

Short communication

Determination of traces of chloride and fluoride in H₂SO₄, H₃PO₄ and H₃BO₃ by in situ analyte distillation—ion chromatography

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Abstract

A simple dual vessel in situ analyte distillation (IAD) system has been developed for suppressed ion chromatographic determination of chloride and fluoride ions in complex matrices. In IAD system, water vapours generated from the outer vessel reacts with sulfuric acid generating heat, thus favouring the quantitative distillation of chloride and fluoride within 30 min on water bath temperature (~80 °C). The distilled analytes, as their respective acids in water, were directly injected into an ion-chromatograph. This newly developed method has been applied for analysis of trace impurities in H₂SO₄, H₃PO₄ and H₃BO₃. The detection limits for chloride is 8, 80 and 70 ppb (w/w) for H₂SO₄, H₃PO₄ and H₃BO₃, respectively. For fluoride the detection limits are 6 and 60 ppb (w/w) for H₂SO₄ and H₃PO₄, respectively. The recovery of spikes for both the analytes ranged between 87 and 100%.

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1. Introduction

The determination of trace ionic impurities in concentrated reagents is important in a variety of chemicals and semiconductor material processing. In boric acid, quantitative determination of chloride is an important requirement in the nuclear industries [1]. Boric acid is added to the primary coolant in pressurised water reactors for reactivity control. Excess of chloride ion can lead to stress corrosion of reactor components. Typical procurement specification for chloride ion limit allows a maximum of 0.4 µg/g of boric acid [2]. The spectrophotometric method using mercuric thiocyanate [3] suffers from high blank value and low sensitivity, thus limiting the usefulness of this method. Ion chromatography is an alternate technique to determine such low level of chloride. However, the boric acid matrix complicates the quantitative determination of trace level of chloride by suppressed IC [1,4]. The boric acid matrix was eliminated as trimethyl borate in a vapour phase matrix elimination system for the

determination of trace ions, but the recovery of chloride was very low (25–40%) and inconsistent [4].

In semiconductor industry, the purity of the reagents such as H₂SO₄ [5] and H₃PO₄ [6], used for wafer cleaning operation, has a direct impact on the reliability of the device and yield [7]. The determination of anions in concentrated acids has been a difficult analytical challenge [8,9]. For weakly ionized acids like phosphoric acid, methods have been developed using ion exclusion chromatography as a pre-treatment step for isolating contaminant anions with low pK_a values from the matrix acid [10–12]. On the other hand, strong acids have continued to present a challenge. Since these acids are almost totally ionised, the predominant anions cannot be completely eliminated by ion exclusion. The most widely used approach is to dilute the concentrated acids in order to reduce matrix interference on the chromatographic separation, thus compromising the detection limit. Even in this case, when sulfuric acid concentration is higher than 60 ppm, the chloride response is affected [13]. Column switching method has been employed for the determination of chloride in sulfuric acid [14]. A recent development in the ion chromato-

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graphic determination of anionic impurities in concentrated acid is the use of a cryptand-based anion exchanger column. This column was applied for the determination of anionic impurities in H_2SO_4 [9] and for the determination of chloride and sulfate in etchants [15] comprised of acetic acid, nitric acid and phosphoric acid used in the wafer cleaning operation.

The conventional distillation of halogen acids (HX, X = Cl, F) [16,17], fluosilicic acid (H_2SiF_6) [18] and chlorine [19] has been applied for the separation of fluoride and chloride from various types of matrices followed by titrimetric and spectrophotometric determination. These distillation systems are complicated and the distillates obtained are not suitable for the analysis of high purity materials using ion chromatograph. Recently, in situ analyte distillation (IAD) system has been developed for the spectrophotometric determination of boron in a variety of complex matrices [20]. This paper describes an in situ, sub-boiling distillation system for the separation of trace level of chloride and fluoride in concentrated high-boiling strongly and weakly ionized acids (H_2SO_4 , H_3PO_4 and H_3BO_3) followed by suppressed ion-chromatographic determination.

2. Experimental

2.1. Chemicals

All reagents and eluents were prepared from deionised water. High purity deionised water with specific resistance of $18\text{ M}\Omega\text{ cm}$ was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Samples of Guaranteed Reagent (GR) grade 98% (w/w) H_2SO_4 , pure grade 85% (w/w) H_3PO_4 (E. Merck, India), H_3BO_3 of Suprapur grade (E.

Merck, Germany) and Aristar grade (BDH, UK) were used. Sulfuric acid (GR grade) was heated till fuming over the hot plate in a clean environment to get rid of chloride and fluoride, stored in an airtight quartz container at room temperature and used for phosphoric acid and boric acid samples.

2.2. Instrumentation and chromatographic conditions

Analysis were carried out on a Dionex (USA) DX-300 IC system, which consists of an advanced gradient pump (AGP-1), a liquid chromatographic module (LCM-3) and a conductivity detector (CDM-3). Separation was carried out on a IonPac AS 17 ($250\text{ mm} \times 4\text{ mm}$) column (Dionex) with an IonPac AG 17 ($50\text{ mm} \times 4\text{ mm}$) guard column. Anion self-regenerating suppressor (ASRS, 4 mm) from Dionex was used in the recycle mode to reduce the conductivity of the eluent, which was 20 mM NaOH at a flow rate of 1 ml min^{-1} . For sample loading, a Rheodyne injection valve (model 9126) with a $50\text{ }\mu\text{l}$ sample loop (PEEK) was used. Data acquisition and processing was performed with chromatography software (AIMIL Winacds 6.2) through an advanced computer interface.

2.3. Sample preparation in IAD system

For the analysis of H_2SO_4 , the quartz vessel containing 1.8 g of sample solution was kept in side a high density poly ethylene (HDPE) vessel containing 5 ml of water (Fig. 1). The outer vessel was tightly closed, heated over a water bath at around $80\text{ }^\circ\text{C}$ for $\sim 30\text{ min}$. After cooling to the room temperature, the inside vessel was removed, the outer container was closed well and swirled to collect the condensate formed on the walls of the vessel. The volume of the solution

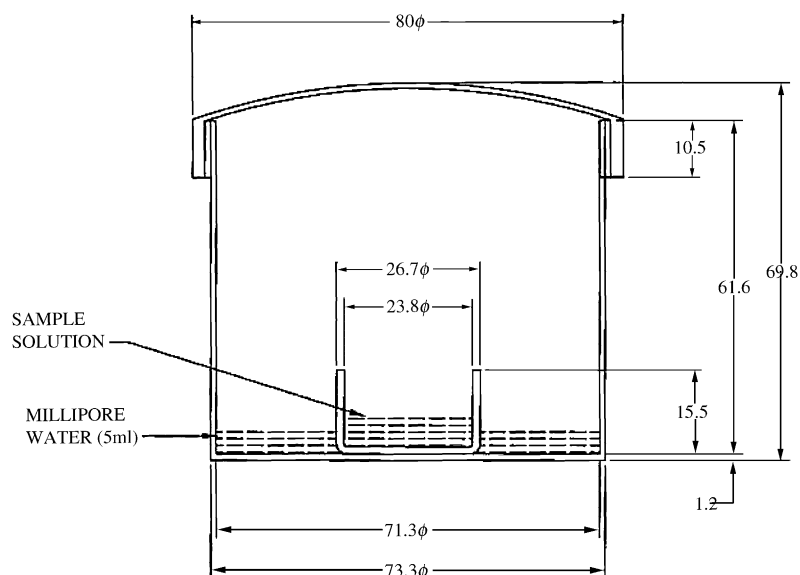


Fig. 1. In situ analyte distillation (IAD) system (dimensions in mm).

(~4 ml) was weighed to find out the dilution factor and injected into the ion-chromatograph. For the analysis of H_3BO_3 and H_3PO_4 , the sample (0.5 g) taken in the inner container was kept inside the outer container, added 0.5 ml of concentration H_2SO_4 into the sample container through Eppendorf micropipette by slightly opening the outer container, closed immediately and the experiment was repeated as described above. To prevent the contamination of analytes, the quartz and HDPE vessels were thoroughly leached and rinsed with de-ionised water. The vessels were filled with de-ionised water when not in use.

3. Results and discussion

3.1. Mechanism and optimisation of the IAD system

On heating the IAD assembly over a water bath, water vapours generated from the outer vessel reacts with sulfuric acid generating heat, which favours the quantitative release of respective halogen acids. The dimension of the inner vessel is to be small to prevent the condensation of halogen acids on its wall. In the absence of a carrier gas, the volatile acid vapours were evolved only from the surface of the sample solution. The surface area/ml of sample solution depends on the sample volume and geometry of the container dimension, which are crucial for quantitative distillation of analytes. The arched roof of the outer vessel prevents the falling of the condensate into the sample solution. The pool of water was acting as a source for water vapour and sink for respective halogen acids. When a teflon vessel was used as an inner container, fluoride got leached out from the teflon vessel and contaminated the distillate. The use of a polypropylene (PP) vessel eliminated the contamination of analytes, but it was attacked by sulfuric acid during distillation and got deformed. Hence, in both aspects, a quartz vessel is superior to teflon and PP containers. The distillation time of around 30 min and 5 ml of water in the outer container were found to be the optimised condition for all the three matrices.

3.2. Sample analysis, accuracy, precision, recovery and detection limits

The developed IC method was applied to sulfuric acid, phosphoric acid and boric acid and the respective chromatogram of trace analytes are presented in Fig. 2. Quantification of analytes was carried out from calibration curves, which were linear ($R^2 > 0.991$) in concentration ranging from 0.01 to 1.0 mg/l. Analysis result of different grades of all the three types of acid samples by suppressed IC along with the specification of impurity levels provided by the manufacturer are presented in Table 2. The chloride value obtained by the proposed IAD—suppressed IC method was found to be within the limits specified by the manufacturers. The reported chloride value in sulfuric acid (GR, grade) is slightly higher than the limits specified by the manufacturer. However, the value varied from one bottle to another. As none of the analysed matrix has specified level for fluoride, the accuracy of the proposed method for fluoride was evaluated by the recovery data, which was found to be ~93%. Precision of the method, expressed as RSD (%) was between 3 and 7% for both the analytes and for all the three matrices (Table 1).

Matrix separation study has been carried out to quantify the amount of the matrix distilled over with the analyte into the distillate. The amount of each matrix taken for this study was same as described in the procedure. The concentration of sulfate and phosphate (by IC) in the distillate was <5 ppm in all the three matrices. But in boric acid matrix, around 100 ppm of boric acid was found in the distillate (by ICP-AES), which did not affect the chloride response as studied earlier [1,4]. The recovery of spikes for both the analytes ranged between 87 and 100% (Table 1). However, the recovery of fluoride in boric acid was poor and inconsistent (36–60%). It may be due to the formation of boron–fluoride complexes, which were not quantitatively distilled off from boric acid. The limit of detection (LOD) was defined as the concentration of the analyte that gives peak height response of three times the standard deviation of the IAD process blank, after performing the experiments ($n = 5$) in the same distilla-

Table 1
Study of recovery of analyte ions after in situ analyte distillation (IAD) and detection limits

Matrix	Added (ng)		Found (ng)		Recovery (%)		LOD (ng.g ⁻¹)	
	F ⁻	Cl ⁻	F ⁻	Cl ⁻	F ⁻	Cl ⁻	F ⁻	Cl ⁻
H_2SO_4	150	500	140 (6)	470 (5)	93	94	6	8
	300	1000	280 (4)	950 (4)	93	95		
H_3PO_4	250	500	230 (8)	460 (7)	92	92	60	80
	500	1000	470 (4)	930 (4)	94	93		
H_3BO_3^a	250	500	120 (25)	460 (5)	48	92	–	70
	500	1000	230 (14)	940 (4)	46	94		

Figures shown in parentheses are percentage relative standard deviation ($n = 3$). Recovery was calculated after correcting the sample values, which are given in Table 2. The LOD values were calculated based on the dilution factor of 2 (1.8 g → 4.0 ml) for sulfuric acid and 9 (0.5 g → 4.4 ml) for phosphoric acid and boric acid, respectively.

^a Suprapur grade (E. Merck, Germany).

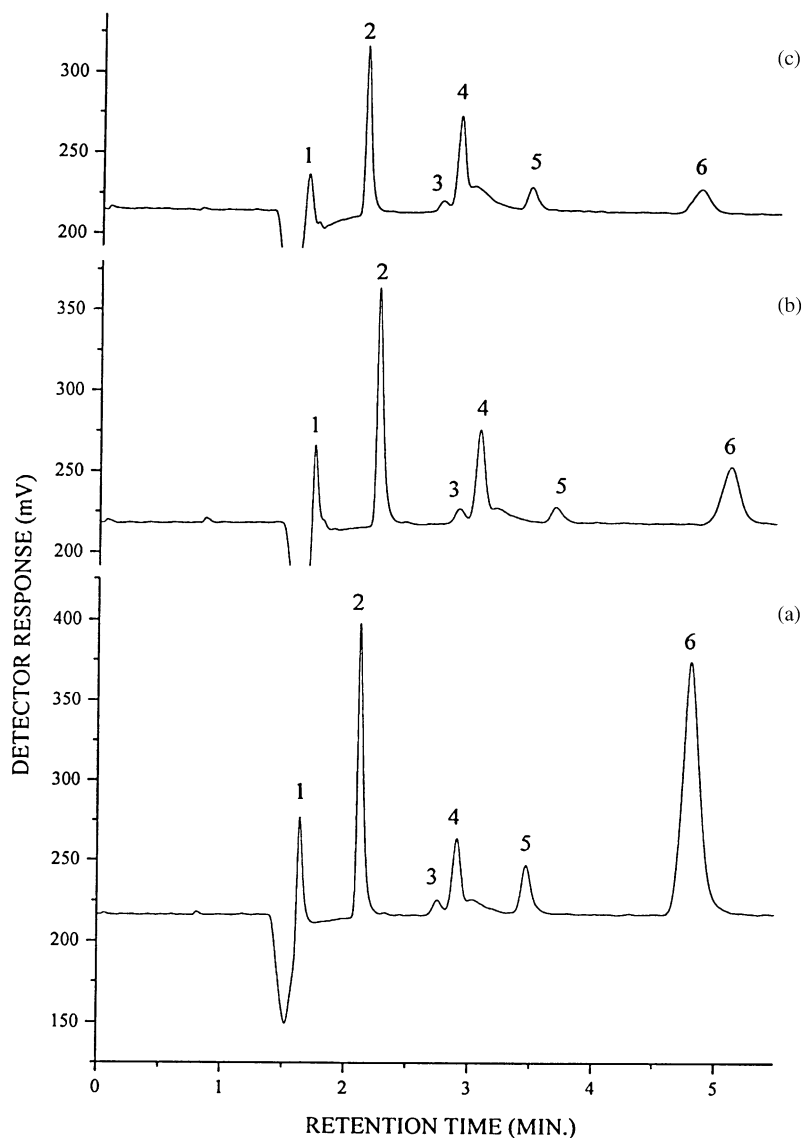


Fig. 2. (a) Chromatogram of fluoride and chloride in sulfuric acid (GR grade, E. Merck, India) after IAD (1.8 g \rightarrow 4.0 ml in water). Peaks: (1) F^- (77 ng/ml); (2) Cl^- (284 ng/ml); (3 and 4) not identified; (5) NO_3^- (not quantified); (6) SO_4^{2-} (5.4 μ g/ml). (b) Chromatogram of fluoride and chloride in phosphoric acid (Pure grade, E. Merck, India) after IAD (0.5 g \rightarrow 4.5 ml in water). Peaks: (1) F^- (67 ng/ml); (2) Cl^- (234 ng/ml); (3 and 4) not identified; (5) NO_3^- (not quantified); (6) SO_4^{2-} (0.30 μ g/ml). (c) Chromatogram of chloride in boric acid (Aristar grade, BDH, UK) after IAD (0.5 g \rightarrow 4.4 ml in water). Peaks: (1) F^- (not quantified); (2) Cl^- (170 ng/ml); (3 and 4) not identified; (5) NO_3^- (not quantified); (6) SO_4^{2-} (0.13 μ g/ml).

Table 2

Trace ion concentrations (μ g $g^{-1} \pm \sigma$) of chloride and fluoride determined by suppressed IC ($n=3$) and comparison with manufacturer's specifications (M)

Analyte	$H_2SO_4^a$		$H_3PO_4^b$		H_3BO_3	
	IC	M	IC	M	IC	M
Fluoride	0.16 ± 0.01	n.a.	0.63 ± 0.04	n.a.	n.d.	n.a.
Chloride	0.62 ± 0.02	max. 0.5	2.15 ± 0.07	≤ 5	0.90 ± 0.06^c 1.53 ± 0.06^d	max. 3 n.a.

Sample size and dilution: (1) H_2SO_4 (1.8 g \rightarrow 4.0 ml); (2) H_3PO_4 (0.5 g \rightarrow 4.5 ml); (3) H_3BO_3 (0.5 g \rightarrow 4.4 ml). n.d.—not determined; n.a.—not available.

^a GR grade (E. Merck, India).

^b Pure grade (E. Merck, India).

^c Suprapur grade (E. Merck, Germany).

^d Aristar grade (BDH, UK).

tion chamber under identical condition. Since no reagent was added into sulfuric acid for its analytes determination, only millipore water (5 ml) was taken in the outer vessel and the experiment was carried out for blank determination. But in the case of boric acid and phosphoric acid, 0.5 ml of sulfuric acid in the inner container and 5 ml of water in the outer container were taken for blank determination. The observed detection limits with their dilution factors are presented in Table 1. As per the specification limits [2,5,6], the detection limits are adequate for the determination of semiconductor grade phosphoric acid, sulfuric acid and nuclear grade boric acid.

4. Conclusion

The proposed IAD system provides a method for the separation of chloride in boric acid, fluoride and chloride in sulfuric acid and phosphoric acid followed by normal suppressed ion-chromatographic determination without any special column. In situ operation results in a very low process blank with minimum dilution (1:2 for sulfuric acid and 1:8 for boric acid and phosphoric acid) leading to low detection limit for the analysis of semiconductor grade sulfuric acid and phosphoric acid and nuclear grade boric acid. The sample pretreatment set up is simple and inexpensive. Large number of IAD systems can be handled at a time on a water bath with a reasonable time-duration (30 min). The limitations of this method are that it is not suitable for low boiling acids (HF, HCl, HNO₃, etc.) and that the number of analytes (chloride and fluoride) is limited.

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