Simultaneous determination of fluoride species plus acid anions in etching baths by ion chromatography with dual detection

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Ion Chromatography

Summary

This poster presents a straightforward ion chromatographic determination of HF, HNO_3, short-chain organic acids and H_2SiF_6 in etching bath samples. Standard ions such as fluoride, nitrate, acetate and sulfate are determined via suppressed conductivity detection while dissolved silicate is spectrophotometrically detected in the same run after downstream post-column reaction (PCR) as molybdosilicic acid. Analytical results of several commercial HF-HNO_3-H_2SiF_6 mixtures obtained by ion chromatography (IC) and titration showed good agreement, which confirms the applicability of the presented «dual detection» IC method for controlling the composition of acidic texturing baths.

Introduction

Energy production from renewable sources such as biomass, biogas, biofuels, water and wind power or solar energy is becoming increasingly important for our energy-hungry society. Particular interest is given to solar energy, which by human criteria is inexhaustible. Solar cells used in photovoltaic units convert the sun`s radiation energy directly into electric energy.

Solar cells are manufactured from monocrystalline and polycrystalline silicon wafers whose surface is treated in etching baths before being spiked with foreign atoms (P, B). The quality of the surface treatment and therefore the quality of the solar cells depends primarily on the composition of the etching bath, in particular on its fluorosilicate concentration. To reduce both costs and waste, any etching bath should be maximally used. Bath utilization is enhanced by replenishing the used etching solutions with concentrated acids. The dissolution of silicon in the etching bath can be described by the following equation:

$$3\ Si\ +\ 4\ HNO_3\ +\ 18\ HF\ \longrightarrow\ 3\ H_2SiF_6\ +\ 4\ NO\ +\ 8\ H_2O.$$

The anions of interest can be determined quickly and precisely by titration and ion chromatography (IC).

The poster describes an ion chromatographic method that permits silicate, fluoride and other anions (CH_3COO^-, NO_3^-, SO_4^{2-}) to be determined with a single injection. Separation takes place on a high-performance anion exchange column. The «dual detection» technique is used: whereas the silicate determination takes place by post-column derivatization with subsequent UV/VIS detection at a wavelength of 410 nm, the remaining anions are determined by suppressed conductivity detection.

Instrumentation

- 858 Professional Sample Processor
- 850 Professional IC Anion – MCS
- Lambda 1010 UV/VIS Detector
- 771 IC Compact Interface
- Post-column reactor (not shown)

Method description

The dissolution of silicon in HF-HNO_3 etching baths leads to the formation of SiF_6^{2-}. Under the given alkaline eluent conditions, SiF_6^{2-} completely hydrolyzes into undissociated orthosilicic acid and fluoride:

$$Na_2SiF_6\ +\ 4\ NaOH\ \rightarrow\ Si(OH)_4\ +\ 6\ NaF.$$

After separation of the resulting HF-HNO_3-$Si(OH)_4$ mixture, the fluoride, nitrate, sulfate and acetate anions are determined by suppressed conductivity detection. The determination of the undissociated orthosilicic acid is achieved by downstream UV/VIS detection at 410 nm after post-column reaction with molybdate:

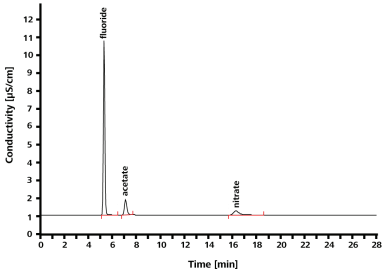
$$H_4SiO_4 + 12\ MoO_4^{2-} + 24\ H^+\ \rightarrow\ H_4[Si(Mo_3O_{10})_4] + 12\ H_2O.$$

Preliminary tests revealed that injection of a Na_2SiF_6 solution results in a fluoride and silicate peak whose areas correspond to those obtained from the single standards of identical concentration. This method assumes the absence of other fluoride or silicon sources.

a) Conductivity detection

Standard: 25 mg/L fluoride, 20 mg/L acetate, 10 mg/L nitrate

Column:	Metrosep A Supp 15 – 250
Column temp.:	45 °C
Eluent:	3.5 mmol/L Na_2CO_3 3.0 mmol/L $NaHCO_3$
Flow:	0.7 mL/min
Loop:	1.5 µL



While acetate and nitrate can be determined directly, the concentration of hydrofluoric acid has to be calculated as the difference between the total fluoride content and the complexed-fluoride content in the hexafluorosilicate:

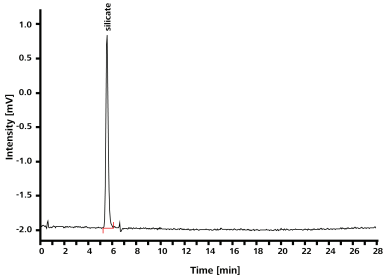
$$[HF] = [F^-]_{total} - [F^-]_{hexafluorosilicate}$$

b) Spectrophotometric detection after PCR

In a subsequent post-column reaction orthosilicic acid, generated from SiF_6^{2-}, reacts with Na_2MoO_4 to molybdosilicic acid, which is spectrophotometrically detected at 410 nm.

Standard: 10 mg/L silicic acid in NaOH

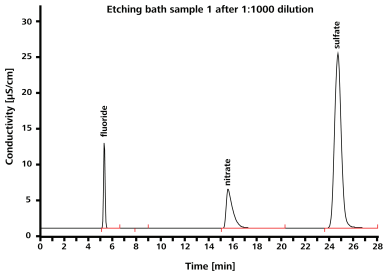
Column:	Metrosep A Supp 15 – 250
Column temp.:	45 °C
Eluent:	3.5 mmol/L Na_2CO_3 3.0 mmol/L $NaHCO_3$
Flow:	0.7 mL/min
Loop:	1.5 µL
PCR reagent:	200 mmol/L nitric acid 20 mmol/L Na_2MoO_4
PCR flow:	0.25 mL/min
Wavelength:	410 nm



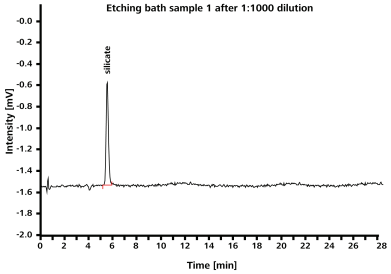
Etching bath samples

Chromatographic conditions correspond to those previously described for the standards.

a) Conductivity detection



b) UV detection after PCR



Comparison titration – IC

Chromatographic results were validated by comparing them with those obtained by titration with 1 mol/L NaOH. According to IC, the content of several components had to be calculated.

	Sample 1			Sample 2			Sample 3			Sample 4		
	Si	HF[a]	HNO_3[b]	Si	HF[a]	HNO_3[b]	Si	HF[a]	HNO_3[b]	Si	HF[a]	HNO_3[b]
IC [g/L]	3.3	22.4	216.6	34.7	47.2	248.4	17.6	98.9	504.4	19.3	94.8	516.8
Titration [g/L]	3.7	26.4	224.3	28.1	48.4	255.9	17.6	86.2	476.1	18.1	80.7	478.1
RSD_{IC} [%]	2.2	1.2	0.3	1.8	5.6	0.6	2.0	2.0	0.4	2.2	3.1	0.7
$RSD_{Titration}$ [%]	1.2	3.3	0.3	0.5	2.4	1.1	0.4	1.3	0.6	0.2	1.8	1.1

[a]calculated from the difference between the total fluoride content (conductivity channel) and the complexed fluoride content in the hexafluorosilicate (UV channel), [b]calculated from the NO_3^- content

References

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