



Determination of anionic impurities in sulfuric acid using ion chromatography

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Keywords

Dionex IonPac AS19 column,
Dionex IonPac AS23-4 μ m column,
Dionex ICS-5000+ HPIC system,
Dionex ICS-6000 HPIC system,
suppressed conductivity detector

Goal

To develop direct injection methods for the determination of anionic impurities in concentrated sulfuric acid

Introduction

Sulfuric acid is used in the manufacturing processes of many products in a wide range of industries. Trace ionic impurities in concentrated sulfuric acid can have a direct impact on the yield and reliability of chemical and semiconductor material processes such as wafer cleaning. However, the determination of anionic impurities in concentrated acids has been an analytical challenge; for example, the titration method is cumbersome, tedious, and uses hazardous chemicals. Ion chromatography is a promising alternative technique to determine low levels of anionic impurities. However, while low concentrations of contaminating anions in weaker acids such as hydrofluoric acid and phosphoric acid can be determined using online ion-exclusion sample preparation, that approach cannot be used for a strong acid like sulfuric acid.^{1,2} In sulfuric acid, the high concentration of sulfate limits the amount that can be injected into the anion-exchange column, thus limiting method sensitivity. Therefore, in this application, we take an approach similar to the approach for determining anionic contamination in another strong acid, nitric acid.³ In this approach, the concentrated sulfuric acid sample is diluted, and a volume that has been empirically determined to avoid overloading a high-capacity column is injected. We developed two methods for this analysis: Method 1 uses a Thermo Scientific™ Dionex™ IonPac™ AS19 column with a hydroxide eluent to determine fluoride, chloride, bromide, nitrite, and

nitrate; Method 2 uses a Thermo Scientific™ Dionex™ IonPac™ AS23-4µm column with a carbonate/bicarbonate eluent to determine phosphate. Key performance parameters were evaluated including response linearity for each analyte, limits of detection, and accuracy.

Experimental

Equipment

Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system including*:

- Dionex ICS-5000+ DP Pump module
- Dionex ICS-5000+ EG Eluent Generator module with high-pressure degasser module
- Dionex ICS-5000+ DC Detector/Chromatography module with conductivity detector
- Dionex AS-AP Autosampler with 250 µL sample syringe (P/N 074306) and 1200 µL buffer line (P/N 074989) and 10 mL vial trays

*These methods can also be run on a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system or Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system

Software

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS), version 7.2 SR4

Method 1 consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 500 Continuously Regenerated Anion Trap Column (P/N 075550)
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 2 mm (P/N 082541)

Method 2 consumables

- Thermo Scientific™ Dionex™ EGC 500 K₂CO₃ Eluent Generator Cartridge (P/N 088453)
- Thermo Scientific™ Dionex™ EPM 500 Electrolytic pH Modifier (P/N 088471)
- Thermo Scientific™ Dionex™ EGC 500 Carbonate Mixer Kit, 4 mm (P/N 088468)
- Thermo Scientific™ Dionex™ AERS™ 500 Carbonate Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 085029)

- Thermo Scientific™ Dionex™ CRD 300 Carbonate Removal Device, 4 mm (P/N 064637)
- Thermo Scientific™ Dionex™ VP Vacuum Pump (P/N 066463)

Reagents and standards

- Deionized water (DI), Type I reagent grade, 18 MΩ·cm resistivity or better
- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anion standards

Samples

Sulfuric acid 93–98%, TraceMetal™ (Fisher Scientific P/N A510-P500)

Chromatographic conditions

Method 1

Columns:	Dionex IonPac AS19 Analytical, 2 × 250 mm (P/N 062886) Dionex IonPac AG19 Guard Column, 2 × 50 mm (P/N 062888)
Eluent:	Eluent: 14 mM KOH from 0–25 min, 14–50 mM KOH from 25–30 min, 50 mM from 30–40 min*
Eluent source:	Dionex EGC 500 KOH cartridge with CR-ATC 500
Flow rate:	0.3 mL/min
Column temp.:	30 °C
Injection volume:	25 µL (Full loop)
Detection:	Dionex AERS 500 (2 mm) Suppressor, recycle mode, 38 mA current
Detection temp.:	35 °C
Suppressor compartment:	20 °C
Background conductance:	<0.5 µS/cm
System backpressure:	~2000 psi
Noise:	<2 nS/cm
Run time	46 min

* Method returns to 14 mM KOH for 6 min prior to injection

Method 2

Columns:	Dionex IonPac AS23-4µm Analytical, 4 × 250 mm (P/N 302555) Dionex IonPac AG23-4µm Guard, 4 × 50 mm (P/N 302556)
Eluent:	4.5 mM K ₂ CO ₃ /0.8 mM KHCO ₃
Eluent source:	Dionex EGC 500 K ₂ CO ₃ Eluent Generator Cartridge with Dionex EPM 500 Electrolytic pH Modifier
Flow rate:	1 mL/min
Column temp.:	30 °C
Injection volume:	25 µL (Full loop)
Detection:	Suppressed conductivity, Dionex AERS 500 Carbonate suppressor (4 mm), recycle mode, 32 mA current, with CRD 300 in vacuum mode
Detection temp.:	35 °C
Suppressor compartment:	20 °C
Background conductance:	<1.8 µS/cm
System backpressure:	~3300 psi
Noise:	<2 nS/cm
Run time	30 min

Standards preparation

Stock standard solutions

Prepare stock standard solutions (1000 mg/L) by dissolving the appropriate amounts of the required analytes in 100 mL of DI water according to Table 1.

Table 1. Masses of compounds used to prepare 100 mL of 1000 mg/L ion standards.

Analyte	Compound	Amount (mg)
Fluoride	Sodium fluoride (NaF)	221.0
Chloride	Sodium chloride (NaCl)	164.9
Nitrite	Sodium nitrite (NaNO ₂)	150.0
Bromide	Sodium bromide (NaBr)	128.8
Nitrate	Sodium nitrate (NaNO ₃)	137.1
Phosphate	Potassium phosphate, monobasic (KH ₂ PO ₄)	143.3

Working standard solutions

Six anion standard solution, 10 mg/L

Accurately pipette 1 mL of each single standard stock solution (Table 1) into a 100 mL volumetric flask and fill to the mark with DI water.

Calibration standards 0.5–500 µg/L

Prepare 500, 200, 100, 50, 25, 10, 5, 2, 1, and 0.5 µg/L standards by diluting the six anion standard solution (10 mg/L) with DI water.

Sample preparation

Add 100 µL of sulfuric acid to 99.9 mL of DI H₂O and mix well to prepare a 0.018 M sulfuric acid solution. This concentration was selected in order to avoid exceeding the column capacity while minimizing the need for dilution.

Results and discussion

Separation

The Dionex IonPac AS19 column, in combination with the Dionex IonPac AG19 guard column, is designed for the determination of inorganic anions and oxyhalides using isocratic or gradient elution with an hydroxide eluent.⁴ Electrolytic eluent generation simplifies the method, avoids manual eluent preparation, improves reproducibility, and provides a high degree of automation.

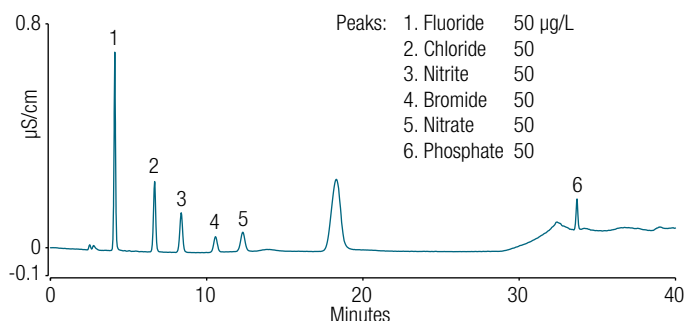


Figure 1. Separation of a six anion standard mixture using Method 1

Figure 1 shows that fluoride, chloride, nitrite, bromide, nitrate, and phosphate were well resolved under the conditions given as Method 1. Under these conditions, phosphate elutes after sulfate, which has a retention time (RT) of 20 min, rendering phosphate determination in sulfuric acid difficult.

The Dionex IonPac AS23-4µm column is a high-capacity anion exchange column specifically designed for use with carbonate/bicarbonate eluents for the determination of trace disinfection byproducts, such as chlorite, bromate, and chlorate together with common inorganic anions, including bromide.⁵ The high capacity of the column, the excellent resolution of inorganic anions, and the elution of phosphate before sulfate (RT= 22 min) makes this column a primary candidate for this application. To simplify the method and avoid manual eluent preparation, the Dionex IonPac AS23-4µm column was used with automated carbonate/bicarbonate eluent generation. We also used the Dionex CRD300 Carbonate Removal Device to remove carbonate from

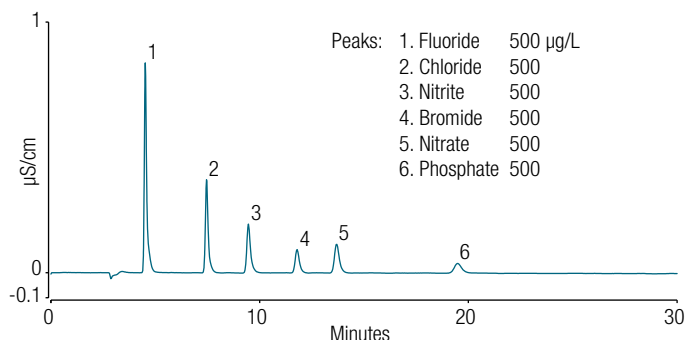


Figure 2. Separation of a six anion standard mixture using Method 2

the eluent and sample before it enters the conductivity cell, thereby reducing the background conductivity and improving detection limits. To set up the Dionex CRD 300 Carbonate Removal Device in vacuum mode, see the Dionex CRD 300 device⁶ and VP pump manuals⁷ and Application Note 72209⁸ for more information. Figure 2 shows that fluoride, chloride, nitrite, bromide, nitrate, and phosphate were resolved using a Dionex IonPac AS23-4µm column.

Method calibration ranges, limits of detection (LOD), and limits of quantitation (LOQ)

Table 2 summarizes the calibration, LOD, and LOQ of fluoride, chloride, nitrite, bromide, and nitrate using Method 1. Table 3 summarizes the calibration, LOD, and LOQ of phosphate using Method 2. Calibration standards were prepared ranging from 0.5 to 500 µg/L. The levels that were used to construct calibration curves of each anion are summarized in Tables 2 and 3. Figures 3–8 show examples of the calibration curves of fluoride, chloride, nitrite, bromide, nitrate, and phosphate.

Table 2. Calibration, LOD, and LOQ of five anions using Method 1

Analyte	Range (µg/L)	Coefficient of Determination (r^2) Linear fitting	LOD (µg/L)	LOQ (µg/L)	LOD in concentrated sulfuric acid (mg/L)	LOQ in concentrated sulfuric acid (mg/L)	LOD in 10% (w/w) sulfuric acid (µg/L)	LOQ in 10% (w/w) sulfuric acid (µg/L)
Fluoride	1–50	0.9998	0.19	0.64	0.19	0.64	19.4	65.3
Chloride	0.5–50	0.9999	0.05	0.17	0.05	0.17	5.10	17.3
Nitrite	2–50	0.9998	0.37	1.23	0.37	1.23	37.8	126
Bromide	5–50	0.9998	1.50	5.00	1.50	5.00	153	510
Nitrate	2–50	0.9999	0.47	1.55	0.47	1.55	48.0	158

Table 3. Calibration, LOD, and LOQ of phosphate using Method 2

Analyte	Range (µg/L)	Coefficient of Determination (r^2) Linear fitting	LOD (µg/L)	LOQ (µg/L)	LOD in concentrated sulfuric acid (mg/L)	LOQ in concentrated sulfuric acid (mg/L)	LOD in 10% (w/w) sulfuric acid (µg/L)	LOQ in 10% (w/w) sulfuric acid (µg/L)
Phosphate	50–500	0.9994	12.6	42	12.6	42	1.29	4.29

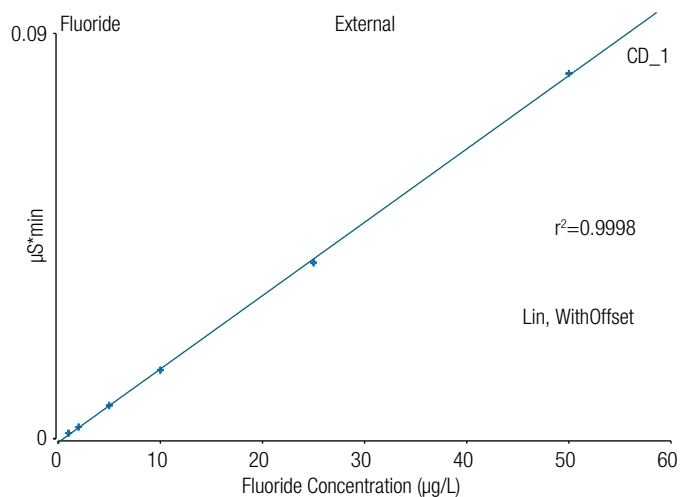


Figure 3. Fluoride calibration curve using Method 1

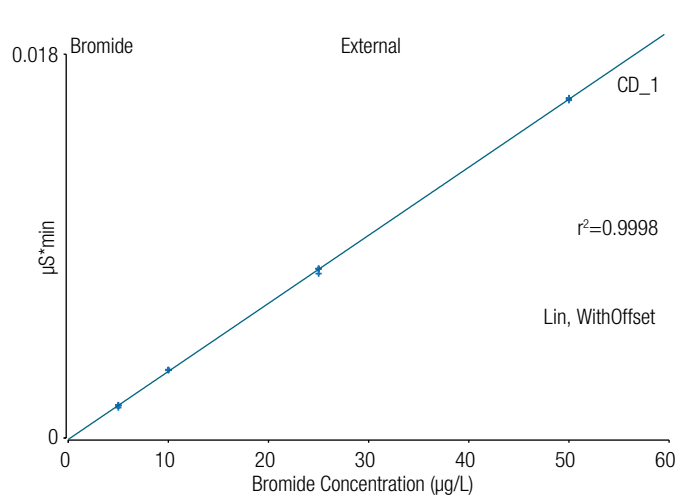


Figure 6. Bromide calibration curve using Method 1

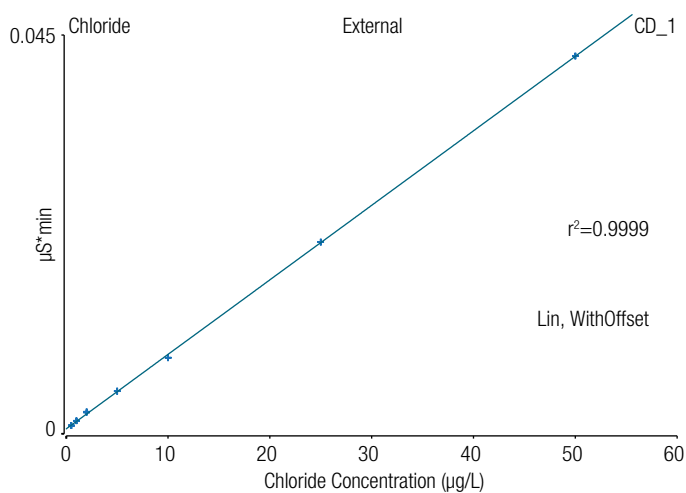


Figure 4. Chloride calibration curve using Method 1

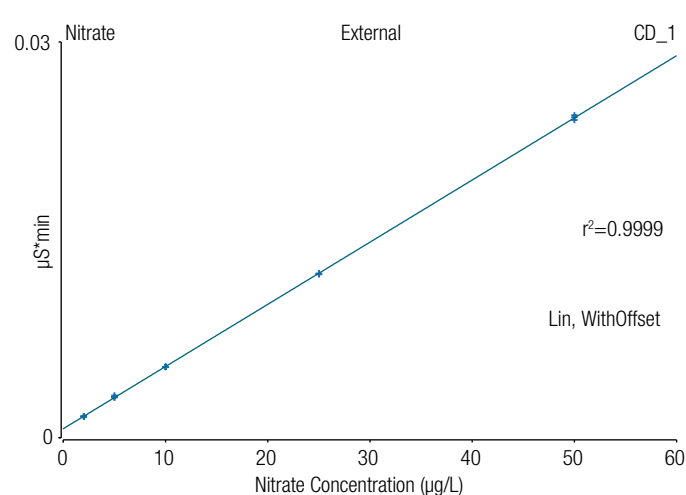


Figure 7. Nitrate calibration curve using Method 1

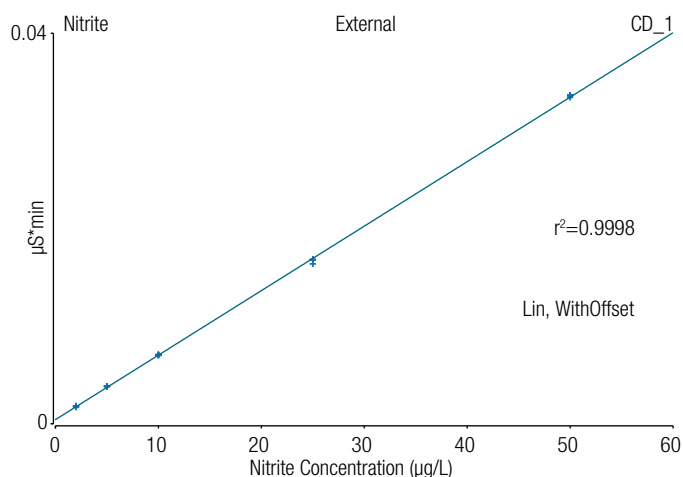


Figure 5. Nitrite calibration curve using Method 1

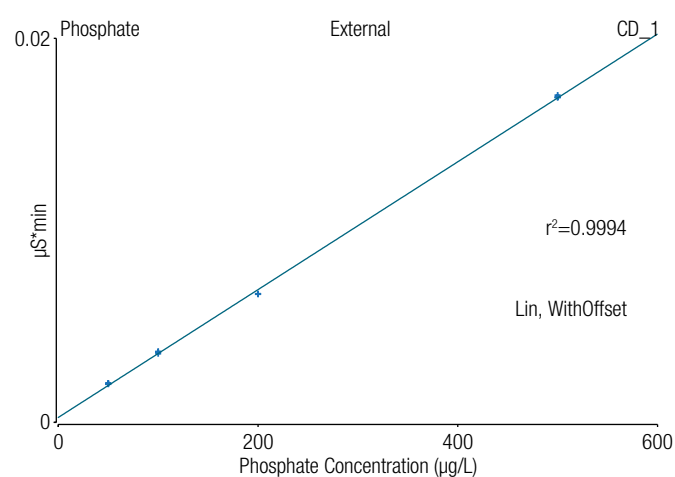


Figure 8. Phosphate calibration curve using Method 2

Signal-to-noise ratios (S/N) of 3 and 10 were used for the determinations of the LOD and LOQ, respectively.⁹ To determine the LOD and LOQ, the baseline noise was first determined by measuring the peak-to-peak noise in a representative one-minute segment of the baseline where no peaks elute but close to the peak of interest. The signal response was determined from the average peak height of three injections of the lowest concentration calibration standard.

Sample analysis and accuracy

Method 1 was developed to determine five anionic impurities (fluoride, chloride, bromide, nitrite, and nitrate) in sulfuric acid. Figure 9 shows the overlay of sample vs. sample spiked with 10 µg/L of six anion standards. The Dionex IonPac AS19 column achieves excellent resolution and sensitive detection for the five anions.

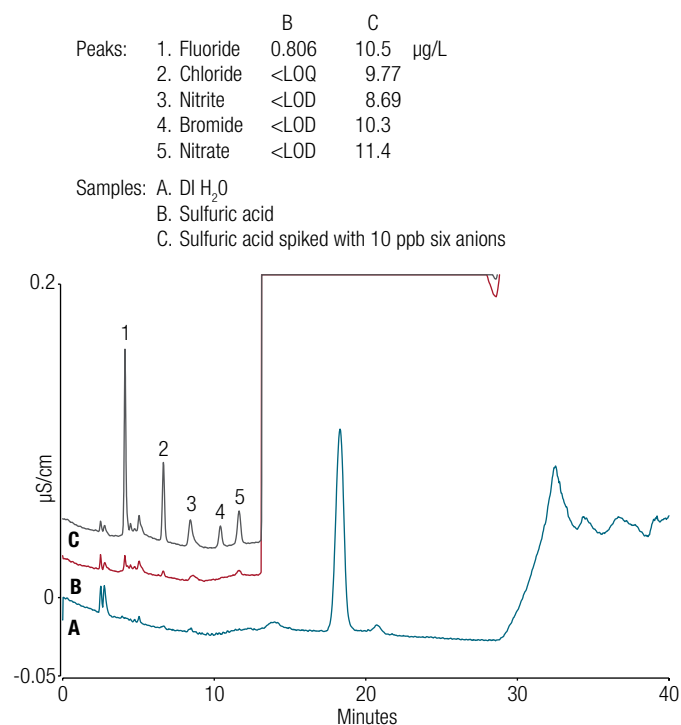


Figure 9. Overlay of chromatograms of sample vs. sample spiked with 10 µg/L of the six anions standards mix using Method 1

Method 2 was initially developed to determine all six anionic impurities in sulfuric acid. Figure 10 shows the overlay of sample vs. sample spiked with 50 µg/L of six anionic standards. As shown in Figure 10, the sample has a strong influence on the separation. Integration of the peak and quantification of fluoride, chloride, bromide, nitrite, and nitrate is difficult due to baseline instability after their elution. Phosphate is not affected and elutes fully resolved from the large sulfate peak. Therefore, Method 2 is only suitable for the determination of phosphate, which cannot be determined by Method 1.

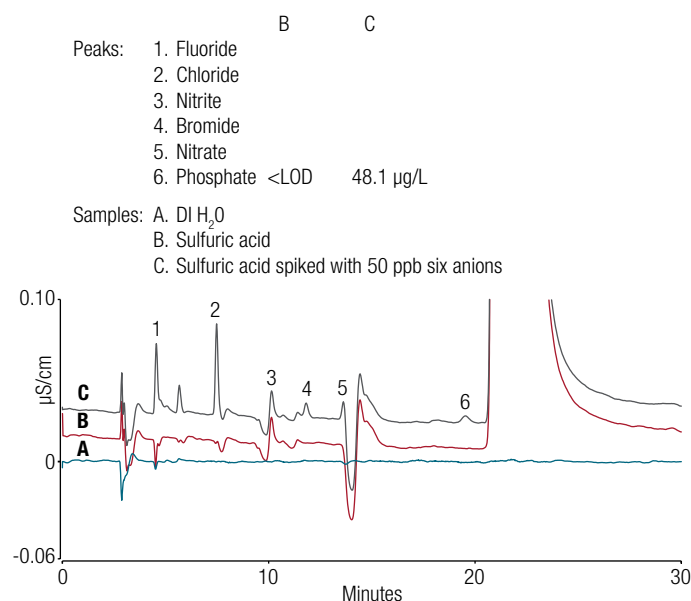


Figure 10. Overlay of chromatograms of sample vs. sample spiked with 50 µg/L of the six anions standards mix using Method 2

The accuracy of the two methods was evaluated through recovery studies using spiked sulfuric acid samples. Table 4 shows the amount detected and the recoveries obtained using Method 1 for fluoride, chloride, bromide, nitrite, and nitrate spiked in sulfuric acid. Table 5 shows the amount detected and the recoveries obtained using Method 2 for phosphate spiked in sulfuric acid. All anions demonstrate acceptable recoveries (85–115%). The lower recovery for nitrite can be explained as a result of its oxidization to nitrate in the spiked sulfuric acid sample before injection.

Table 4. Recoveries of five anions spiked in sulfuric acid using Method 1

Analyte	Found (µg/L)	Added (µg/L)	Recovery (%)
Fluoride	0.806	10	97.3
Chloride	<LOQ	10	97.7
Nitrite	<LOD	10	86.9
Bromide	<LOD	10	103
Nitrate	<LOD	10	114

Table 5. Recovery of phosphate spiked in sulfuric acid using Method 2

Analyte	Found (µg/L)	Added (µg/L)	Recovery (%)
Phosphate	<LOD	50	96.2

Table 6. Precision

Analyte	Method	Standard Concentration (µg/L)	Retention Time Precision (RSD)	Peak Area Precision (RSD)
Fluoride	1	10	0.05	0.60
Chloride	1	10	0.03	0.17
Nitrite	1	10	0.02	0.66
Bromide	1	10	0.10	0.43
Nitrate	1	10	0.03	0.01
Phosphate	2	200	0.04	0.28

Precision

Table 6 shows retention time and peak area precisions from three standard injections. The excellent retention time stability and peak area precision are consistent with results obtained when using an electrolytically generated high-purity eluent. The use of such eluent also simplifies the method by eliminating the need for manual eluent preparation and by reducing the time for method development.

Conclusion

This study demonstrated that anionic impurities such as fluoride, chloride, nitrite, bromide, and nitrate can be determined accurately in sulfuric acid using Method 1. Method 1 uses a Dionex IonPac AS19 column with hydroxide eluent, which is ideal for separating a wide range of inorganic anions with high sensitivity.

The anionic impurity phosphate can be determined accurately in sulfuric acid using Method 2. Method 2 uses a Dionex IonPac AS23-4µm column with carbonate eluent, which is ideal for determining phosphate in sulfuric acid because it elutes before sulfate.

Both methods use eluent generation to consistently produce eluent by adding only DI water to the system.

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