

Trace anion determination in concentrated hydrofluoric acid solutions by two-dimensional ion chromatography II. Method performance study with a hydroxide eluent and a low noise suppressor

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Abstract

The two-dimensional ion exclusion chromatography/ion chromatography (ICE–IC) approach is considered to be the method of choice for the determination of trace anions in concentrated hydrofluoric acid (48–50%, w/w). In order to achieve lower detection limits, this method was for the first time used with electrolytically generated and purified hydroxide eluents in combination with a low noise electrochemical suppressor. Compared to carbonate based eluents, the achieved gain in peak height sensitivity for chloride, sulfate, nitrate and phosphate is a factor of 6, 7, 16 and 13, respectively. The instrumental detection limits, based on the background noise, are 2, 0.2, 0.4 and 1.4 $\mu\text{g}/\text{kg}$ HF 50% (w/w) for the same anions. Their method detection limits, calculated according to SEMI, are all within the 6–10 $\mu\text{g}/\text{kg}$ HF 50% (w/w) range and thus at least 10 times lower than the current Tier C grade requirements. The chromatographic run time could be shortened with some 10 min by the use of a relatively fast high-capacity hydroxide selective anion exchange column.

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1. Introduction

A comprehensive literature survey of the ICE–IC method used for the analysis of trace anions in concentrated hydrofluoric acid (HF) has already been given in Part I [1]. This method is routinely used in our production environment for the analysis of chloride, sulfate, nitrate and phosphate. The ICE separations are done onto the IonPac ICE-AS1 column with water as a carrier. For the IC part, an IonPac AS9-HC column is used with a carbonate based eluent (see Table 3 for further details).

Because of the higher residual background conductivity ($\sim 15 \mu\text{S}$) and the associated background noise typical for carbonate eluents, the detection of anions at trace level

(<50 $\mu\text{g}/\text{kg}$ HF 50%, w/w) is seriously hampered, especially for sulfate and phosphate.

In an attempt to determine the true anion levels in our own products and those of competitors, work was undertaken to improve the sensitivity of the method. This could be achieved by using a high capacity hydroxide-selective column with electrolytically prepared and cleaned KOH eluent as well as a low noise electrochemical suppressor.

The present paper (Part II) discusses some of the optimization work which has been done. The results of the method validation realized according to SEMI regulations will also be given for parameters such as method detection limits (MDL), accuracy and precision. Analysis results will also be presented for some electronic grade HF samples from European, American and Japanese producers. Besides the classical anions mentioned above, at least three or four other, mostly unidentified, analyte peaks were generally observed in their chromatograms.

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2. Experimental

2.1. Reagents

All synthetic mixtures used during the optimization and validation work were prepared from electronic grade concentrated HF (48–50%, w/w) samples obtained from different manufacturers.

The mixtures were prepared by weight in 50 or 100 ml pre-cleaned HDPE bottles and always contained 20% (w/w) of HF. Cleaning of the bottles was achieved by soaking them for at least 48 h with 10% (v/v) electronic grade hydrogen peroxide (30%, w/w). On the moment of use, these bottles 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.

2.2. Instrumentation

Ultra-pure water (resistivity > 18 M Ω cm) was produced 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.

All experiments were run on a DX-500 system comprised of an LC 20 chromatography enclosure with Rheodyne injection valve, a GP50 gradient pump with PEEK flow path and a CD20 conductivity detector. The hydroxide eluents were generated with a RFC-30 module equipped with an EGC-II KOH cartridge.

The injection valve was fitted with a 0.82 ml sample loop constructed from PEEK tubing (0.03 in. or 0.75 mm internal diameter). 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 \times 9 mm) using UP water as the eluent, delivered by an ALLTECH model 426 mono-piston HPLC pump which was controlled manually. An IonPac AG10 column (50 mm \times 4 mm) was installed as a *trap column* on the water feeding line to retain eventual impurities.

A flow-rate of 0.50 ml/min was used to establish the cut (8.5–14.5 min). From 15 to 35 min, the flow-rate was increased to 1.00 ml/min to speed up the HF elimination from the exclusion column. Between 35 and 40 min, the ICE column was stabilized again at 0.50 ml/min waiting for the next sample.

A two-position six-port electric valve (Fluid processor Rheodyne EV-750 AL) was further used to isolate the cut window fraction. This valve was also piloted through the PeakNet software controlling the DX 500 system.

An IonPac AG18 (50 mm \times 4 mm) column was used as *concentrator* for all trials. The *analytical separation* was done on the hydroxide selective and fast IonPac AS18 column (250 mm \times 2 mm) with 75 μ eq total capacity. The eluent flow-rate was maintained at 0.25 ml/min.

Two different electrochemical suppressors (in 2 mm version) were used during this study: the ASRS ULTRA during the optimization work and the more recently available ASRS ULTRA II for the validation work and the unknown sample analysis. The latter model exhibits faster start-up time and a much lower background noise (typically < 2 nS).

Fig. 1 shows a schematic of the complete set-up of this integrated ICE–IC application.

The waste flows of both valves were collected in a 5 l plastic bottle containing an excess of concentrated caustic soda. The whole instrumental set-up was put in a well ventilated fume hood.

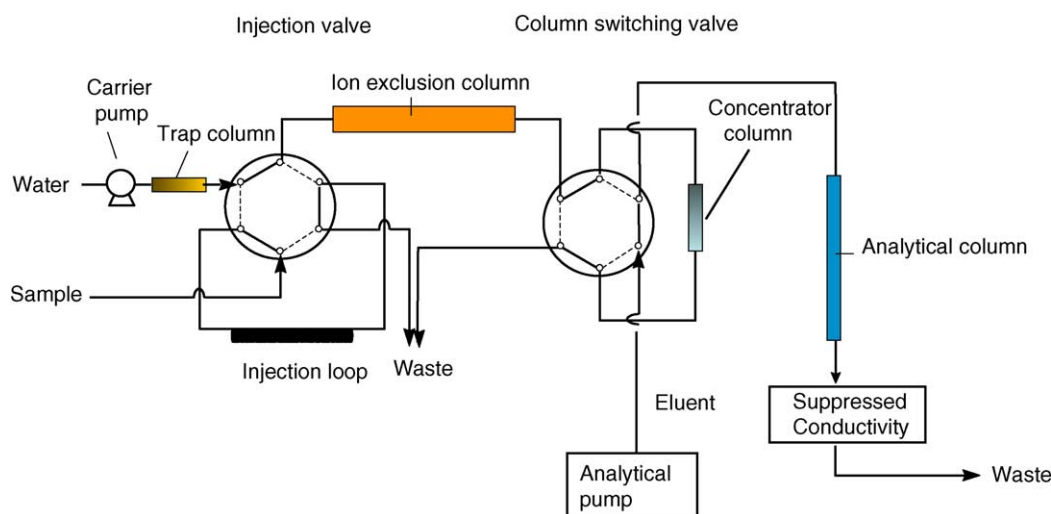


Fig. 1. Plumbing diagram of the ICE–IC approach used for the analysis of anions in concentrated hydrofluoric acid.

3. Discussion of the results

3.1. Optimization of the IC gradient

The way how the cut window was selected has already been discussed in Part I [1]. Initial trials showed that with hydroxide eluents, a gradient was needed in order to obtain a good separation of chloride from the remaining fluoride whilst still having a reasonable retention time and sensitivity for phosphate, being one of the late eluting anions.

The gradient was optimized on a 20% (w/w) HF solution spiked with 1 mg/kg of chloride, sulfate, nitrate and phosphate.

The RFC-30 parameters which were varied are the *start* and *end* KOH concentrations (mM), the *gradient time* (min) and the *start time* (min). The gradient time is the time needed to reach the end final KOH concentration from the start concentration. The start time is the time at which the gradient is started from within the method file.

The measured response factors were the sensitivities for all four anions (chloride, sulfate, nitrate and phosphate), expressed as peak height (μS) and the resolution between all major peak pairs (calculated according to the PeakNet software) including the fluoride matrix peak. All these factors are reported in the peak analysis table available in the standard PeakNet report templates.

It became soon clear that the response factors showing the greatest variability are the peak heights (P_h) for sulfate (factor 2.4) and phosphate (factor 4) and the resolution factors (R_f) between the peak pairs F/Cl (factor 1.3) and NO_3/PO_4 (factor 2.9).

A global response factor (Π) was then calculated for all experimental conditions by multiplying the values of the response factors mentioned in the preceding paragraph, i.e.

$$\Pi = P_h(\text{SO}_4) \times P_h(\text{PO}_4) \times R_f(\text{F/CL}) \times R_f(\text{NO}_3/\text{PO}_4)$$

The global response factors calculated for the different gradient elutions are presented in Table 1. The values obtained for an isocratic elution with 25 mM KOH are given for comparison (see first line).

The experimental conditions giving the overall best performance are a *start* eluent concentration of 10 mM, a *final* eluent concentration of 40 mM, a *gradient time* of 5 min and a *start gradient time* of 19 min.

Under these conditions, the analytical separation part only takes some 35 min bringing the total analysis time (including the ICE matrix elimination and column re-equilibration) close to 50 min. Compared to our older eluent/column combination; this constitutes a time gain of some 10 min for each sample [7].

3.2. Sensitivity

Under the optimum gradient parameters (10/40/5/19), the peak height sensitivities, expressed as $\mu\text{S}\cdot\text{kg}/\text{mg}$ of added anion in 50% (w/w) HF solutions, are typically about 114 for chloride, 92 for sulfate, 50 for nitrate and 17 for phosphate.

Compared to the previously used carbonate/bicarbonate eluent [7], the gain in sensitivity is a factor of 5.5, 7.1, 15.6 and 13.2, respectively (Table 2).

To obtain the actually measured peak heights for the diluted HF samples, the data from Table 2 still have to be divided by the dilution factor (2–2.5).

3.3. Influence of the carrier flow-rate

The influence of the carrier flow-rate used for the ICE separation on the final peak areas in the ICE–IC chromatogram was studied in the range from 0.46 to 0.52 ml/min, corresponding to deviations of -8 and $+4\%$ from the nominal flow-rate of 0.50 ml/min. A 20% (w/w) HF solution spiked with 1 mg/kg of the four analyte anions was used for these trials.

As can be seen from Fig. 2, this parameter is very important. For a flow-rate increase of only 4%, the fluoride peak area increases by a factor four and already 50% of the chloride peak area is lost. The incidence on the peak areas is much smaller for the other anions.

The accuracy and precision of the pump used to feed the water to the ICE column are therefore very important. This was in fact the reason why we used a HPLC pump rather than some low cost reagent pump.

Table 1
Global response factors (Π) calculated for different gradient conditions (see Section 3.1)

Preconcentration column	Sc (mM)	Fc (mM)	Gt (min)	Sg (min)	$P_h(\text{SO}_4)$ (μS)	$P_h(\text{PO}_4)$ (μS)	$R_f(\text{F/Cl})$	$R_f(\text{NO}_3/\text{PO}_4)$	Π
AG18, 4 mm	25	25	0	14.5	54.8	3.8	1.43	5.77	1742
AG18, 4 mm	20	30	25.5	14.5	47.3	4.8	1.23	7.51	2097
AG18, 4 mm	10	25	2	16.5	58	4.2	1.28	2.95	920
AG18, 4 mm	10	30	3	17.5	80.7	7.2	1.17	4.67	3175
AG18, 4 mm	10	40	4	18.5	110.3	14.6	1.09	2.82	4950
AG18, 4 mm	10	40	5	19	102	14.4	1.14	3.66	6128
AG18, 4 mm	7.5	40	4	18.5	114	15	1.09	2.62	4883
AG18, 4 mm	5	35	3	18.5	97.8	10.4	1.15	3.29	3848

Sc, start eluent concentration (mM); Fc, final eluent concentration (mM); Gt, gradient time (min); Sg, start time gradient in method file (min); Ph, peak height; Rf, resolution factor between a given peak pair. The data for an isocratic elution with 25 mM KOH are given for comparison.

Table 2

Comparison of peak height sensitivities ($\mu\text{S kg/mg HF } 50\%$, w/w) between carbonate and hydroxide based eluents, when used for the determination of trace anions in hydrofluoric acid (ICE–IC approach)

	Chloride	Nitrate	Sulfate	Phosphate
$\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$	20.8	7.0	5.9	1.3
NaOH	113.6	49.6	92.0	17.2
Gain	5.5	7.1	15.6	13.2

Old chromatographic conditions with carbonate/bicarbonate eluents [6].

ICE separation: sample volume: 0.75 ml; analytical column: IonPac ICE-AS1 (250 mm \times 9 mm); trap column: IonPac AG10 (50 mm \times 4 mm); eluent: water; eluent flow-rate: 0.50 ml/min; cut window from 7.5 to 12.5 min.

IC analysis: analytical column IonPac AS9-HC (250 mm \times 2 mm); eluent: 1.5 mM $\text{NaHCO}_3 + 6.5$ mM Na_2CO_3 ; eluent flow-rate: 0.25 ml/min; detection: suppressed conductivity, ASRS ULTRA in external water mode (100 mA); run time: 50 min.

Current chromatographic conditions with hydroxide eluents

ICE separation: sample volume: 0.82 ml; analytical column: IonPac ICE-AS1 (250 mm \times 9 mm); trap column: IonPac AG10 (50 mm \times 4 mm); eluent: water; eluent flow-rate: 0.50 ml/min from 0 to 20 min and 1.00 ml/min after from 20 to 35 min; cut window from 8.5 to 14.5 min.

IC analysis: analytical column IonPac AS18 (250 \times 2 mm); eluent: 10 mM from 0 to 19 min, linear increase from 10 to 40 mM from 19 to 24 min, 40 mM from 24 to 40 min; eluent flow-rate: 0.25 ml/min; detection: suppressed conductivity, ASRS ULTRA II in external water mode (25 mA); run time: 25 min.

3.4. System blanks

The system blanks – hereafter simply referred to as blanks – obtained with the IonPac ICE-AS1 column were determined for chloride, sulfate, nitrate and phosphate in order to check if this column was really compatible with trace analysis.

Before determining the blanks, the injection loop and IC system were rinsed with UP water. Afterwards, three consecutive injections of UP water were done followed by a single injection of an aqueous multi-anion standard (chloride, sul-

Table 3

Typical system blanks ($\mu\text{g/l}$) for the determination of trace anionic impurities in HF with the ICE–IC approach

	Chloride	Sulfate	Nitrate	Phosphate
System blanks (with Ionpac ICE-AS1 column)				
Trial 1	– ^a	0.30	1.5	– ^a
Trial 2	– ^a	0.33	1.0	– ^a
Trial 3	– ^a	0.27	0.8	– ^a
Best estimate	<0.7	0.3	<1	<0.2

^a Not detected, masked by a residual fluoride peak.

fate, nitrate and phosphate) at 0.05 mg/l. All blank values obtained are summarized in Table 3.

The experiments indicate that fluoride is only washed out very slowly from the IonPac ICE-AS1 column. Because chloride is masked by the remaining fluoride peak, an upper limit of 0.7 $\mu\text{g/l}$ can only be given for the chloride blank. The sulfate blank was fairly constant (~ 0.3 $\mu\text{g/l}$) and approximately 100 times lower than the blank values reported by other authors for the previously described IonPac ICE-AS6 column (see refs. [6,7] and [9] from Part I [1]). The nitrate system blanks showed a slight decrease on going from trial 1 to 3, indicating that the system was still slightly polluted at the beginning of the trials. An upper blank of about 1 $\mu\text{g/l}$ was therefore given. The phosphate peak could never be detected during these trials. The reported phosphate blank of 0.2 $\mu\text{g/l}$ is an upper limit based on a minimum detectable peak height.

3.5. Calibration issues

Because the recoveries of the ICE pre-separation depend on the HF concentration [1], samples and standards were matrix matched and always contained between 19.8 and 20.2% (w/w) of HF.

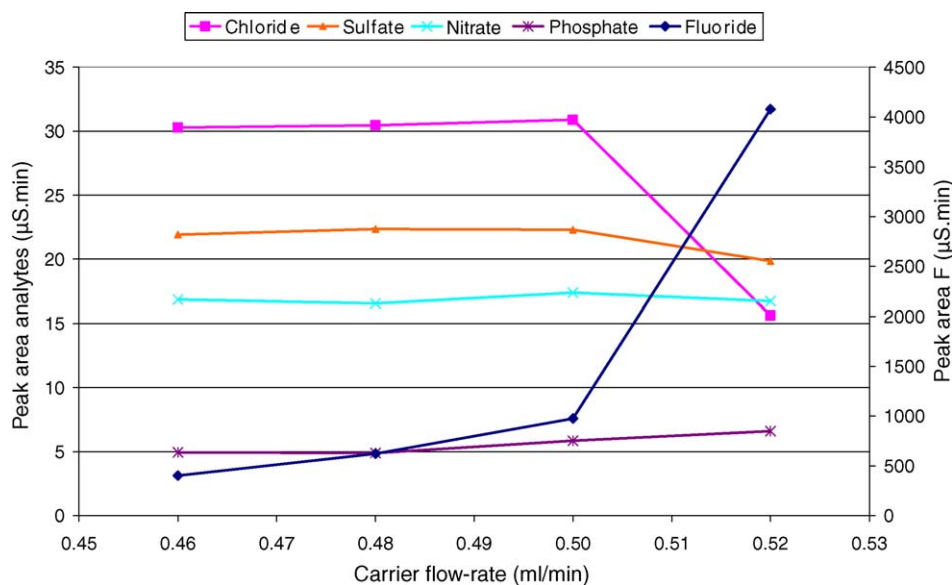


Fig. 2. Influence of the carrier flow-rate on the fluoride and analyte peak areas.

The anion levels in the real HF samples were determined by using the method of standard addition. A very pure HF sample, spiked with increasing analyte concentrations (0.02–0.10 mg/kg of diluted HF solution), was used to establish a calibration line. As no HF sample is completely free of anionic impurities, only the slope of this calibration line can be used to estimate the concentration of the other unknowns.

It has already been shown that when ortho-phosphate (OP) is added to HF (spiked sample), a part of it is transformed into mono-fluorophosphate (MFP) [1]. A peak corresponding to MFP is then also found back in the final ICE–IC chromatogram (retention time 27.7 min). In the case of unspiked samples, it is generally not possible to detect the MFP peak as their total phosphorus concentration is very low (see Table 4).

In practice, a fairly constant peak area ratio MFP/OP of 0.11 ± 0.02 was observed over the concentration range 0.02–1.0 mg added $\text{PO}_4/\text{kg HF 20\%}$ (w/w). This makes it possible to neglect the MFP peak and to obtain accurate total phosphate levels by a calibration based on the OP response only. These findings support the hypothesis of several authors that a chemical equilibrium might exist between all involved species [3]. In that case the ratio of MFP to OP is indeed expected to be constant and independent of the total phosphorus level, as long of course as the HF concentration is kept constant. This was indeed the case, as samples and standards were always diluted to $20.0 \pm 0.2\%$ (w/w) HF.

Table 4

Impurity levels for a few anions in commercially available hydrofluoric acids ($\mu\text{g}/\text{kg}$)

Sample	[HF] (w/w, %)	Chloride	Sulfate	Nitrate	Phosphate
A	40	<MDL	17	36	<MDL
B	48	59	58	73	14
C	49	27	10	100	<MDL
D	49	– ^a	20	35	<MDL
E	50	21	12	80	<MDL
F	49	40	12	27	<MDL

<MDL, below method detection limit (see Table 5).

^a Sample contaminated during transport, value not reported.

Fig. 3 shows typical calibration lines for chloride, sulfate, nitrate and phosphate in the range between 0.02 and 0.08 mg/kg HF 20% (w/w) of added anion. Sample F was used for the preparation of all standard solutions (see next section). At least three injections were done at each concentration level. The correlation coefficients for the calibration lines (ordinary linear regression) were 0.9937, 0.9985, 0.9972 and 0.9997, respectively.

3.6. Analysis results for some commercially available concentrated hydrofluoric acids

Table 4 shows the obtained anion levels on some high purity HF samples. Their origin has been omitted because of confidentiality.

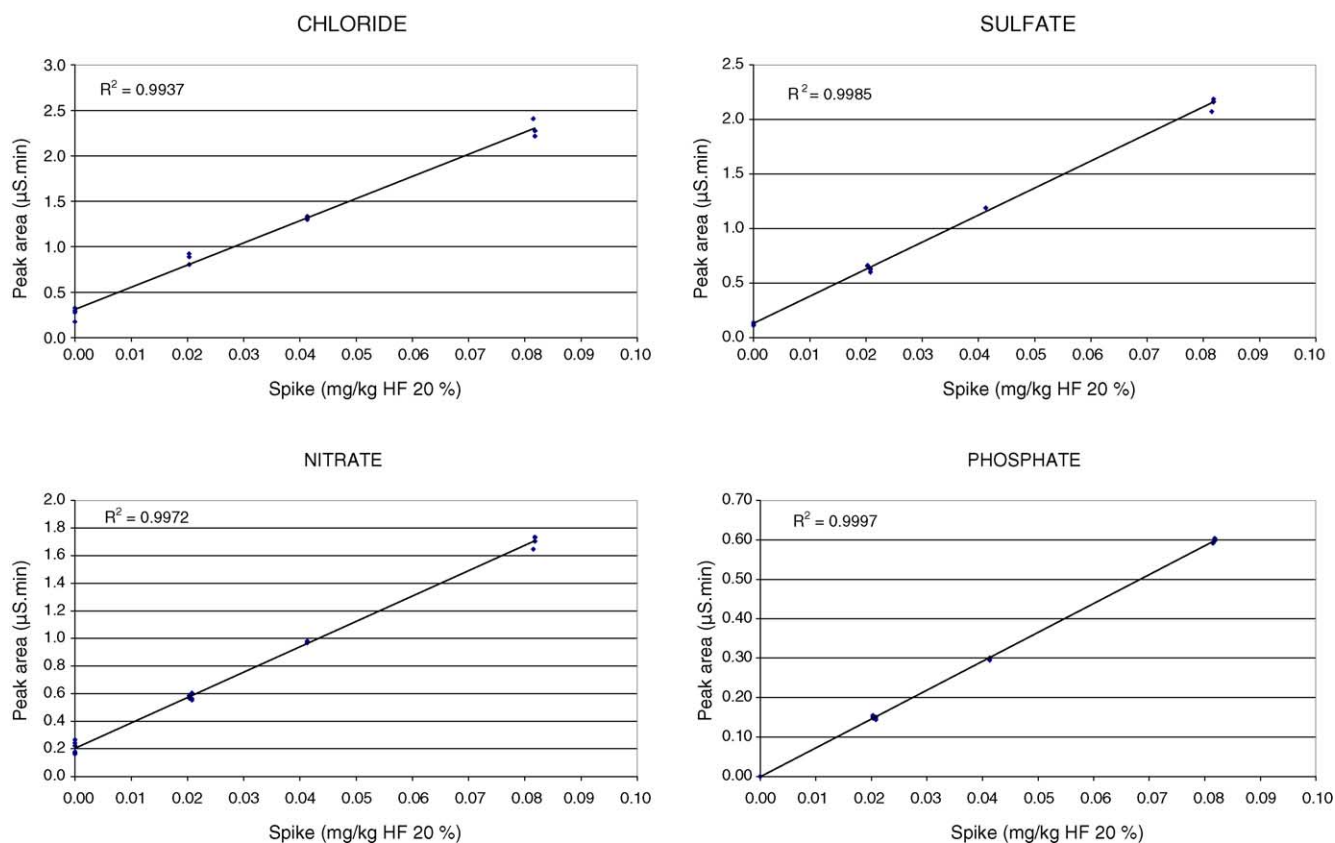


Fig. 3. Examples of calibration graphs in the range 0–0.08 mg/kg HF 20% (w/w).

Two of them are available in small quantities from major chemical reagents suppliers (A and B). Sample A is an analytical grade reagent, whilst sample B is a double distilled acid conditioned in a PTFE bottle. Samples C–F are all semiconductor grade samples put at our disposal by major American, European and Japanese producers.

Phosphate was only detected in sample B. Chloride levels were from <MDL – 60 $\mu\text{g}/\text{kg}$; sulfate levels from 10 to 60 $\mu\text{g}/\text{kg}$ and nitrate levels from 30 to 100 $\mu\text{g}/\text{kg}$.

Fig. 4 shows the obtained chromatograms for samples A and B (diluted to 20%, w/w) and of the same samples spiked with 0.1 and 0.08 mg/kg HF 20% (w/w) of the four anions, respectively.

When the time window between 25 and 35 min was zoomed in, a small MFP peak became visible as well as some other unknown peaks. No effort was yet made to identify them, but their concentration should be at the low $\mu\text{g}/\text{kg}$ level. Only for sample B, a rather important peak was observed between nitrate and phosphate. Addition

experiments indicated that most probably this impurity was chlorate.

3.7. Method validation according to SEMI

The ability of the proposed analytical method to support the latest (Tier C) guideline for hydrofluoric acid [2] was checked through a validation study performed in accordance with a specific SEMI procedure; including such parameters as method detection limits (MDL), accuracy and precision [4].

3.7.1. MDL and accuracy

Because of the lack of available Standard Reference Materials in complex matrices, such as HF, validation mainly relies on a spike recovery testing and on the determination of the MDL through a calibration curve. Both parameters can be obtained through a single series of experiments.

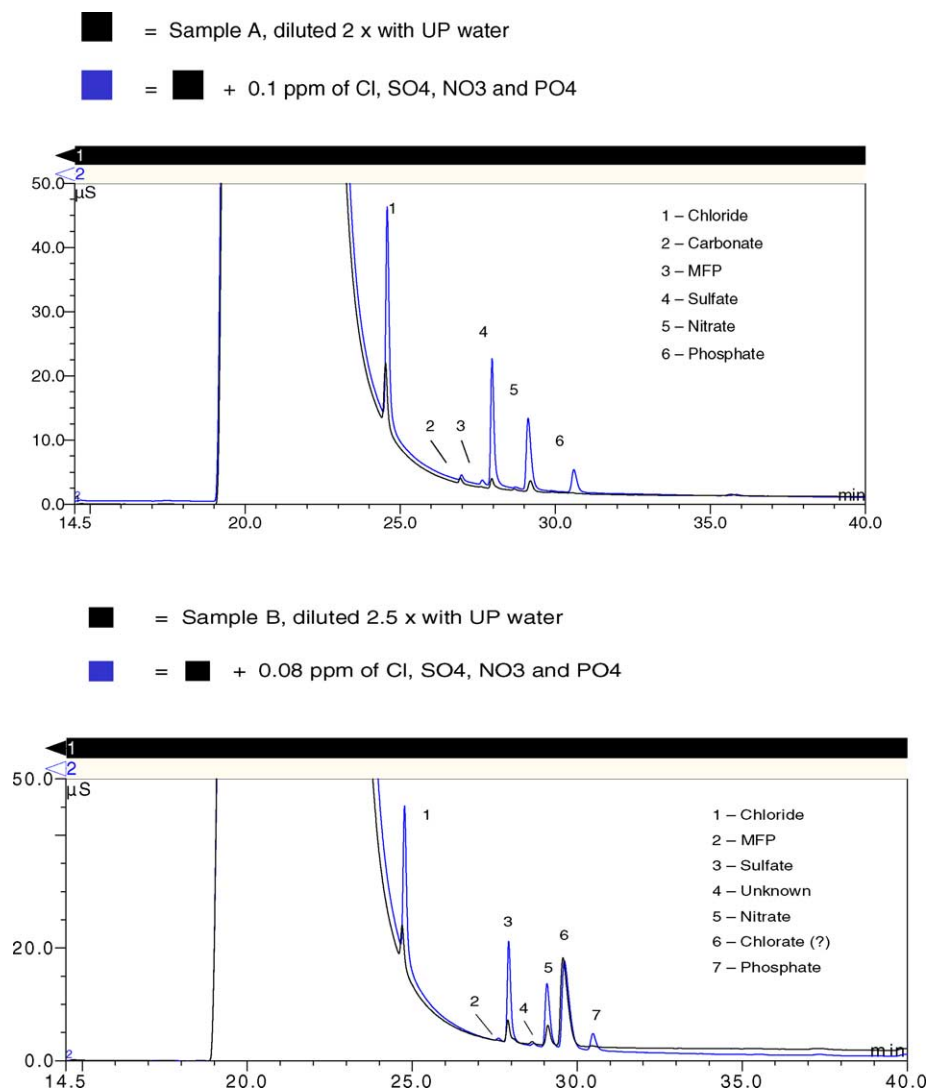


Fig. 4. Example chromatograms obtained for the analysis of ultra pure HF samples by the ICE-IC approach.

Table 5

Method detection limits obtained with carbonate and hydroxide based eluents for the determination of some anions in concentrated HF

	Chloride	Sulfate	Nitrate	Phosphate
Old MDL (carbonate)	0.011	0.031	0.0074	0.043
New MDL (hydroxide)	0.009	0.006	0.0068	0.0088
Gain	1.2	5.2	1.1	4.9

All values are expressed in mg/kg HF 50% (w/w) and calculated according to [5].

Old MDL's were based on a calibration curve (ordinary linear regression using peak area) build with four measurements of the following solutions: HF 49% unspiked, spiked with 0.05 ppm and spiked with 0.2 ppm of each anion.

New MDL's were based on a calibration curve (ordinary linear regression using peak area except for chloride) build with three measurements of the following solutions: HF 49% unspiked, spiked with 0.05 ppm, spiked with 0.1 ppm and spiked with 0.2 ppm of each anion.

MDL values were determined in accordance with a SEMI guideline [5]. It requires the establishment of a calibration curve with at least two different concentration levels, not including the blank. Triplicate analysis of each standard is needed. Moreover, the concentration levels investigated must either span the specification or include it as a level. The calculated MDL values are not allowed to exceed the specification.

In practice, four calibration standards were prepared from samples F or C (for chloride only) with added amounts of 0, 0.02, 0.04 and 0.08 mg/kg HF 20% (w/w). The spike of 0.04 mg/kg HF 20% (w/w) corresponds to 0.10 mg/kg HF 50% (w/w) which is also the proposed specification level for all anions in the new Tier C guideline.

Table 5 shows the MDL values which were obtained by an ordinary least squares regression based on peak height for chloride and peak area for the other anions. The obtained calibration lines were already shown in Fig. 3. All MDL calculations were done using the software program MDL Estimator [6].

As can be seen, the MDL values obtained by using hydroxide eluents are within the 6–10 µg/kg HF 50% (w/w) range and thus at least 10 times lower than the Tier C grade requirements.

Compared to our current method using carbonate/bicarbonate eluents [7], the gain in MDL is about a factor of 5 for phosphate and sulfate. For chloride and nitrate, only slightly better MDL values were obtained. It has to be repeated that the SEMI way of calculating limits is rather severe because it includes the global uncertainty of the calibration line. The instrumental detection limits, based on the background noise only, are significantly lower. Values of 2, 0.2, 0.4 and 1.4 µg/kg HF 50% (w/w) were computed for chloride, sulfate, nitrate and phosphate, respectively.

According to the SEMI rules [4], the accuracy was assessed through a spike recovery test based on the analysis of at least two samples and two spiked samples. The spike level must be half of the proposed specification. Spike recoveries on these individual samples should be between 75

Table 6

Accuracy of the method proposed for the determination of several anions in HF (recovery testing performed according to [4])

	Chloride	Sulfate	Nitrate	Phosphate
Sample F, #1	13.6	4.9	13.3	nd
Sample F, #2	–	4.9	9.2	nd
Average	–	4.9	11.2	nd
Sample F spiked, #1	35.5	26.6	31.2	20.7
Sample F spiked, #2	–	24.9	31.2	20.2
Sample C, #1	10.8 ^a	–	–	–
Sample C spiked, #1	31.5 ^a	–	–	–
Recovery 1	21.9	21.7	20.0	20.7
% Recovery 1	108	107	99	102
Recovery 2	20.7	20.0	20.0	20.2
% Recovery 2	101	96	96	97
Average recovery	104	101	97	100
% Recovery range	7	10	3	5

The spike level on the diluted samples (F and C) was 20.3 µg/kg HF 20% (w/w). All concentration values mentioned in the above table are expressed in µg/kg HF 20% (w/w).

^a Based on peak height data. #1 and #2, first and second sample preparation; nd, not detected.

and 125% of the expected value. Furthermore, the difference between the recoveries (%) obtained for the two samples may not exceed 35%.

Table 6 shows the results of the spike recovery tests. The results initially obtained for chloride on sample F #2 (unspiked and spiked) were rejected because of some identified problem and therefore repeated on sample C.

The average recovery for samples spiked with only 0.05 mg/kg HF 50% (w/w) (half of the Tier C guideline) is 104, 101, 97 and 100% for chloride, sulfate, nitrate and phosphate, respectively. These results are excellent and much better than what is required by SEMI. In addition, all recovery ranges (between 2.6% for nitrate up to 10.4% for sulfate) are also well below 35%.

3.7.2. Method precision

According to the SEMI procedure [4], the relative standard deviation (RSD%) obtained for the repeated injections of the spiked samples may not exceed 20%.

The obtained RSD% values for the three injections of the samples spiked at the 0.05 mg/kg HF 50% (w/w) level are shown in Table 7. For chloride, a much better precision (~1% RSD) was obtained by working in peak height. For the other anions, RSD ranged between 1 and 5% for peak area

Table 7

Relative standard deviations (RSD%) obtained for the three injections of the spiked samples F and C

Solution	Cl	SO ₄	NO ₃	PO ₄
Spiked sample F, #1	7.0	0.7	1.5	2.3
Spiked sample F, #2	–	2.8	4.8	2.3
Spiked sample C, #1	1.1 ^a	–	–	–

Spike level was 0.05 mg/kg HF 50% (w/w).

^a RSD% was based on peak height. #1 and #2, first and second sample preparation.

measurements. These precision data are very good and again much better than what is requested for by SEMI.

4. Conclusions

When the ICE–IC method for the anion analysis in concentrated hydrofluoric acid is used with an electrolytically generated and purified hydroxide eluent, a hydroxide selective high capacity anion exchange column and a low noise electrochemical suppressor, it is possible to achieve much better peak height sensitivities and significantly lower detection limits.

Compared to the currently used method within Solvay using a carbonate/bicarbonate eluent run onto the Ion-Pac AS9-HC column, the gain in peak height sensitivity ($\mu\text{S}\cdot\text{kg}/\text{mg}$ HF 50%, w/w), is a factor of 6 for chloride, 7 for nitrate, 16 for sulfate and 13 for phosphate [7].

The instrumental detection limits of the new method, calculated from the background noise and sensitivities, were estimated at 2, 0.2, 0.4 and 1.2 $\mu\text{g}/\text{kg}$ HF 50% (w/w) for chloride, sulfate, nitrate and phosphate, respectively.

For ordinary least square regressions based on peak areas (except for chloride), the method detection limits calculated according to SEMI [5], are 9, 6, 7 and 9 $\mu\text{g}/\text{kg}$ HF 50% (w/w) for the same anions in the same order. It has to be remembered that this way of calculating yields always much higher values because it includes the global uncertainty of the calibration line.

The newly achieved MDL values with a KOH eluent are all at least one order of magnitude below the Tier C guideline for HF [2], even for sulfate and phosphate.

The method has been further validated according to the SEMI regulations for such parameters as accuracy and precision. The average recovery for samples spiked with only 0.05 mg/kg HF 50% (w/w) is 104, 101, 97 and 100% for chloride, sulfate, nitrate and phosphate, respectively. The precision of the method, evaluated through the relative standard deviation of repeated injections at the 0.05 mg/kg HF 50% (w/w) level, is also very good and typically a few % for all anions.

All validation results are much better than what is required by SEMI. This confirms the potential of this method for reliable trace analysis of current and future semiconductor grades of HF.

References

- [1] K. Vermeiren, J. Chromatography A 1085 (2005) 60.
- [2] Book of SEMI International Standards 2004, Chemical Reagents Volume, Semiconductor Equipment and Materials International, Mountain View, CA, 2004, C28-0704.
- [3] L. Vanatta, D. Coleman, J. Chromatogr. A 804 (1998) 161.
- [4] Book of SEMI International Standards 2004, Chemical Reagents Volume, Semiconductor Equipment and Materials International, Mountain View, CA, 2004, C1-0704.
- [5] Book of SEMI International Standards 2004, Chemical Reagents Volume, Semiconductor Equipment and Materials International, Mountain View, CA, 2004, C10-0299.
- [6] T. Bzick, Air Products and Chemicals Inc., MDL software and manual.
- [7] D. Boyer, Solvay Fluorides, Alorton, IL, USA, personal communication.