Analysis methods for meso- and macroporous silicon etching baths

Julia B. Nehmann[1], Sarah Kajari-Schröder[1] and Detlef W. Bahnemann[2]

[1]Institut für Solarenergieforschung Hameln/Emmerthal (ISFH), Germany
[2]Institut für Technische Chemie, Leibniz Universität Hannover, Germany

Motivation

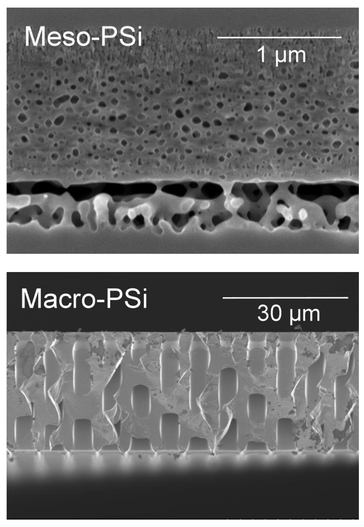
- Analysis of etching baths for porous silicon (PSi):

  Meso-PSi: HF (19.5 mol·L^{-1}) + ethanol
  Macro-PSi: HF (1.5 mol·L^{-1}) + acetic acid

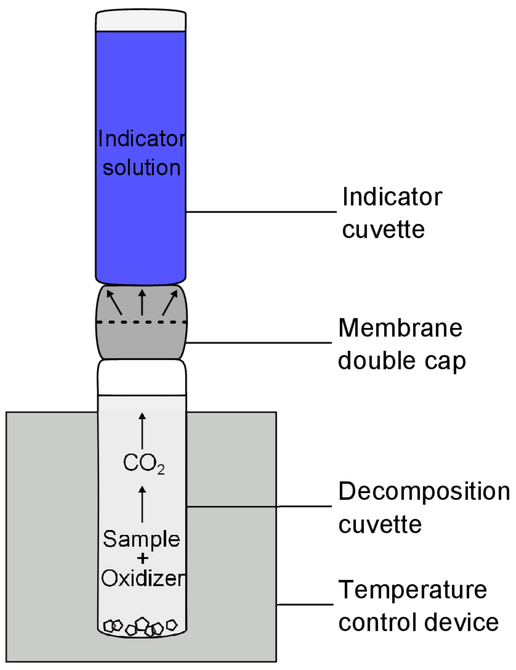
- Constant process conditions for homogeneous pore formation

→ Requires analysis of chemical composition of electrolytes

- Methods for determination of HF and organic contents described



Determination of Organics



Heating the sample at 100 °C for 2 hours sets CO_2 free and leads to a color change of the indicator solution.

P. Prütz, "TOC wastewater analysis". Hach Lange. www.hach-lange.de.

Observed color changes: 0 ppm, 10 ppm, 25 ppm, 35 ppm, 50 ppm TOC (from left to right).

Cuvette test system:

- By HACH LANGE
- Analysis of wetting agents ethanol and acetic acid
- Determination of "Total Organic Carbon" = TOC

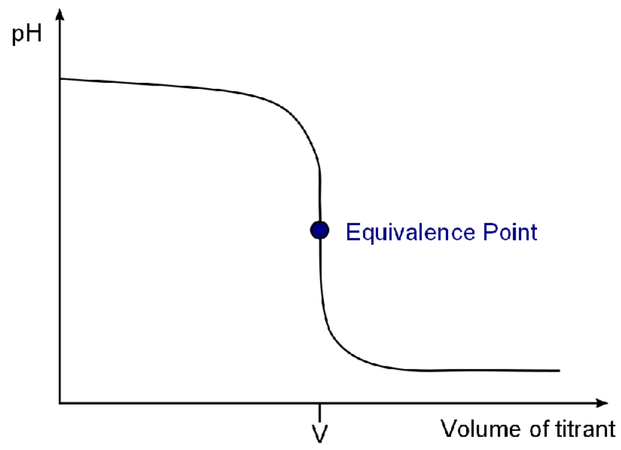
→ Measurement range: 2 – 65 ppm TOC
→ Relative error: 2.3%

Determination of HF

Titration:

1. Adjustment to pH 6.5 – 7.5 with NaOH
2. Titration with $La(NO_3)_3$ for determination of HF

$La^{3+} + 3\ F^- \rightarrow LaF_3$
$La^{3+} + 3\ H_2O \rightarrow La(OH)_3 + 3\ H^+$

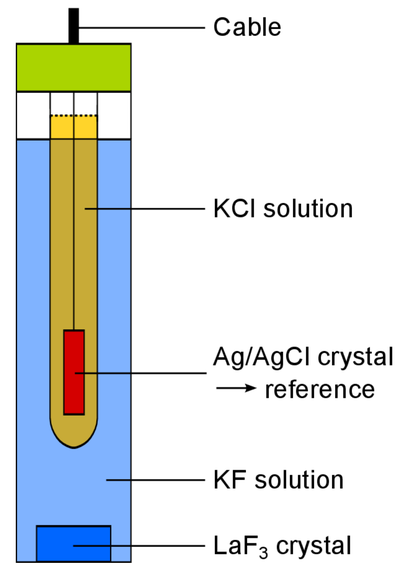


The volume of the titrant at the equivalence point is used for the calculation of the HF concentration.

W. Weinreich et al. *Talanta* **71**, 2007, 1901-1905.

Fluoride Ion-Selective Electrode:

→ Direct measurement of HF in sample

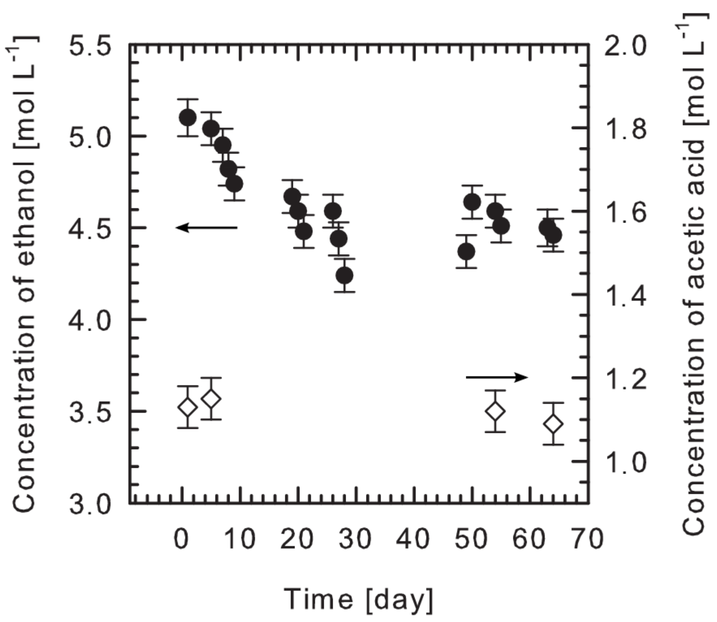


Schematic diagram of a Fluoride Ion-Selective Electrode (F-ISE).

Parameter	Titration	F-ISE
Measurement method	Indirect	Direct
Measurement range	> 50 mmol·L^{-1}	0.05 – 50 mmol·L^{-1}
Time for measurement	15 min	5 min
Time for calibration	5 min[a]	15 min[b]
Suitable for acetic acid containing electrolytes?	No	Yes
Relative error	± 3.3%	± 1.5%
Standard deviation *(40 samples)*	± 0.3%	± 0.3%
Inline analysis possible?	Yes	Yes

[a]once a week [b]directly before measurement

Application to Etching Baths for Porous Silicon

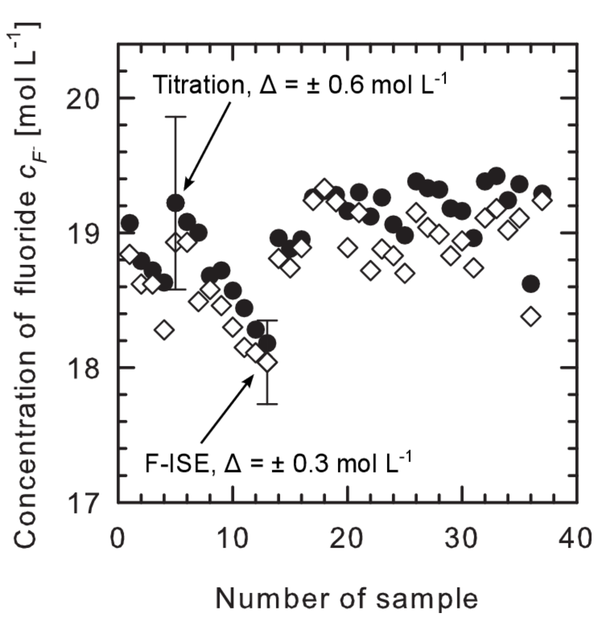


Development of organic contents in Meso- and Macro-PSi baths over time.

- Monitoring the constituents of the etching baths for porous silicon over time
- Meso-PSi: Titration, cuvette test method
- Macro-PSi: F-ISE, cuvette test method
- Loss of HF due to evaporation during etching
- Enlargement of bath lifetime due to replenishment of HF

Conclusion:

→
- Keeping etching parameters constant due to stable HF concentration
- Constant process conditions achieved
- Homogeneous pore formation



Comparison of HF concentrations determined by titration and F-ISE.

Institut für Solarenergieforschung Hameln / Emmerthal
Am Ohrberg 1, D-31860 Emmerthal, Germany, Tel.: +49 (0) 5151 999-100, Fax: +49 (0) 5151 999-400