Trace anion determination in concentrated hydrofluoric acid solutions by two-dimensional ion chromatography
I. Matrix elimination by ion-exclusion chromatography

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Abstract

Since years, ion exclusion chromatography (ICE) has been the standard method to separate strong acid analyte anions from concentrated weak acid matrices such as hydrofluoric acid (HF). In this work, the commercially available IonPac ICE-AS1 column was used to separate trace levels of chloride, nitrate, sulfate and phosphate from HF solutions at 20% (w/w). The efficiency of the separation was studied in more detail using techniques such as ion chromatography (IC), inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (ICP-MS). For 20% (w/w) HF solutions and at a water carrier flow-rate of 0.50 ml/min, the cut window was set from 8.5 to 14.5 min. Under these conditions, analyte recoveries of better than 90% were obtained for chloride, nitrate and sulfate, but only about 75% for phosphate. The HF rejection efficiency was better than 99.9%. It was found that the ICP techniques, measuring total element levels and not species, yielded significantly higher recoveries for phosphorus and sulfur compared to IC. Evidence will be given that part of the added phosphorus ($\sim$15% for an addition of 10 mg PO_4/kg) is present as mono-fluorophosphoric acid (H_2FPO_3). In the case of sulfate, the difference between IC and ICP-MS could be attributed to an important matrix effect from the residual HF concentration.
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1. Introduction

Over the past decade, ion chromatography (IC) became the most popular analytical technique for the determination of trace anions in concentrated hydrofluoric acid (HF) solutions (48–50%, w/w) and replaced traditional wet chemistry methods detailed in references [1,2].

The direct injection of diluted HF solutions ($\sim$5%, w/w) minimizes matrix effects, but allows only to achieve detection limits in the concentrated acid in the range of 250–500 μg/kg because of the dilution of the anions of interest [3].

To meet the quality requirements for the use of HF in the semiconductor manufacturing process, such as the specifications and guidelines set by the semiconductor equipment and materials international (SEMI) organization [1], new methods have been developed.

The most popular one, developed by Watanabe et al. [4], uses a two dimensional ion chromatography approach comprising several steps. First of all, the analyte anions are separated from the HF matrix by ion-exclusion chromatography (ICE). A carefully selected fraction – called hereafter "cut window" fraction – and containing the major percentage of each analyte, is then sent to a concentrator column. The fractions preceding and following this fraction are directed to waste. The impurities, accumulated onto the concentrator, are finally separated on an analytical column and detected by conductivity after electrochemical suppression of the eluent conductivity.

Regarding its application to concentrated HF solutions, the several author groups agreed on the fact that the method works reasonably well for chloride and nitrate, however disagree on its potential for reliable trace determination of sulfate and phosphate [7,9]. Amongst the reported problems are the rather high and irreproducible sulfate blanks as well as the sensitivity variations for phosphate.

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The above mentioned IC-ICE method is also the one used by Solvay for quite some time albeit that the ion exclusion column originally used by all research groups (IonPac ICE-AS6, [4–9]) was replaced by the ICE-AS1 in order to avoid the sulfate bleeding.

Using a carbonate/bicarbonate eluent, our actual method detection limits for chloride and nitrate compare favorably well to the SEMI specifications for Tier C HF [1,10]. However, for sulfate and phosphate there is clearly a lack of sensitivity [10]. For that reason, it was decided to study the ICE-IC method over from the beginning. The present paper (Part I) deals with some more or less fundamental work related to the ICE separation. In Part II, we will describe how the use of an electrolytically generated and purified hydroxide eluent and a low noise electrochemical suppressor allow to achieve much better detection limits, especially for sulfate and phosphate [11].

2. Experimental

2.1. Reagents

All synthetic mixtures used during this work were prepared from analytical grade HF 40% (w/w) obtained from Merck (Darmstadt, Germany).

The solutions were prepared by weight in 50 or 100 ml pre-cleaned HDPE bottles. Cleaning was achieved by filling the bottles for at least 48 h with 10% (v/v) electronic grade hydrogen peroxide (30%, m/m). On the moment of use, they were rinsed three times with ultra pure (UP) water. Chloride, nitrate, sulfate and phosphate were added from intermediate mixed standard solutions at 100 mg/l, prepared from single ion certified standards – Certipur from Merck (Darmstadt, Germany) – at 1000 mg/l. Mono-fluorophosphoric acid (H_2FPO_3) was purchased as a 70% solution in water from Acros (Geel, Belgium).

2.2. Instrumentation

Ultra-pure (UP) water (resistivity > 18 MΩ cm) was generated by a MAXIMA purification station from Elga (High Wycombe, England), fed by an in-house circuit of desionised water. The unit was equipped with two anion exchange beds in series to achieve very low anion levels.

All chromatography equipment and columns were from Dionex (Sunnyvale, CA, USA), unless otherwise mentioned.

The ion exclusion separations were done on a DX-500 system comprised of an LC 20 chromatography enclosure with a six port Rheodyne injection valve, a GP50 gradient pump with PEEK (PolyEther Ether Ketone) flow path and a CD20 conductivity detector. The whole instrumental set-up was put in a well ventilated fume hood.

The injection valve was fitted with a 0.82 ml sample loop constructed from PEEK tubing (0.03 in. or 0.75 mm i.d.). All HF samples were fed to the sample loop by pneumatic means,

i.e. by putting the HDPE bottles in a chamber pressurized to 25 psi with helium. Pressurization times were typically 2–3 min for the first injection of a sample and 1 min for all further injections.

All ion exclusion separations were done on the IonPac ICE-AS1 column (250 mm × 9 mm) using UP water as the eluent. An IonPac AG10 (50 mm × 4 mm) column was installed on the water feeding line to retain eventual impurities.

A flow-rate of 0.5 ml/min was used to establish the cut. Afterwards, the flow rate was increased to 1.0 ml/min to speed up the HF elimination from the exclusion column.

The IC analysis of the cut window fractions were done on a DX-600 ion chromatograph equipped with a GP50 gradient pump, an EG40 eluent generator, an AS50 autosampler with associated chromatography compartment and an ED50 electrochemical detector used in the conductivity mode. Electrochemical eluent purification (CR-ATC) and eluent neutralisation (ASRS ULTRA II, 4 mm) were used. The current applied to the suppressor was 100 mA.

This system was equipped with an IonPac AS18 column (250 mm × 4 mm) and its associated guard column. Separations were isocratic by using 30 mM KOH as the eluent at a flow-rate of 1.00 ml/min. The injection volume was 25 μl.

All cut window fractions were collected manually in 10 ml polystyrene vials with screw caps and septa, which could be placed directly in the AS50 autosampler. Before use, the vials were soaked during 24 h with UP water.

Total phosphorus was analyzed in the optimum fractions by ICP-OES on an ULTIMA spectrometer (Jobin-Yvon/HORIBA) equipped with special UV optics. Phosphorus was analyzed using its emission wavelength at 177.440 nm. Standard plasma operating conditions were used.

Total sulfur was analyzed by ICP-MS on an ELEMENT 2 (THERMO-FINNIGAN, Bremen) double focusing mass spectrometer operated in medium resolution ($R \geq 4000$). The ^{32}S isotope was used for quantification. The ICP-MS was equipped with an inert sample introduction system (ELEMENTAL SCIENTIFIC Inc., Omaha, NE) comprising of a PFA spray chamber and a PFA micro-concentric nebulizer operating in the free aspiration mode (flow-rate 0.1 ml/min).

3. Results and discussion

3.1. Setting of the "cut window"

In a first part of this study, the "cut window" was determined. This was achieved by recording the conductivity profiles of the eluate from the ion-exclusion column during matrix separations of solutions containing different HF concentrations (0, 5, 10 and 20% by weight), each spiked with chloride, sulfate, nitrate and phosphate at the 10 mg/kg level.
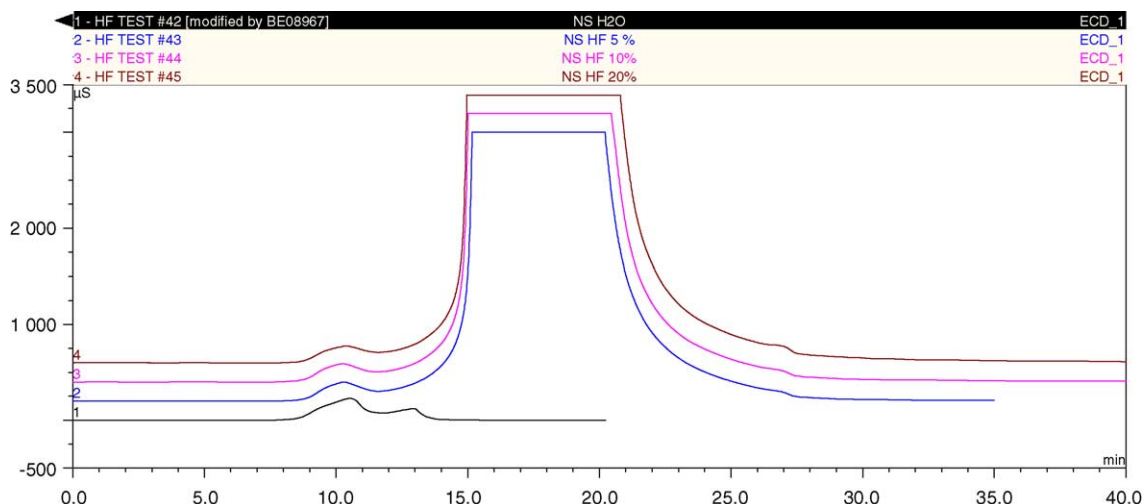
Fig. 1. Separation by ion exclusion chromatography of a mixture of chloride, nitrate, sulfate and phosphate – each added at 10 mg/kg – from HF matrices at different concentrations. Sample volume: 0.82 ml; analytical column: IonPac ICE-AS1 (250 mm × 9 mm); trap column: IonPac AG10 (50 mm × 4 mm); eluent: water; eluent flow-rate: 0.50 ml/min; detection: non suppressed conductivity.

For these experiments, the outlet from the IonPac ICE-AS1 column was directly fed to the conductivity cell; i.e. there was no electrochemical suppression.

Fig. 1 shows an overlay of the conductivity profiles which were obtained for the different HF concentrations. Each separation was continued until the initial baseline conductivity was achieved.

As can be seen from the lower trace, the injection of an aqueous standard of chloride, nitrate, sulfate and phosphate shows two peaks, probably corresponding to a beginning separation among anions derived from strong (hydrochloric, nitric and sulfuric acid) and weaker (orthophosphoric acid) mineral acids.

The profiles obtained for the solutions containing HF all show the same first peak, but the second one is masked by the HF matrix. One can also see that the matrix peak gets broader and broader as the HF concentration increases.

Based on a visual inspection of these profiles, it was decided to set the cut window from 8.5 to 14.5 min and to check what the recovery would be under these circumstances.

3.2. Recovery of analyte anions

To determine the recovery, the same solutions as those described in previous section were used. However, the outlet of the exclusion column between 8.5 and 14.5 min was now collected and analysed by IC. Calibration was performed with aqueous standards containing chloride, nitrate, sulfate and phosphate in the 0–6 mg/l range. A 20% (w/w) HF blank was chromatographed and analysed in parallel.

Recoveries, R (%), were calculated, according to the following formula:

$$R\,(\%) = 100 \left[\frac{C_f V_f}{C_{inj} V_{inj}} \right]$$

where each symbol has the following meaning:

C_f (μg/ml), analyte concentration measured in the cut window fraction after subtraction from the HF blank. In practice, the applied correction was small. It was thereby assumed that the HF blanks were proportional to the HF concentration.

V_f (ml), volume of the cut window fraction (under the flow-rate conditions used $V_f = 3.00$ ml).

C_{inj} (μg/ml), analyte concentration in the solution injected onto the exclusion column. C_{inj} was obtained by multiplying the analyte concentration in mg/kg (ppm) by the density of the different HF solutions (kg/l). The latter were determined by weighing a fixed volume of the prepared mixtures.

V_{inj} (ml), injection volume (in our study V_{inj} was 0.82 ml).

The recoveries obtained for the analyte anions under study are presented in Fig. 2 for HF concentrations of 0, 5, 10 and 20% (w/w), respectively. The 0% values correspond to the recoveries in pure water. For chloride and nitrate, the recoveries are always above 90% and did not depend on the HF concentration. However, those for sulfate and phosphate are significantly lower. In contrast with sulfate, the phosphate recovery dropped as the HF concentration increased (from about 80 % in pure aqueous solutions to only 63 in a 20% (w/w) HF matrix).

The reproducibility of the ICE separation was also checked by the repeated chromatography of a HF 20% (w/w) solution spiked with chloride, nitrate, sulfate and phosphate at the 10 mg/kg level.

The relative standard deviation (%) on the recoveries obtained for four separations (two on the first day of analysis and two on the day after) was 0.4% for chloride, 0.7% for nitrate, 0.8% for sulfate and 2.3% for phosphate.
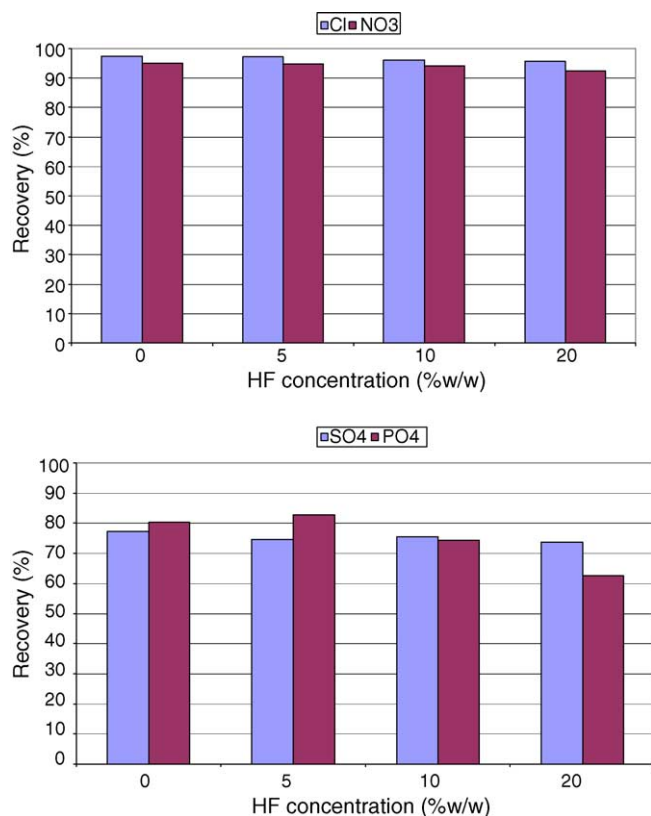
Fig. 2. Recoveries (%) with which chloride, nitrate, sulfate and phosphate can be isolated from HF matrices with ion exclusion chromatography. ICE separation: sample volume: 0.82 ml; analytical column: IonPac ICE-AS1; trap column: IonPac AG10 (4 mm); eluent: water; eluent flow-rate: 0.50 ml/min from 0 to 20 min and 1.00 min after 20 min; collection of cut window fractions from 8.5 to 14.5 min. IC analysis of cut window fractions: sample volume: 25 μl; analytical columns IonPac AG18 (50 mm × 4 mm) + AS18 (250 mm × 4 mm); eluent: 30 mM KOH; eluent flow-rate: 1.00 ml/min; detection: suppressed conductivity, ASRS ULTRA II in external water mode (100 mA).

3.3. Efficiency of the matrix removal

The residual concentration of fluoride measured in the fraction corresponding to the cut window was also determined and typically around 10 mg/l F. For a HF solution at 20% (w/w), this corresponds to a rejection efficiency of the matrix better than 99.95%.

Most of the fluoride comes off the exclusion column with the later eluting fractions. The HF concentrations in the second and third 3 ml fractions (the corresponding time windows are 14.5–20.25 min and 20.25–23.25 min) were approximately 3 and 0.1 M, respectively.

3.4. Particular behavior of phosphate and sulfate

In order to get a better understanding of the low recovery values for sulfate and phosphate, it was decided to prepare two more cut window fractions from the HF 20% (w/w) solution spiked with all four analyte anions at 10 mg/kg. These fractions were again analyzed by IC but also by inductively coupled plasma optical emission spectrometry (ICP-OES) for total phosphor and by inductively coupled plasma mass spectrometry (ICP-MS) for total sulfur as the instrument blank obtained with the latter technique for sulfur was much lower than for the OES spectrometer. For completeness, two later eluting 3 ml fractions were also collected and analyzed by ICP-OES (for P) or ICP-MS (for S). Note that ICP-OES and ICP-MS both measure total element levels, whatever the species under which phosphorus and/or sulfur may be present.

3.4.1. Phosphate

As can be seen from Table 1 (Experiment I), the phosphor recovery for the cut window fraction as measured by ICP-OES is roughly 20% higher than the one calculated from the IC data. The ICP-OES data further show that about 25% of the injected phosphate is eluting in the second 3 ml fraction and is thus lost for analysis. The phosphor content in the last 3 ml fraction is negligible small.

The chromatograms obtained on the cut window fractions of the spiked HF samples always revealed a small unknown peak, eluting between carbonate and sulfate (retention time ~5.4 min). This peak became more important as the HF concentration of the matrix and the added phosphate level increased. It was therefore suggested that part of the added phosphate, in the presence of the HF matrix, is reacting to form a complex phosphorus species.

The combination of HF and H_3PO_4 has already been described in the literature and is known as monofluorophosphoric acid (H_2FPO_3) [12]. MFP will be used

Table 1

Distribution of sulfur and phosphorus species over different eluate fractions collected during the separation by ion-exclusion chromatography of sulfate and phosphate from 20% (w/w) HF solutions

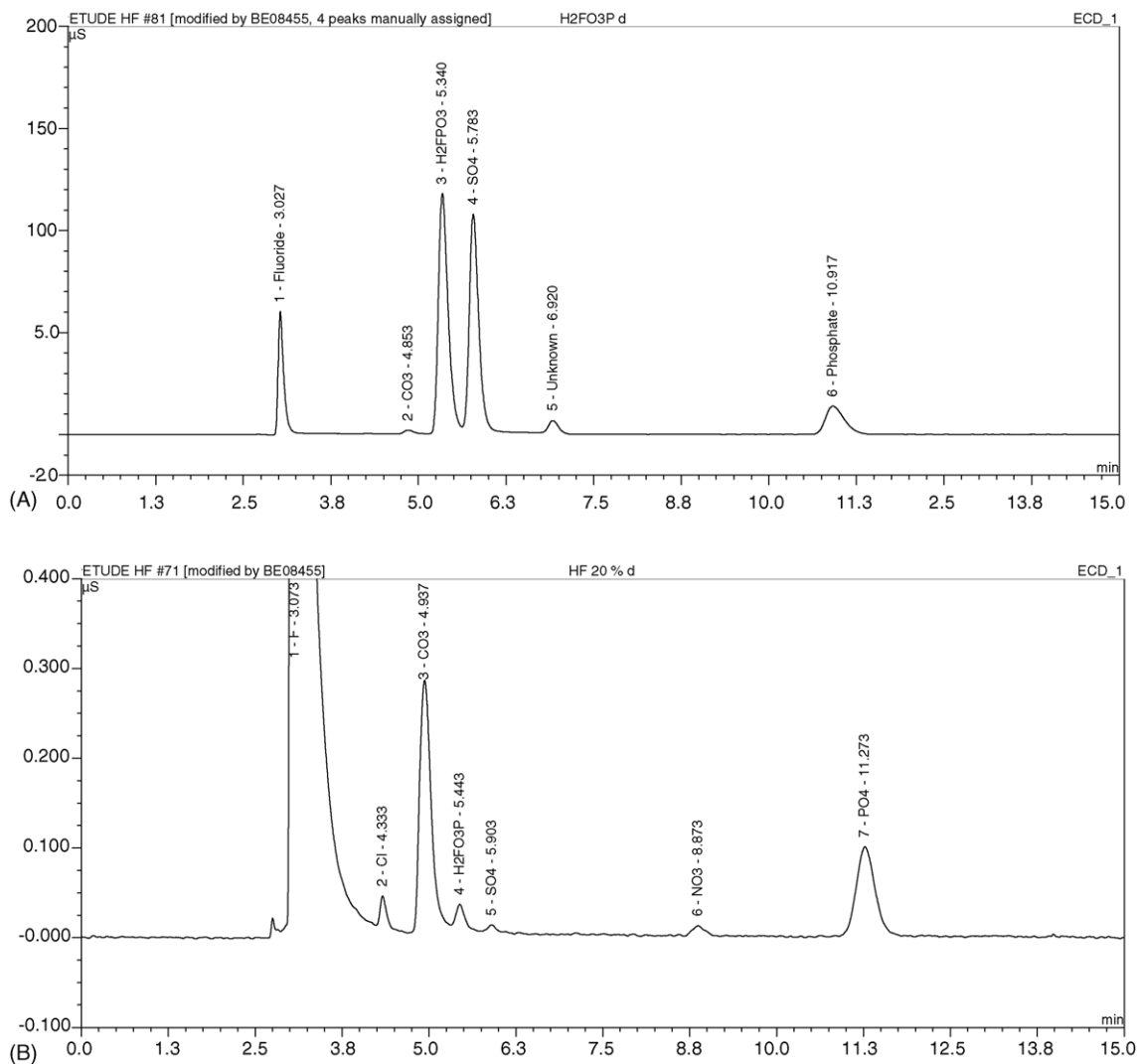|	Cut window fraction (3 ml)		Second 3 ml fraction	Third 3 ml fraction
Time window (min)	8.5–14.5		14.5–20.25	20.25–23.25
	PO_4 (IC)	PO_4 (ICP-OES)	PO_4 (ICP-OES)	PO_4 (ICP-OES)
Experiment I	63	75	26	0.4
	SO_4 (IC)	SO_4 (ICP-MS)	SO_4 (ICP-MS)	SO_4 (ICP-MS)
Experiment II	84	91	3.0	0.7

Chromatographic conditions as in Fig. 2.

Fig. 3. Chromatograms obtained for a standard solution containing 32 mg/l H_2FPO_3 (mono-fluorophosphoric acid) and 10 mg/l SO_4 (A) and for analysis of the optimum fraction obtained during the separation by ion exclusion of a 20% by weight HF solution spiked with 5 mg PO_4/kg (B). Chromatographic conditions as in Fig. 2.

as the acronym of H_2FPO_3 through the remainder of this paper.

The identity of this small peak was verified by comparison of its retention time in the cut window chromatograms (Fig. 3B) with the one obtained for an aqueous MFP standard (see Fig. 3A). As can be observed, the retention times are in pretty good agreement. Although no formal evidence was given, all our observations indicate that this small peak could effectively be MFP.

The chromatogram in Fig. 3A shows also peaks corresponding to free fluoride and orthophosphate. By comparison with aqueous standards of these ions which gave comparable signals, it was possible to estimate their concentration level and to calculate a molar F/PO_4 ratio of 1.03. As the obtained value is very close to unity, it can be assumed that both ions are not present as impurities in the concentrated acid but are produced by hydrolysis with water according to the reaction [12]:

$$H_2FPO_3 + H_2O \Leftrightarrow HF + H_3PO_4$$
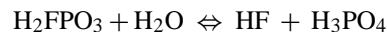
From the areas of the F, MFP and PO_4 peaks in the chromatogram of Fig. 3A, and knowing the sensitivity for fluoride and phosphate anions, it was possible to estimate the sensitivity for the MFP peak with suppressed conductivity. This allowed us to calculate how much of the total phosphorus in the optimal fraction was approximately present as MFP.

For experiment I (Table 1), it was calculated that the MFP peak was roughly equivalent to an additional 7.5% orthophosphate. When this percentage is added to the one obtained for free orthophosphate, an overall recovery of 70% is obtained, which is already in better agreement with the 74.5% obtained by ICP.

So, the apparent discrepancy between the IC and ICP-OES data stem from the presence of another phos-
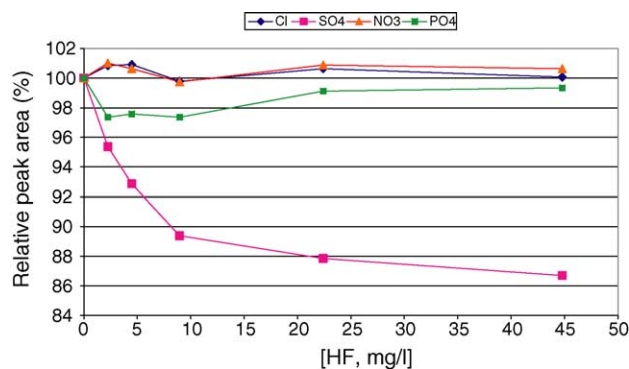
Fig. 4. Matrix effects experienced by chloride, nitrate, sulfate and phosphate during their IC analysis in solutions containing some free HF. Anion concentrations were 3 mg/l each. Chromatographic conditions as for the analysis of the cut window fraction in Fig. 2.

phorous compound, most probably mono-fluorophosphate (MFP).

3.4.2. Sulfate

The sulfate recovery determined by ICP-MS on the cut window fraction of experiment II (Table 1) was 91% and thus about 9% higher than the one calculated for the same fraction from the IC measurements. The ICP-MS data further indicate that the second and third 3 ml fractions are only responsible for a few per cent of the injected sulfate.

It was found that the anomaly between the IC and ICP-MS data could be explained by a rather severe matrix effect from the residual HF on the sulfate response by IC. It has to be remembered that the sulfate concentrations in the cut window fractions were obtained through an external calibration and not determined by standard addition.

To study this matrix effect, a series of solutions were prepared containing 3 mg/l of all analyte anions (chloride, sulfate, phosphate and nitrate) and HF concentrations ranging from 0 mg/l (pure aqueous solutions) to about 45 mg/l (2.3 mM). The 3 mg/l level is comparable to the typical analyte concentrations in the cut window fraction and the HF concentration in the same fractions varies slightly from one series of experiments to another (between 10 and 30 mg/l HF). All solutions were injected in triplicate. Peak areas were averaged and normalized to the mean peak areas obtained for the pure aqueous standard.

In Fig. 4, those relative peak areas are plotted as a function of the HF concentration. As can be seen, the response is almost not affected for chloride and nitrate over the entire HF concentration range. A small matrix effect can be observed for phosphate (~2%); however the suppression effect on sulfate (lower trace) is much more pronounced: at 10 mg/l HF (0.5 mM), already 11% of the peak area is lost. The same

effect was observed for peak height responses as well as when sulfate was the only anion which was present.

This important matrix effect on sulfate is strange because its peak is eluting well after the fluoride peak (see also Fig. 3B). For chloride, eluting just after the HF peak, there is almost no effect.

4. Conclusions

Chloride and nitrate can be isolated from concentrated HF solutions (20%, w/w) by ion-exclusion chromatography with recoveries over 90%.

The remaining HF concentration in the cut window fractions is very low (10–20 mg/l), corresponding to a matrix rejection efficiency better than 99.9%.

The sulfate recovery for the same ICE separation, as determined through a sulfur determination by ICP-MS, is also about 90%. However, only about 80% is found by IC analysis as sulfate. It was proved that sulfate is experiencing a severe matrix effect in IC from the remaining HF. It should therefore be quantified in the cut window fraction by the method of standard addition. The reason for this matrix effect is yet unknown.

In the case of HF doped with phosphate, about 75% of the injected amount is found back in the cut window fraction. Evidence was given that phosphorus exists in this fraction as two different species: orthophosphate constituting the major part of the total phosphorus (~85%) and mono-fluorophosphate (MFP) accounting typically for about 15% of the total P. The analytical consequences of these observations will be discussed in Part II [11].

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