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

Formulae:	MW:	CAS:	RTECS:
H_2SO_4	98.08	7664-93-9	WS5600000
H_3PO_4	98.00	7664-38-2	TB6300000

METHOD: 7908, Issue 2 **EVALUATION: FULL**

Issue 1: 10 May 2014
Issue 2: 16 November 2023

OSHA: 1 mg/m³ (H_2SO_4 & H_3PO_4)
NIOSH: 1 mg/m³ (H_2SO_4 & H_3PO_4); STEL: 3 mg/m³ (H_3PO_4)
OTHER OELS: [1,2]

PROPERTIES [3]:
H_2SO_4: Liquid, mp = 10 °C; bp = 337°C
H_3PO_4: Solid (often used in an aqueous solution), mp = 42.4°C; bp = 407 °C

SYNONYMS: H_2SO_4: hydrogen sulfate, oil of vitriol; H_3PO_4: ortho-phosphoric acid

SAMPLING

SAMPLER:	FILTER, 37-mm diameter quartz fiber; or polytetrafluoroethylene (PTFE), 0.45 µm pore size
FLOW RATE:	1 to 5 L/min
VOL-MIN:	15 L
-MAX:	1000 L
SHIPMENT:	4 °C
SAMPLE STABILITY:	Filter: at least 7 days at room temp. (See Evaluation section); Extract: 1 week at room temp. and at 4 °C thereafter to 28 days [4,5]
BLANKS:	3 field blanks minimum per set

ACCURACY*

RANGE STUDIED:	0.005 to 2.0 mg/sample
BIAS*:	Negligible [5]
OVERALL PRECISION $(\hat{S}_{rT})$*:	H_2SO_4 = 0.107; H_3PO_4 = 0.106 [6]
EXPANDED UNCERTAINTY*:	less than 23% for both H_2SO_4 and H_3PO_4 [5]

* Accuracy calculations were determined using references 5 and 7 rather than the traditional NIOSH accuracy criteria.

MEASUREMENT

TECHNIQUE:	ION CHROMATOGRAPHY (IC) with conductivity detection
ANALYTES:	Sulfate (SO_4^{2-}) ion, phosphate (PO_4^{3-}) ion
EXTRACTION:	Aqueous solution of sodium carbonate / sodium hydrogen carbonate
INJECTION VOLUME:	50 µL
ELUENT:	2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$, flow rate 1.5 mL/min
COLUMNS:	Pre-column, anion-exchange column and suppressor column
CALIBRATION RANGE:	H_2SO_4 = 0.06 mg/L to 10 mg/L; H_3PO_4 = 0.1 mg/L to 10 mg/L
ESTIMATED LOD:	H_2SO_4 = 0.001 mg/sample (quartz), 0.0003 mg/sample (PTFE); H_3PO_4 = 0.0005 mg/sample (quartz or PTFE) [8]
PRECISION $(\hat{S}_r)$:	H_2SO_4 = 0.043; H_3PO_4 = 0.032 [4,6]

APPLICABILITY: The working range for H_2SO_4 is (at least) 0.008 to 1.0 mg/sample and for H_3PO_4 is 0.004 to 1.0 mg/sample for a 420 Liter air sample [6,8]. This method has been updated to include sample storage study and filter variability information.

INTERFERENCES: Particulate salts of sulfate or phosphate will give a positive interference. Both quartz fiber and PTFE filters may have a variable sulfate background.

OTHER METHODS: This procedure, which is consistent with ISO 21438-1 [5], replaces NIOSH 7903 [9] 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), ≥18 MΩ-cm resistivity
2. Sodium carbonate (Na_2CO_3), anhydrous, American Chemical Society (ACS) analytical grade
3. Sodium hydrogen carbonate ($NaHCO_3$), ACS analytical grade
4. Extraction & eluent stock solution: 0.27 M Na_2CO_3 / 0.03 M $NaHCO_3$; dissolve 2.86 g Na_2CO_3 and 0.25 g $NaHCO_3$ 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_2CO_3 / 0.0003 M $NaHCO_3$; transfer 10 mL of 0.27 M Na_2CO_3 / 0.03 M $NaHCO_3$ stock solution to a 1 L volumetric flask, dilute to the mark with deionized water, stopper and mix thoroughly.
6. Sulfate (SO_4^{2-}) ion and phosphate (PO_4^{3-}) 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-µm 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 or 15-mL, plastic (e.g., polypropylene), with screw caps
6. Volumetric flasks, 25- to 1000-mL
7. Pipets, 50- to 10,000-µL
8. Beakers, 25- to 100-mL
9. Water purification system, to prepare greater than or equal to18 MΩ-cm resistivity deionized water
10. Bottles, polyethylene, 100-mL
11. Syringes, plastic, 5-mL
12. Syringe filter cartridges, with 0.8-µm pore size PTFE membrane filters
13. Micro-syringes, 50-µL, 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 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 [10,11].

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 (0.0027 M Na_2CO_3 / 0.0003 M $NaHCO_3$), rinse material from the inside surfaces of the cassette into the vessel. Add extraction solution into the vessel until a final volume of 5 mL is reached.

NOTE: If field desorption is not possible, filters may be stored within the cassettes or transferred to 15-mL polypropylene tubes for shipment to laboratory. However, samples should be prepared in a timely manner after receipt by the laboratory. See Evaluation Section for more information.

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 [12].
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:

NOTE: If samples were not field desorbed, begin sample preparation with Step 3.

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 0.06 to 10 mg/L of sulfate and phosphate. Modify the range of calibration standards depending upon the working range for your instrumentation. 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 0.06 to 10 mg/L of sulfate and phosphate ion per sample by preparing a calibration graph of anion peak height (μS [micro siemens]) vs. concentration (mg/L).
13. Analyze at least one calibration standard per ten samples to confirm that instrument calibration is maintained over the course of the analytical run.
14. Check recoveries with QC samples of at least one media blank (minimum of 3) and at least one spiked media blank per twenty samples (or batch). QC values should be within established control limits. If not, the batch is considered out of control and corrective actions taken before more samples are analyzed.
15. Analyze working standards together with samples, reagent blanks, field blanks, and QC samples.

MEASUREMENT:

16. Set the ion chromatograph to desired eluent flow rate, e.g.,1.5 mL/min, and column pressure, e.g., 1.1 x 10^5 kPa, and other conditions as specified by the instrument manufacturer.
17. 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:

18. Calculate the mass concentration of each anion, C (mg/m^3), in the air volume sampled, V (L):

$$C = \left(\frac{((C_1 * V_1 * F_d) - (C_0 * V_0)) * 1000}{V} \right) * F_c$$

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 L, of the field blank test solutions;
V_1 = volume, in L, 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:

Reported recoveries of sulfuric acid were greater than 95% over the range of 0.1 to 2 times the limit value on 0.45-µm pore size PTFE filters [13]. Greater than 95% recovery of extracts of sulfuric acid and phosphoric acid collected on quartz fiber filters was found four weeks after sample collection with extracted samples stored at room temperature for 7 days and under refrigeration thereafter [4]. The validated measuring range extends to 1 mg/m^3 [6]. 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 [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 [4]. 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^3 [14]. The method has also been field tested for sulfuric acid measurements at sample volumes of up to nearly 2,000 liters [15]. The analytical figures of merit for the method satisfy performance criteria specified in an applicable consensus standard [16]. Issue 1 validation data are found in references 4, 6, and 13 and the user check report is found in reference 14.

Issue 2 Revisions:
In this issue, the calibration range is updated to match what was used for the new studies, and information on the storage stability of samples, i.e., the need for field desorption, and filter variability is added.

In ISO 21438-1 [5] samples are reported to be stable for 4 weeks; however, sample preparation includes field desorption of quartz fiber filters and users are cautioned about anecdotal evidence relating to the storage of quartz fiber filters. NIOSH conducted a series of storage stability studies to test the necessity of field desorption, fully described in [8]. In one study quartz fiber filters were spiked with sulfuric and phosphoric acids at 2 levels (10 µg and 40 µg). Filters were stored at ambient temperature, either within a closed-faced cassette (CFC) assembly or in 15-mL polypropylene tubes, and analyzed at Days 0, 7, and 14. For sulfuric acid spikes, sample stability was affected by spike level. For this reason, quartz fiber filter samples containing sulfuric acid should be prepared within 7 days of sampling. Phosphoric acid quantitatively recovered regardless of concentration or storage vessel over the 14 days of the study, however, the recovery did decline over the storage period.

In another study PTFE filters were spiked with sulfuric and phosphoric acid at 4 levels within the analytical range of the method (10, 40, 160, and 1000 µg), separately and in combination [16]. Samples were stored within acid-resistant cassettes at ambient temperature. No significant difference was found between acids spiked separately or in combination. Sample storage stability varied based upon spike level and the results at the 160 and 1000 µg levels were found to be significantly different ($p=0.0060$). For nearly all of the spike levels, the samples were found to be stable for 28 days. Outliers in the reported storage stability study may be due to issues with spiking relatively large acid volumes onto filters and handling spiked filters where the liquid was still present, neither of which would be conditions encountered with field samples.

NIOSH also conducted studies on the background levels of sulfuric and phosphoric acid in quartz fiber and PTFE filters [16]. Quartz fiber filters were tested from three manufacturers. Multiple lots were tested, when available. A sulfuric acid background was found on all filters, with % RSDs ranging from 7 to 69%. No phosphoric acid was detected on the quartz fiber filters. PTFE filters were tested from two manufacturers. Multiple lots were tested, when available. One lot (of three tested) from a single manufacturer had a variable sulfuric acid background (110% RSD) and one filter from the other manufacturer had a sulfuric acid response.

In each instance, the responses were near the LOD. No phosphoric acid background was detected on the PTFE filters. Method users are encouraged to adequately assess and understand the background response when analyzing samples for sulfuric acid.

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