

# Determination of trace anions in hydrofluoric acid by ion chromatography

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## ABSTRACT

A method for the chemical analysis of trace phosphate and sulfate found in 4.9% hydrofluoric acid is described. Analysis to sub-ppm levels is required to determine the trace quantities of contaminants in hydrofluoric acid used in the etching process for submicron technologies.

In the laboratory, experiments were conducted to determine the amount of phosphate and sulfate in the hydrofluoric acid. Success was achieved by diluting 49% hydrofluoric acid, and by using a weak eluent of sodium carbonate and sodium bicarbonate in the analysis of these anions to the detection limits of 7.8  $\mu\text{g/l}$  by ion chromatography. The run time is approximately 20 min.

## INTRODUCTION

With the growth of the semiconductor industry, there has been an increase in the need to develop methods for trace anion analysis. This demand has been the justification for a search for more powerful analytical techniques, including chromatographic methods. The result of these efforts has been the basis for developing a method for the detection of anions in hydrofluoric acid.

Because of its rapidity and efficiency in quantifying anions in aqueous samples, the application of ion chromatography (IC) in unification with conductivity detection and an automated system has been an especially important development. This type of chromatography provides accurate data on anions found in 4.9% hydrofluoric acid. This system offers the sensitivity needed to distinguish between anions and generates highly useful results, making it an excellent method for characterizing hydrogenphosphate and sulfate detected in dilute HF [1]. This paper describes the experimental methods used in analyzing  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  in HF in the  $\mu\text{g/l}$  range. This method was developed using a fully automated system for data collection and presentation.

## EXPERIMENTAL

### Apparatus

A Model 4500 series ion chromatograph [2] furnished with a gradient pump (GPM), a conductivity detector (CDM), an autosampler (including plastic vials for 5-ml and filterless caps provided from Dionex) and an eluent degas module (EDM). The columns used were a Dionex IonPac AS4A analytical column, 250 mm  $\times$  4 mm I.D., packed with 15- $\mu\text{m}$  polystyrene-divinylbenzene substrate agglomerated with a 0.05- $\mu\text{m}$  diameter anion-exchange aminated latex particles [3], a HPIC-AG4A guard column, trace anion concentrator-1 (TAC-1), an anion trap column (ATC) and an anion micromembrane suppressor-II (AMMS-II) was used [4] (Dionex, Sunnyvale, CA, USA).

### Materials

Ultrapure dionized distilled water free from interferences at the minimum detection limit of each constituent was used and degassed using the EDM. Reagent-grade sulfuric acid, sodium hydrogen-carbonate, and sodium carbonate were used. Ultrapurity-grade  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  standards were used. Reagent-grade HF was used. The volumetric flasks, sample bottles, vials, pipette tips, and beakers are cleaned according to suggested procedures [5,6].

### Eluent preparation

A solution of 0.9 mM  $\text{Na}_2\text{CO}_3$  and 0.85 mM  $\text{NaHCO}_3$  is prepared by dissolving 0.382 g  $\text{Na}_2\text{CO}_3$  and 0.286 g  $\text{NaHCO}_3$  in ultrapure deionized distilled water to a final volume of 1000 ml. Eluent flow-rate was set to 2.0 ml/min at room temperature and degassed using the EDM.

### Standard and regenerant preparation

Standards were prepared by diluting stock solutions (1000 ppm) of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  to make concentrations, detailed in the figure legends. A regenerant of 0.0125 M  $\text{H}_2\text{SO}_4$  was prepared from reagent-grade concentrated  $\text{H}_2\text{SO}_4$ .

### Sample preparation

HF (49%) was diluted 1:10 (v/v) (1 ml 49% HF to 9 ml ultrapure deionized water) using an automatic plastic pipette, plastic volumetric flasks, plastic pipette tips, and plastic disposable beakers intended for trace level analysis.

### Sample injection

A 5-ml aliquot of each blank, standard and sample is delivered to its designated vial, capped and placed in the autosampler in a precise order. From the autosampler, the aliquot is delivered to the TAC-1 through the sample port at a flow-rate of 5 ml/2.4 min.

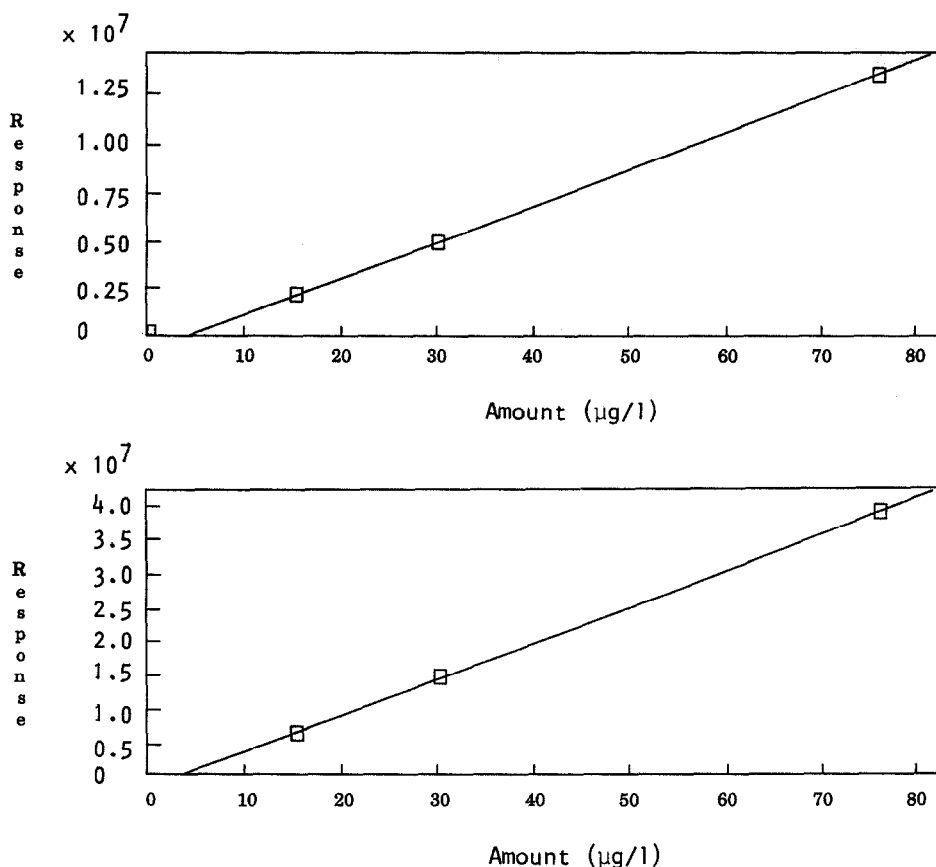


Fig. 1. Calibration curves of phosphate (top) and sulfate (bottom) standards at 15, 30 and 75  $\mu\text{g/l}$ . Dionex AS4A, AG4A, TAC-1 and ATC columns were used. Application conditions included the following: the eluent was 0.9 mM  $\text{NaHCO}_3$  and 0.85 mM  $\text{Na}_2\text{CO}_3$  run at a flow-rate of 2.0 ml/min. A conductivity detector was used and the background conductivity was 15  $\mu\text{S}$ . The volume injected was 5 ml. The data acquisition was 18 min.

### Note

Because small sample volumes are used, contamination is to be scrupulously avoided.

### RESULTS

Relatively high concentration of fluoride interferes with the determination of ions such as chloride and nitrate. Sample dilution will not overcome this interference.

The minimum detectable concentration of an anion is a function of sample size and conductivity scale used. The concentrator column was used for the acquisition of ultratrace level ions. A direct injection of the sample insured the reproducibility of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$ . The operation provided a decrease in background noise necessary for a low detection limit [7]. Since the signal to noise level is dependent on the sensitivity of the  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  ions at ultratrace levels, several approaches to decrease background noise required automatic injection of samples, degassed eluents, and no liquid leaks. A stable temperature is also required because temperature fluctuations have been shown to affect precision, sensitivity and reproducibility of conductivity detection in IC [8–11].

In IC, anions are detected by controlling the eluent that increases resolution. In the presence of high levels of  $\text{F}^-$ , this ion was eluted as a very large peak which masked the detection of ions eluting before 7 min [12,13]. A weak eluent is used to increase

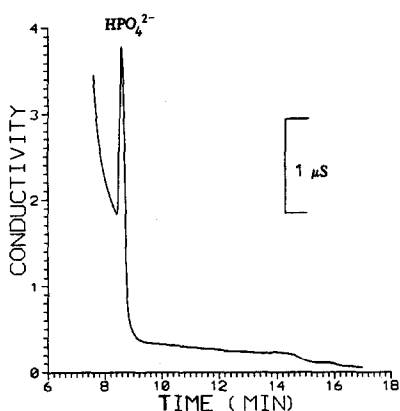


Fig. 2. Chromatogram of conductivity response showing detection of approximately 30  $\mu\text{g}/\text{l}$  of phosphate in 4.9% HF solution diluted by 1:10 (v/v) to 4.9% HF. All other application conditions as in Fig. 1.

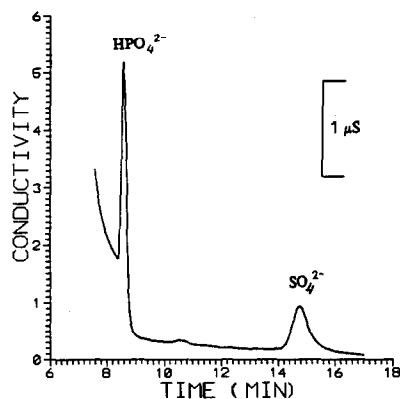


Fig. 3. Chromatogram of conductivity response showing detection of phosphate and sulfate after 4.9% HF is spiked with 75  $\mu\text{g}/\text{l}$  of phosphate and sulfate respectively. All other application conditions as in Fig. 1.

elution time to reveal anions after  $\text{F}^-$  has completely eluted [14]. As this occurs, the column overloads with the  $\text{F}^-$  for approximately 7 min. After complete elution of  $\text{F}^-$  late eluters such as  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  are detected. In analyzing a sample of 4.9% HF, 30  $\mu\text{g}/\text{l}$  of  $\text{HPO}_4^{2-}$  were detected, and no  $\text{SO}_4^{2-}$  was detected. After each run, the system needed a rinse before running the next sample.

The concentration of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  is measured from calibration curves from the standards (see Fig. 1). The instrument detection limit of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  was determined to be 7.8  $\mu\text{g}/\text{l}$  after calculating  $3\sigma(\text{dc}/\text{dx})$  (where  $c$  = peak height and  $x$  = noise ratio); therefore, the sample of 4.9% HF < 7.8  $\mu\text{g}/\text{l}$  of  $\text{SO}_4^{2-}$ . Ion chromatograms of 4.9% HF and a spike HF sample are provided in Figs. 2 and 3. A standard addition method was used to verify the quantification of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  ions because of the overabundance of  $\text{F}^-$  present. Recoveries of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  were in the range of 95–110%.

### DISCUSSION

The limits in IC operations are restricted by the difference between the retention times and concentrations of the ions being analyzed. The adjustment of the strength of sodium carbonate and hydrogen-carbonate combinations significantly controls the retention times of the ions being chromatographed

[14]. The sensitivity for ions at ultratrace levels required a means that provided a decrease in background noise necessary for a low detection limit. The chromatogram of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  displayed a flat baseline for precise quantitation.

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