Specific Targeted Research Project FP6-034472

Water Risk Management in EuRope
WARMER

Multiparametric automatic detection of water quality chemical parameters using a strip of miniaturized ion-selective potentiometric electrodes working in a modular flow-cell

presented by

Prof. Leszek J. Opalski
Institute of Electronic Systems
Warsaw University of Technology, Poland

at the Workshop:

Environmental Risk Management Tools For Water Quality Monitoring

National Oceanographic Centre Southampton (UK), 30th March 2009

Outline

- Expectations
- THE probe (uLFA)
- Problems to be solved
- Measurement procedures used
- Implementation of measurement procedures in uLFA
- Final remarks

Note: the presentation includes contribution from the following WARMER partners:

- WUT-DACh – sensor and meas. procedure development
- WUT-ISE – sensor modelling, data processing, uLFA lab-testing, meas. proc. tuning
- Systea company – design of uLFA hardware, principles of operation
- Sysmedia company – firmware and electronics of uLFA
- MEDBRYT – sensor cells, ISE manufacturing and testing

Expectations

- Capability to determine concentration of selected *set of ions* in water (multi-parameter measurement) using miniaturized Ion Selective Electrodes
- Autonomous operation for 3 – 6 months (long term sensor stability, automatic cleaning)
- Response time: from 1-5 minutes (streams) to 30-120 minutes (sea)
- Measurement uncertainty:

  relative: 10 – 20 % (pX: 0.04 – 0.08)

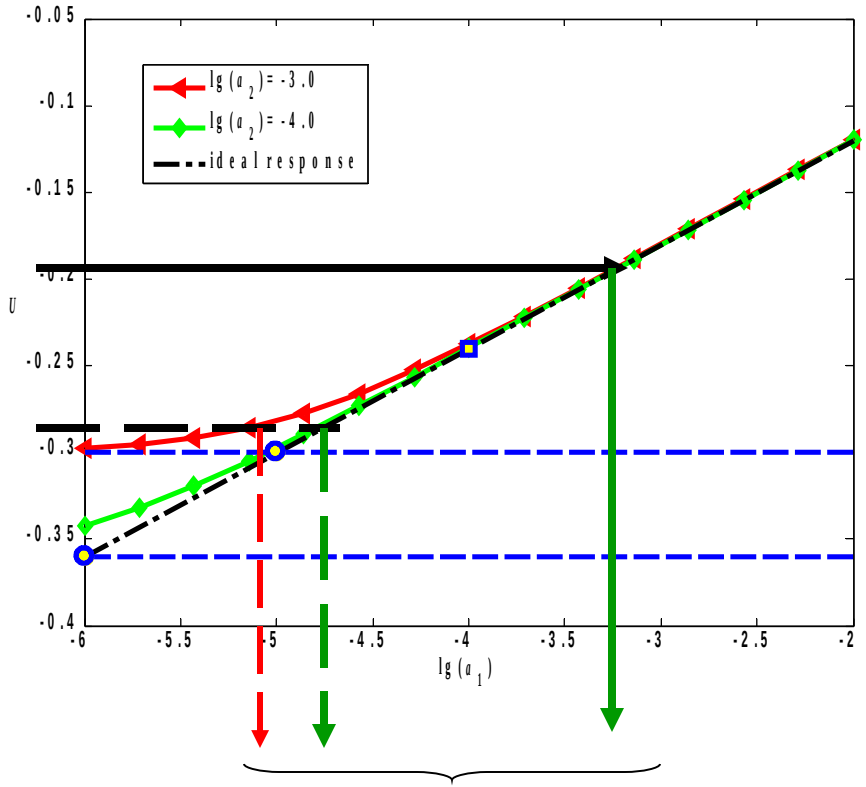
Potentiometric sensors in WARMER

NH4+	1-4pX (1.8-1800 ppm)
NO3-	1-4pX (6.2-6200 ppm)
Na+	1-4pX (2.3-2300 ppm)
K+	1-4pX (3.9-3900 ppm)
Cl-	1-4pX (3.5-3500 ppm)
Pb++	> 50 ppt
Cd++	>10 ppt
Cu++	>6 ppb
Zn++	Extra sensor

There are trade-offs that make satisfaction of all expectations virtually impossible

Potentiometric sensor basics

Sensor response in a binary solution



read-outs

estimates of the main ion activity

Even for ideally modelled and calibrated single sensor there exists an uncertainty of measurement, dependent on sensor selectivity and interfering ion activities

A need for multiparameter approach:

- measurement procedure
- fusion of read-outs from related sensors

$$U = U_0 + \frac{S}{z_m}\lg\left(\sum_{i=1}^{M} K_{m,i}a_i^{z_m/z_i}\right), \qquad K_{m.m} = 1$$

Nikolsky-Eisenmann model

Problems to be solved

- Accuracy/precision requirements

  Major contributors to measurement uncertainty:
  - non-ideality of Ion-Selective Electrodes
  - liquid dosing precision

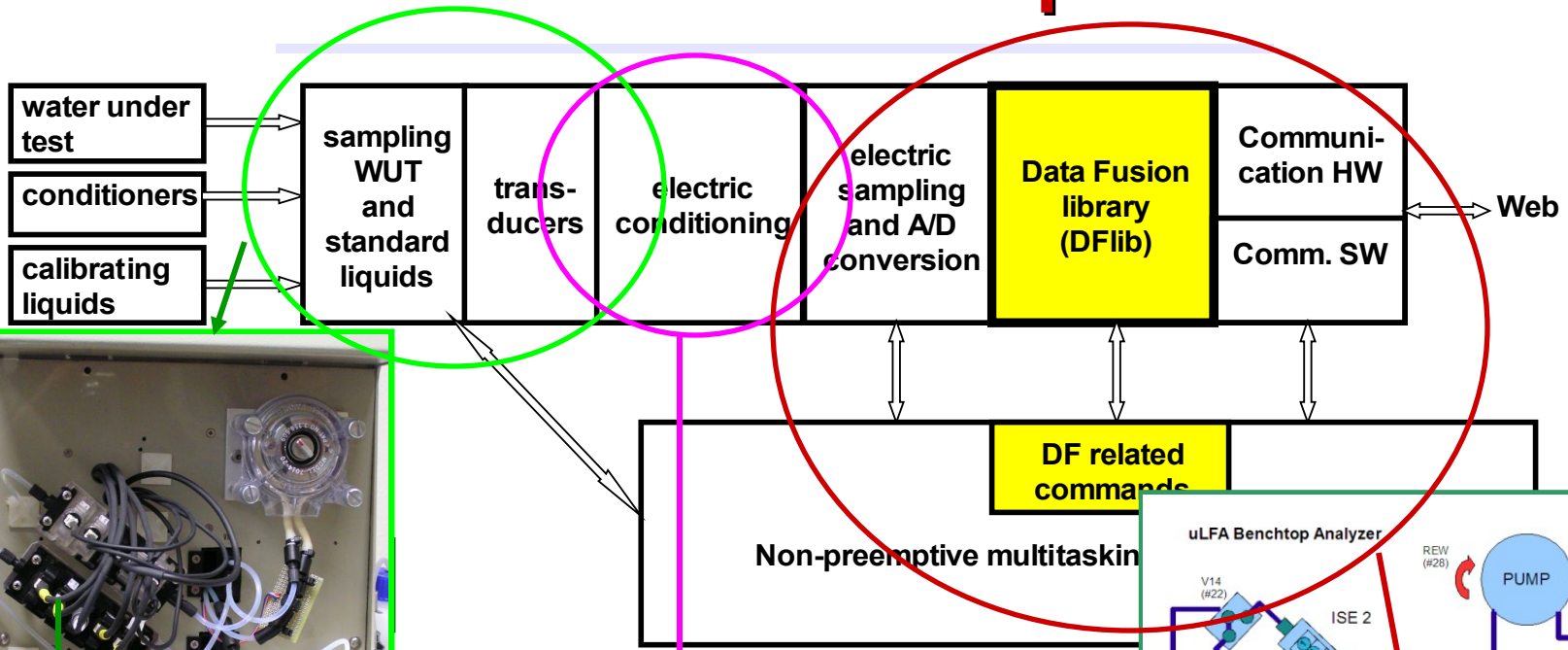
- Lifetime of a stand-alone measurement unit

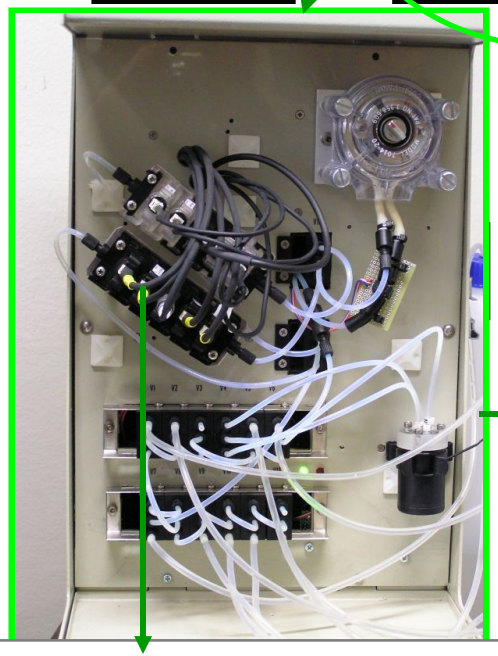
  Limiting factors
  - sensor lifetime
  - volume limitation of standard liquids

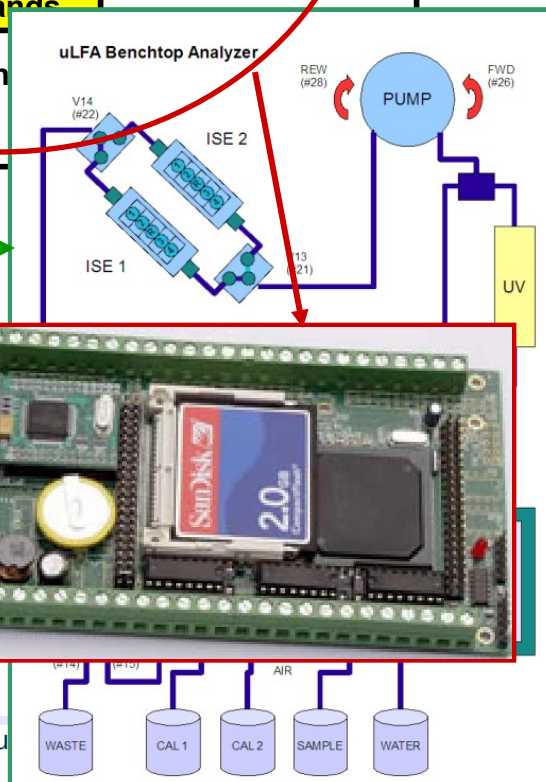
Actions

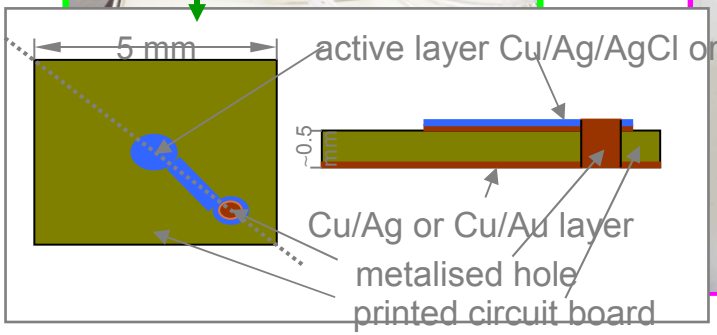
- sensor development
- hydraulic circuit design
- measurement procedure selection
- data processing (multiparameter methods)

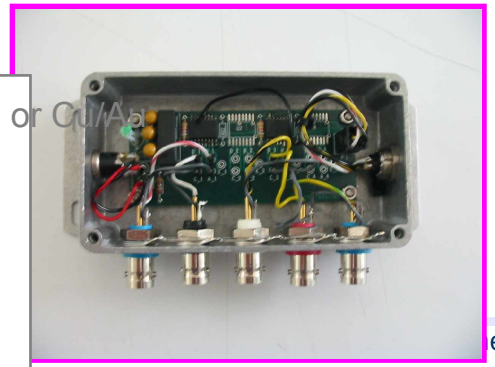
Architecture of the probe







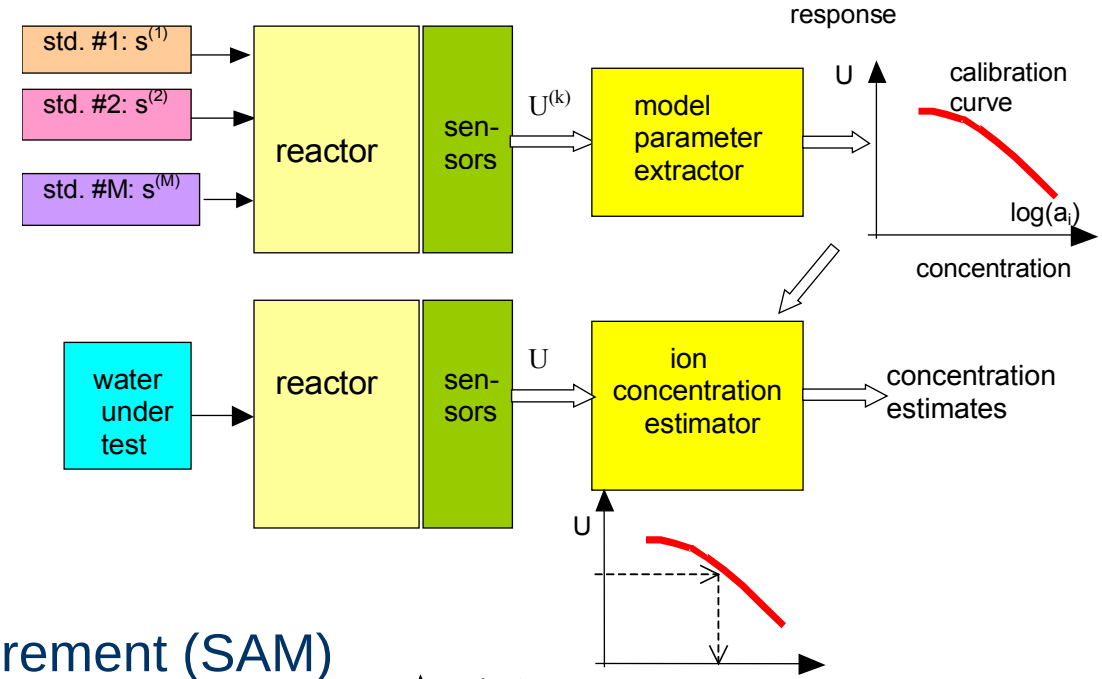




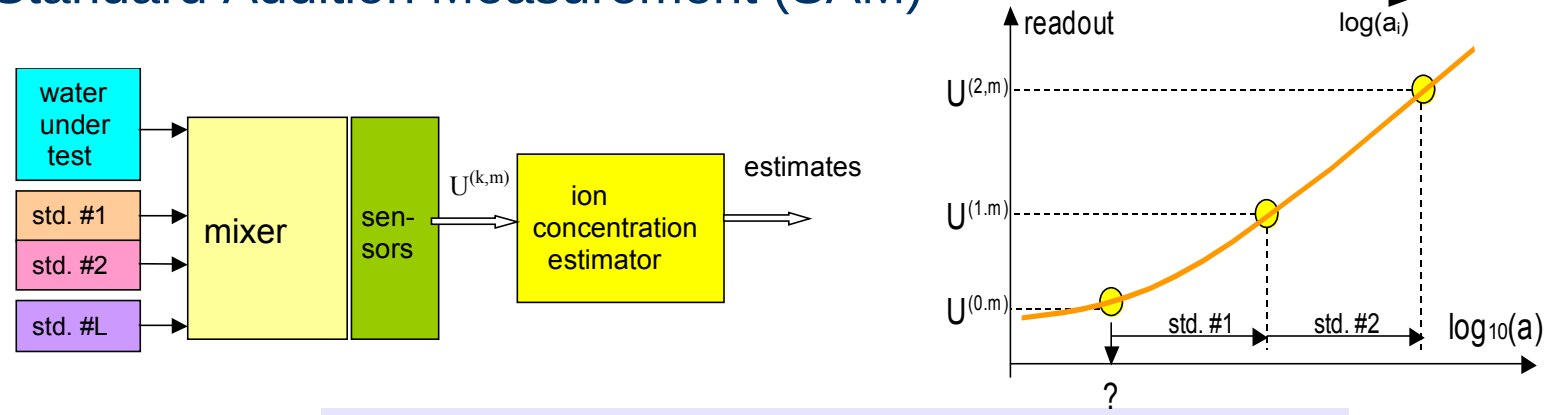
eters..., Sou

Measurement procedures considered

- Pre-Calibration based Measurement (PCM)



- Standard Addition Measurement (SAM)



Implementation of measurement cycles

Laboratory measurement procedures have to be

adapted

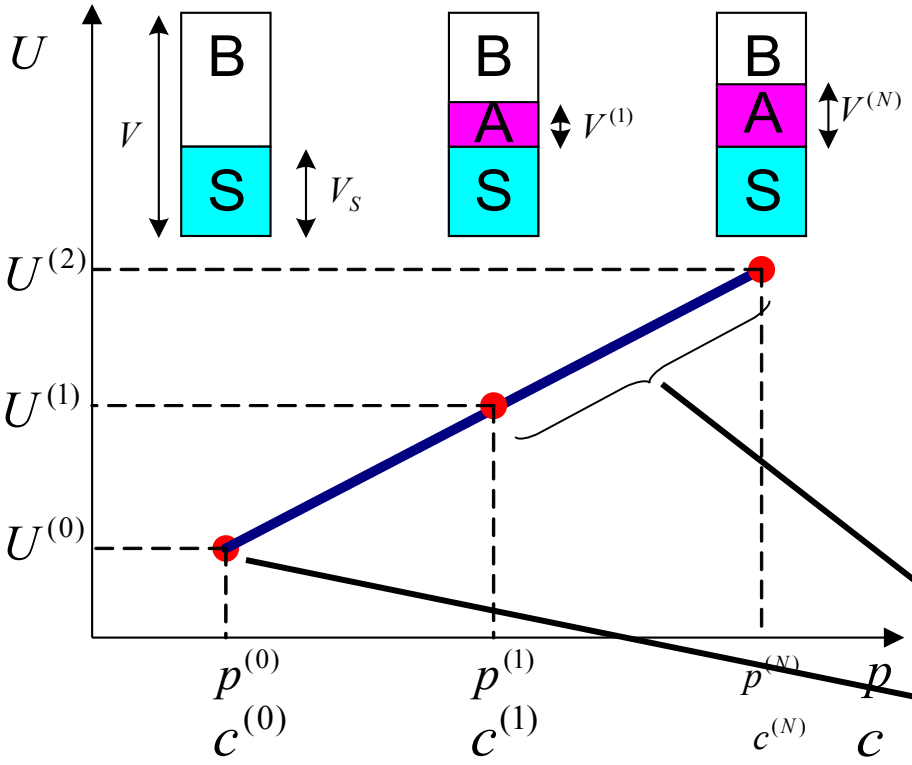
to become appropriate for

on-line automatic measurements

with miniaturized Ion Selective Electrodes

>

Conventional Standard Addition Measurement (CSAM) technique



$$c_m^{(j)} = c_m \frac{V_s}{V} + s_m \frac{V^{(j)}}{V}$$

$$c_i^{(j)} = c_i \frac{V_S}{V}, \quad j = 1,\ldots,N$$

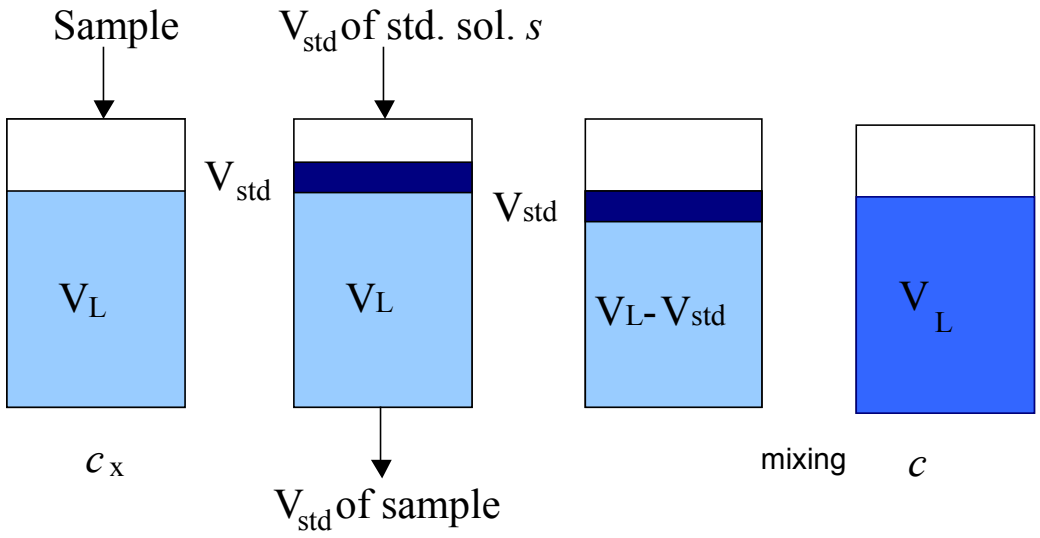
Algorithm

2. Slope calculation

3. Back extrapolation

CSAM technique requires large volume of liquids, and so has to be modified to fit in-situ measurement units that operate stand-alone for months

Fixed volume Std. Addition Method - idea



$$c_x^{(j)} = c_x^{(j-1)}(1-\beta_j) + s_x^{(j)}\beta_j$$

$$\beta_j = \frac{V^{(j)}}{V}$$

$$U \approx U_0 + \frac{S}{z_m}\lg(c_m)$$

- low interferent level sensor approximation

If additions are large enough: $c_m^{(j)} = s_m^{(j)}, j = 1,2$ Then:

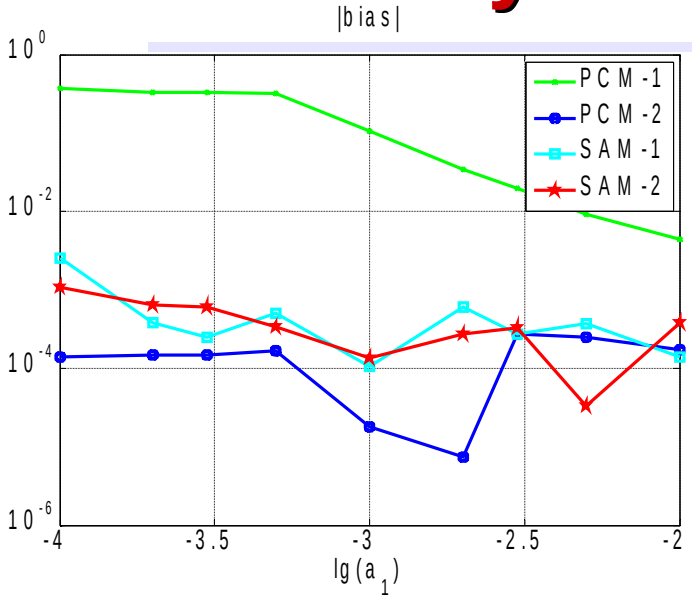
$$S \approx \tilde{S} = z_m \frac{U^{(2)} - U^{(1)}}{\lg(c_m^{(2)}/c_m^{(1)})} \approx z_m \frac{U^{(2)} - U^{(1)}}{\lg(s_m^{(2)}/s_m^{(1)})} \rightarrow c_m \approx \tilde{c}_m = \frac{\beta_1 s_m^{(1)}}{10^{z_m \frac{U^{(1)} - U^{(0)}}{\tilde{S}}} + \beta_1 - 1}$$

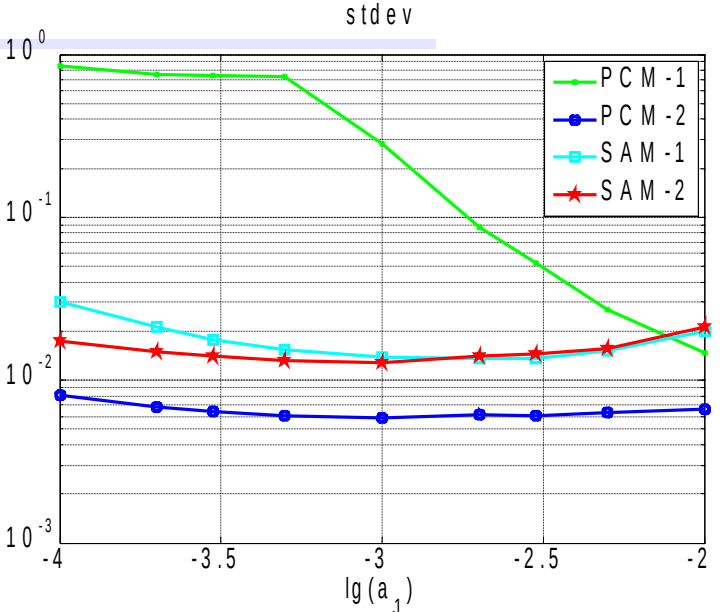
Uncertainty of PCM vs. SAM

a)

$lg(c_2)$=-3

PCM-2 is the best



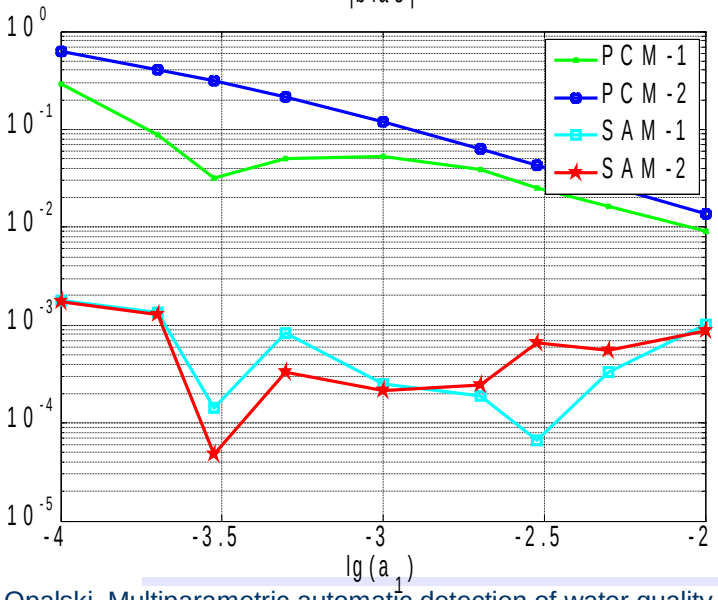


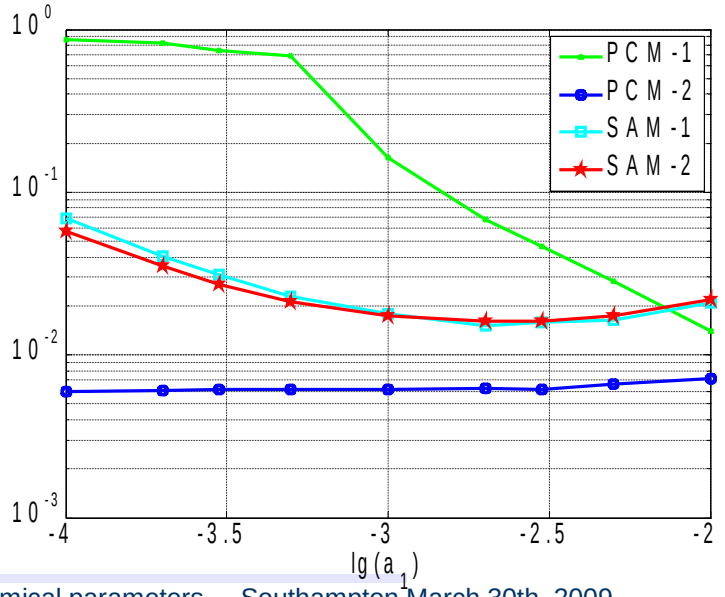
b)

$lg(c_2)$=-3

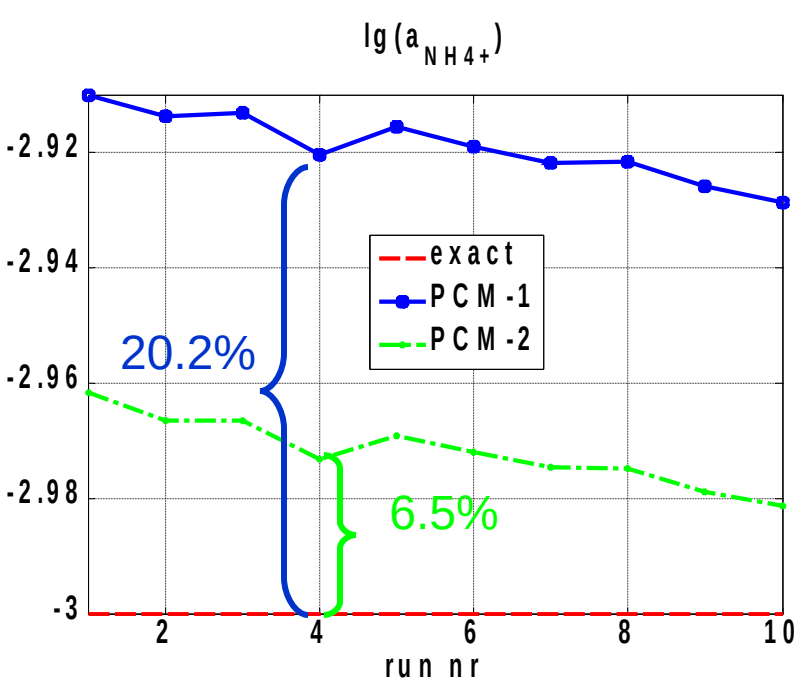
$lg(c_3)$=-1

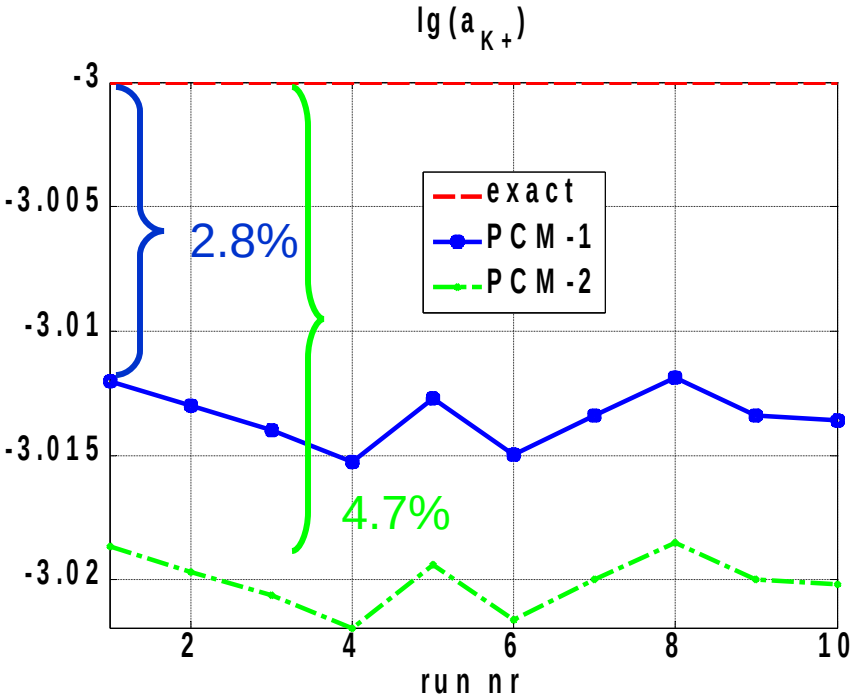
PCM-2 / SAM?





Example results for PCM





Main ion (NH4+) – large accuracy improvement

Interfering ion (K+) – slight accuracy deterioration

Final remarks

Major features of uLFA + WUT-DACh ISEs:

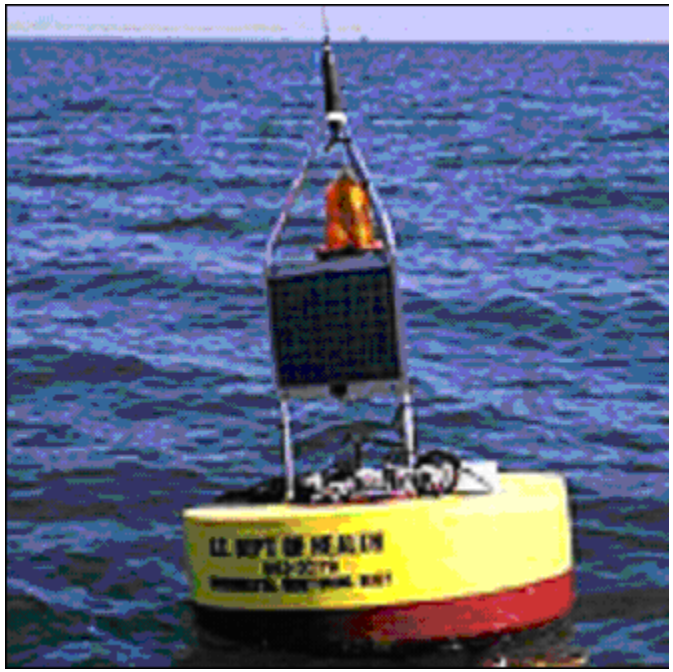
- ready for autonomous long-term operation with remote access/control
- script based programmability of measurement cycles+ multi-tasking firmware
- good repeatability of measurements
- multiparameter built-in capability (up to 8 ions) for enhanced accuracy with low selectivity sensors

Measurement procedure selection – trade-off situation

SAM	PCM	Feature
+		(small) volume of liquids used
+		resistance to ion-matrix effect
	+	precision

Multiparameter (DF) approach improves accuracy, but still

measurement range is limited by sensor selectivity and interferent activity



Thank you for your attention