>3</sub>PO<sub>4</sub> is 0.004 to 1.0 mg/sample for a 420 Liter air sample [3,6].

**INTERFERENCES:** Particulate salts of sulfate or phosphate will give a positive interference.

**OTHER METHODS:** This procedure, which is consistent with ISO 21438-1 [6], replaces NIOSH 7903 [8] for the determination of sulfuric and phosphoric acid in workplace air samples by IC. The main advantage of NIOSH method 7908 is that it can allow for the collection of the inhalable fraction of sulfuric and phosphoric acid aerosols by means of the pre-filter (housed within an optional inhalable sampler).

**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: 0.27 M Na<sub>2</sub>CO<sub>3</sub> / 0.03 M NaHCO<sub>3</sub>; dissolve 2.86 g Na<sub>2</sub>CO<sub>3</sub> and 0.25 g NaHCO<sub>3</sub> in 25 mL of deionized water and swirl to mix. Then bring to 100 mL in a volumetric flask, stopper and mix thoroughly.
5. Extraction & eluent solution: 0.0027 M Na<sub>2</sub>CO<sub>3</sub> / 0.0003 M NaHCO<sub>3</sub>; transfer 10 mL of 0.27 M Na<sub>2</sub>CO<sub>3</sub> / 0.03 M NaHCO<sub>3</sub> stock solution to a 1 L volumetric flask, dilute to the mark with deionized water, stopper and mix thoroughly.
6. Sulfate (SO<sub>4</sub><sup>2-</sup>) ion and phosphate (PO<sub>4</sub><sup>3-</sup>) ion standard solutions, each 1000 mg/L
7. Calibration stock solution, 100 mg/L (as the anion): Place 10 mL aliquots of sulfate and phosphate standard solution into a 100 mL volumetric flask, dilute to the mark and mix thoroughly.

\*See Special Precautions

**EQUIPMENT:**

1. Sampler: filter, 37-mm diameter quartz fiber; or polytetrafluoroethylene (PTFE), 0.45  $\mu$ m pore size, in cassette filter holder manufactured from acid-resistant (chemically inert) material  
NOTE: Quartz fiber filters should be binderless and heat-treated.
2. Personal sampling pump, 1 to 5 L/min, with flexible connecting tubing
3. Ion chromatograph, 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
4. Ultrasonic bath
5. Vessels, 10-mL, plastic (e.g., polypropylene), with screw caps
6. Volumetric flasks, 25- to 1000 mL
7. Pipets, 50 to 10000  $\mu$ L
8. Beakers, 25 to 100 mL
9. Water purification system, to prepare greater than or equal to 18 M $\Omega$ -cm resistivity deionized water
10. Bottles, polyethylene, 100 mL
11. Syringes, plastic, 5 mL
12. Syringe filter cartridges, with 0.8- $\mu$ m pore size polytetrafluoroethylene (PTFE) membrane filters
13. Micro-syringes, 50  $\mu$ L, with 60 mm x 0.6 mm needles
14. Tweezers, PTFE-coated
15. Auto-sampler vials, 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. There is risk of fire and explosion when phosphoric acid has contact with bases, combustible substances, oxidizing agents, reducing agents or water. Avoid physical contact since both sulfuric and phosphoric acid are both corrosive and irritants to eyes, skin, and the respiratory system. These are caustic materials and can react with metals to form flammable hydrogen gas. Do NOT mix with solutions containing bleach or ammonia [9,10].

**SAMPLING, SAMPLE TRANSPORT AND STORAGE:**

1. Calibrate each personal sampling pump with a representative sampler in-line.
2. Sample at an accurately known flow rate between 1 and 5 L/min for a total sample size of 15 to 1000 Liters. Avoid sampler overloading.
3. Immediately after sampling, remove the filter from the cassette with PTFE-coated tweezers and place it in a 10-mL screw-cap plastic vessel. With about 2 mL extraction

- solution (0.27 M Na<sub>2</sub>CO<sub>3</sub> 0.03 M NaHCO<sub>3</sub>), rinse material from the inside surfaces of the cassette into the vessel. Add additional extraction solution into the vessel until a final volume of 5 mL is reached.
4. Submit at least three field blanks for each set of samples collected per day. Handle these in the same way as the field samples; i.e., place each filter into a vessel, add 5 mL of eluent solution and ship it to the lab along with the remaining samples.
  5. Refrigerate all samples that are to be stored overnight (or longer) prior to shipment to the laboratory. Ship all samples to the laboratory in accordance with established chain-of-custody procedures [11].
  6. Refrigerate the samples (4 °C) immediately upon receipt at the lab until ready for analysis.
  7. Analyze samples within 4 weeks of receipt.

**SAMPLE PREPARATION:**

8. Remove sample vessels from storage and bring them to room temperature.
9. Sonicate the samples in an ultrasonic bath for at least 15 minutes and allow to cool for at least 30 minutes.
10. Using 5-mL syringes, filter each sample extract solution through a PTFE filter into clean plastic vessels or into autosampler vials (if autosampler used).

**CALIBRATION AND QUALITY CONTROL:**

11. Through dilution of the calibration stock solution in eluent solution, prepare calibration working standard solutions covering the range of approximately 0.2 to 8 mg/L of sulfate and phosphate. Store working standards in tightly sealed polyethylene bottles. Prepare fresh working standards weekly.
12. Calibrate the ion chromatograph with at least six working standards covering the range of 0.2 to 8 mg/L of sulfate and phosphate ion per sample by preparing a calibration graph of anion peak height (mm or µS [micro siemens]) vs. concentration (mg/L).
13. 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:**

14. Set the ion chromatograph to desired eluent flow rate, e.g., 1.5 mL/min, and column pressure, e.g., 1.1 x 10<sup>5</sup> kPa, and other conditions as specified by the instrument manufacturer.
15. Inject a sample aliquot, e.g., 50-µL, into the chromatograph, and measure the peak heights of the phosphate and sulfate peaks (at retention times of about 9 min and 11.6 min, respectively). If the peak height exceeds the linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

**CALCULATIONS:**

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

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

where:

C<sub>0</sub> = mean concentration, in mg/L, of anion in the field blank test solutions;

C<sub>1</sub> = concentration, in mg/L, of anion in the sample test solution;

V<sub>1</sub> = volume, in liters, of the air sample;

V<sub>0</sub> = 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:

$F_c = 1.021$  for sulfate;  $F_c = 1.031$  for phosphate

#### EVALUATION OF METHOD:

Laboratory testing with generated atmospheres of sulfuric acid mist yielded a collection efficiency of greater than 95% over the range 0.5 to 10 mg/m<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> on 0.45 µm pore size PTFE filters [4]. Greater than 95% recovery of sulfuric acid and phosphoric acid was found four weeks after sample collection. On quartz fiber filters, 97 to 100% recovery of sulfuric acid was found four weeks after sample collection, and no breakthrough was observed at sample loadings of up to 1 mg [3]. Mean analytical recovery determined from the analysis of spiked quartz fiber filters has been found to be in the range of 97 to 100% for both acids [3,4]. The component of the coefficient of variation of the method that arises from analytical variability, determined from the analysis of spiked quartz fiber filters, was 0.7% to 3.2% for phosphoric acid and 0.5% to 2.6% for sulfuric acid [3]. An interlaboratory study with 26 participants found negligible biases and interlaboratory relative standard deviations of 12 to 15% for sulfuric acid and phosphoric acid concentrations between 0.05 and 1 mg/m<sup>3</sup> [12]. The method has also been field tested for sulfuric acid measurements at sample volumes of up to nearly 2,000 Liters [13]. The analytical figures of merit for the method satisfy performance criteria specified in an applicable consensus standard [14]. The back-up data and user check reports are references 4 and 12 respectively.

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