Determination of pH and pCO2 - new autonomous instrumentation for Ferrybox

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[2] Franatech GmbH
[3] GEOMAR

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Outline

- The Ferrybox network to be used for ocean acidification studies in Norway
- New approach/idees and sensor for carbon systems sensors Ferrybox
- Some preliminary tests of the new systems
- Future work

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Motivation

- Assessment of anthropogenic impact on marine carbon system is increasingly demanding

- Support the national monitoring program of marine acidification in Norwegian waters

- Increase knowledge about the inter-annual changes of pH and pCO_2 in a challenging area

- High frequent measurements is needed of carbon speciation in the surface water

- Deployment of cost effective instrumentation capable to detect changes at the level necessary to understand and estimate future trends of ocean acidification

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Norwegian Ferrybox network

Core water sensors
- Inlet temperature
- Temperature
- Salinity
- Turbidity
- Oxygen

Biogeochemical
- Chl fluorescence
- PC Fluorescence
- CDOM Fluorescence
- pH and pCO2

Water samples
- Chl-a
- TSM
- Turbidity
- CDOM
- Nutrients
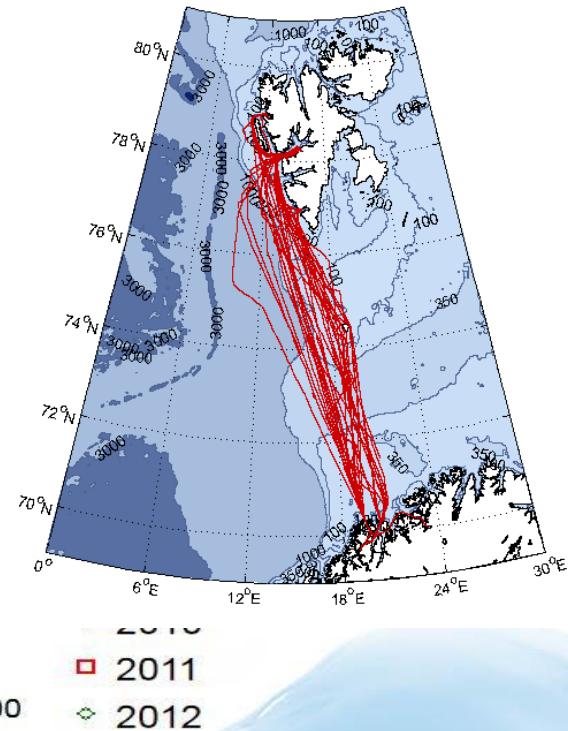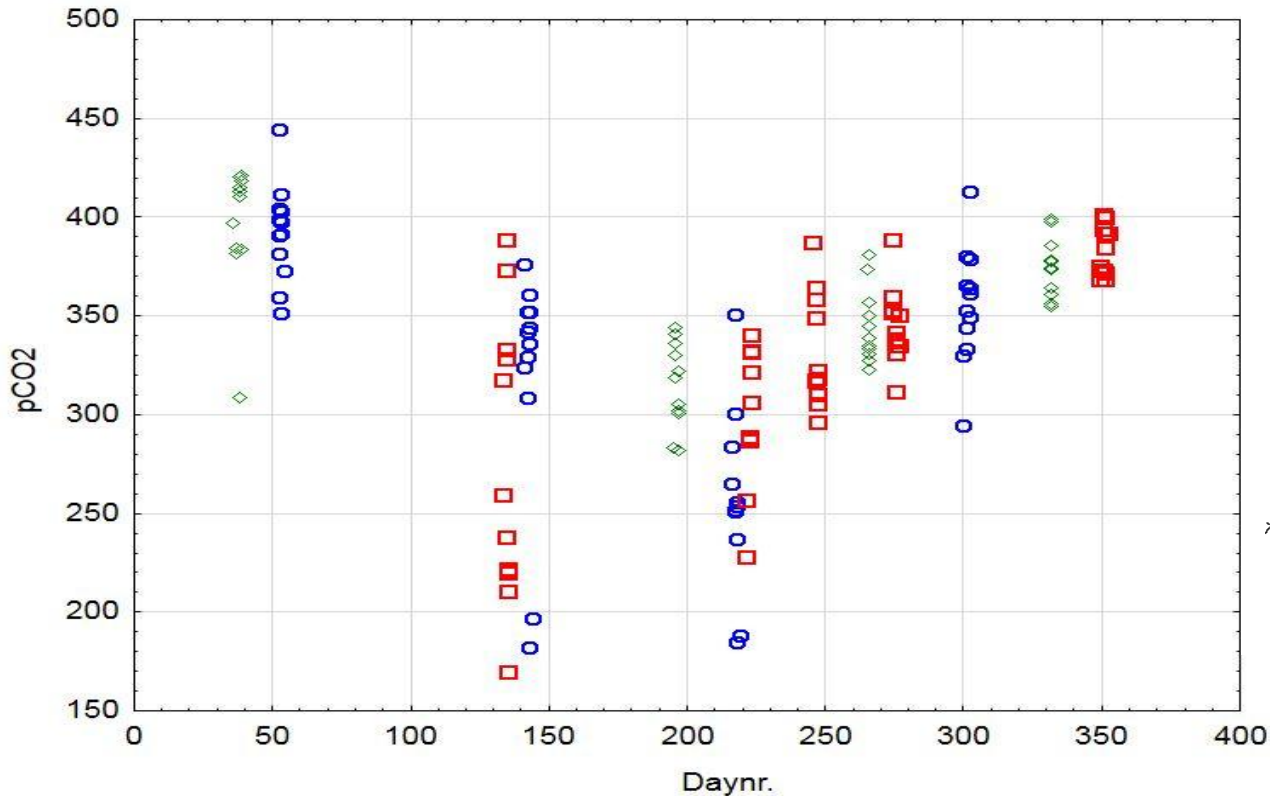- Algal pigment absorbtion
- Algae taxonomy

Deck sensors
- Uppwelling Radiance
- Down welling radiance
- Downwelling Irradiance
- Wind

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Inter-annually variation in pCO₂ in the Arctic waters

From the national monitoring program in the Arctic

Seasonal changes in pCO2 (TOT-pH/AT) categorizead by year

Based on water sampling and At, Ct, pH measurements

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Ferrybox pCO2 and pH

- A new installation combining autonomous pCO_2 and spectrophotometric pH detection will be installed in 2013.

- pH is based on an effective set-up for high resolution absorbance detection of a suitable dye injections. Developed at NIVA.

- pCO2 using combined membrane technology and a new solid state detector. Developed at Franatech.

- Couple the two measurement systems in a compact, reliable Ferrybox set-up requiring minimal maintenance, optimal calibration to performed the needed requirements.

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Recommendations for accuracy and precision of pCO2 meas.

Accuracy. (Values in brackets are calculated by me from the other values)

Demands	Range (µAtm)	Accuracy µAtm)	Accuracy in %
Shall	<= 400	+/- 4	(+/- 1%)
Shall	> 400	(+/- 4 to +/- 20)	+/- 1 %
Should	<= 400	+/- 2	(+/- 0.5 %)
Should	>400	(+/- 2 to +/- 10)	+/- 0.5%

Precision: (Values in brackets are calculated for what in the text)

Demands	Range (µAtm)	Accuracy (µAtm)	Accuracy in %
Shall	<= 400	+/- 2	(+/- 0.5%)
Shall	> 400	(+/- 2 til +/- 10)	+/- 0.5 %
Should	<= 400	+/- 1	(+/- 0.25 %)
Should	>400	(+/- 0.5 to +/-5)	+/- 0.25%

Ref: Ocean Observatories Initiative, 16.11. 2010.

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Preliminary wish list for pCO2 and pH sensor in a Ferrybox

- High accuracy and precision
- Small and cost effective
- Easy installation
- Onboard calibration (Cal. gas, CRM)
- Low calibration frequency
- Fast response time
- Flow trough system (easy water in and out)
- Easy maintenance (membranes, cleaning, dyes...)
- Leakage detection - stop of pumps
- Online operational software interfaced with Ferrybox SW (SST, SSS, pump stop in harbour)
- Handle variable pressures in the Ferrybox due to e.g. blocking of inlets/outlets

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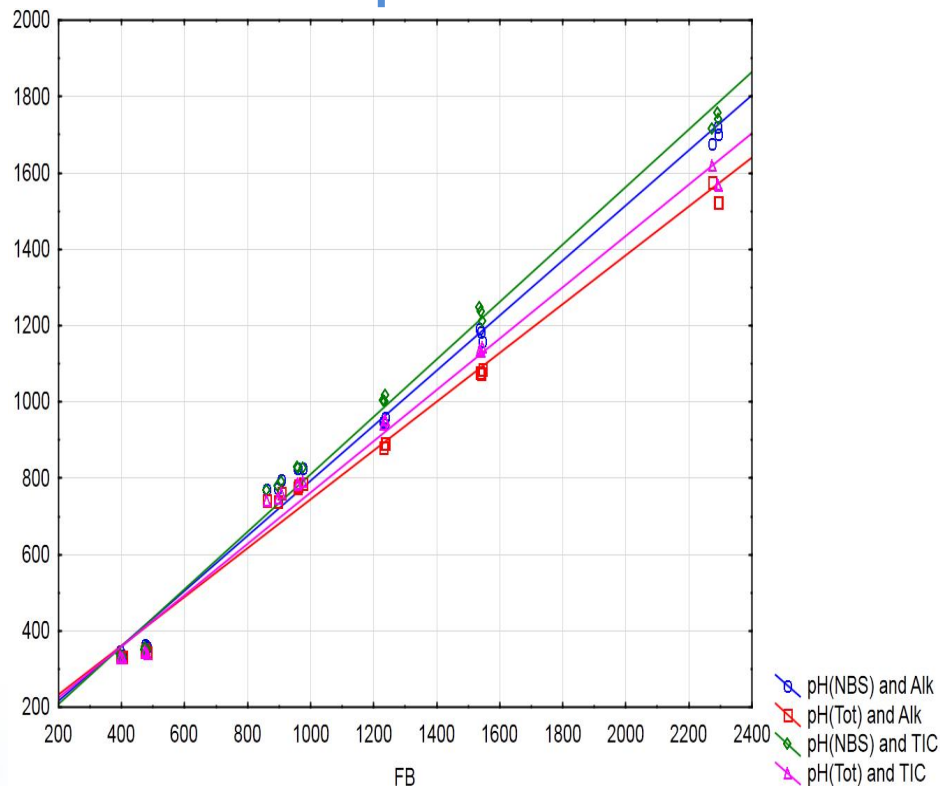# Franatech pCO₂ systems for Ferrybox installations

- Membrane based system
- Solid state detector
- Calibration on-board
- Easy to maintain/replace

- Flow through system
- Uses external pump (Ferrybox)
- Water leakage detector
- Internal logging and on-line SW
- Communication with Ferrybox

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Ongoing technical tests

- Mechancial test on the ship
  - Optimal flow
  - Membrane pressure test
  - Ferrybox pump test
- Technical tests of response time
- Linearity, accuracy and precision
  - compared with calculated $pCO2$ from At, Ct, pH
  - compared to GO $pCO2$ systems
- Calibration with NOAA high precision gas
- Field comparison with GO-$pCO2$ system
- Long term performance test

Preliminary linearity test of Franatech pCO2 sensor with pCO2 calculated from pH, Ct, At as "true" values.

- **What is the true pCO2value?**

- **There are uncertainty in the CO2SYS calculations equations (10%)**

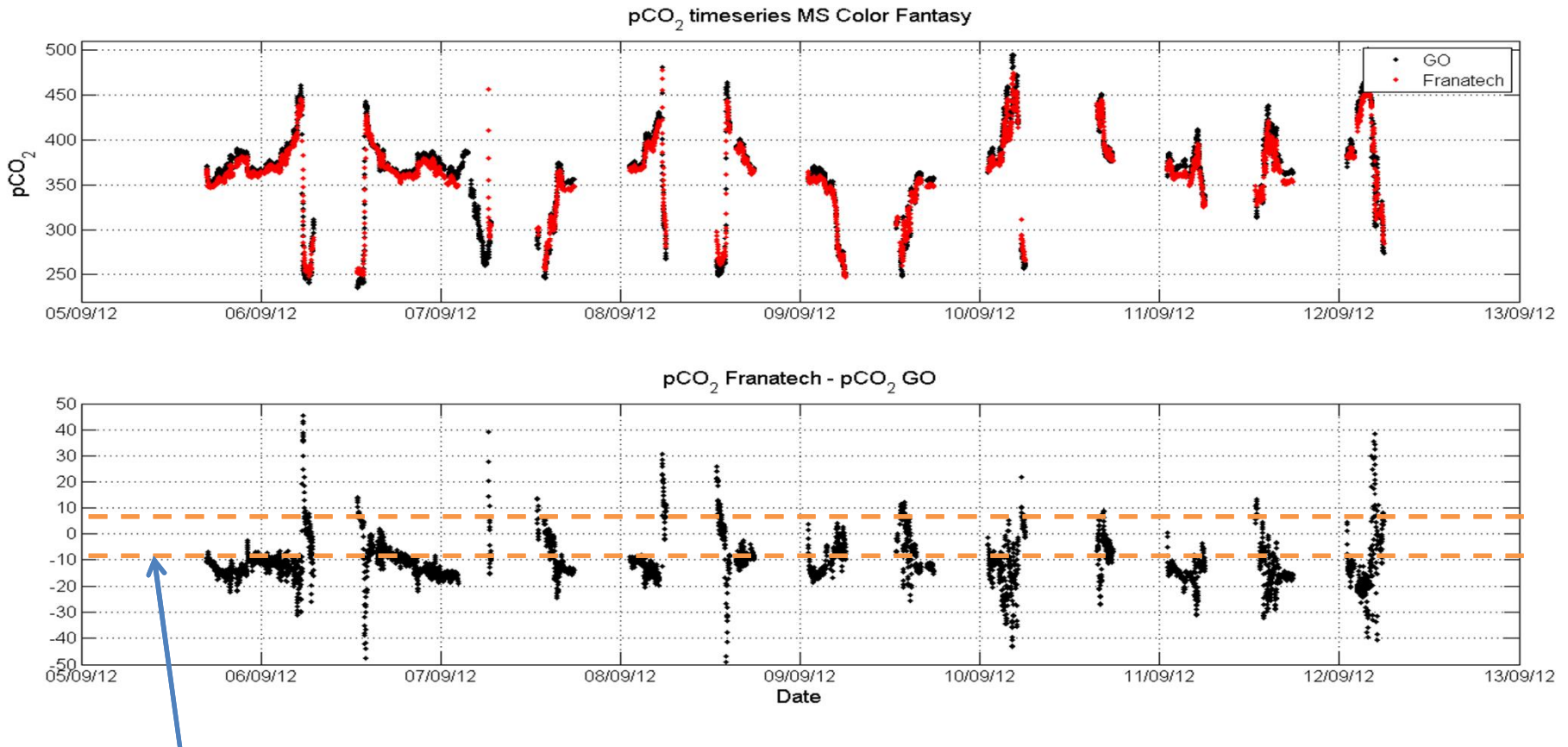- **Good linearity over the concentration range 0-2000 ppm**

FB: pH(NBS) and Alk: $r^2 = 0,9904$
FB: pH(Tot) and Alk: $r^2 = 0,9854$
FB: pH(NBS) and TIC: $r^2 = 0,9914$
FB: pH(Tot) and TIC: $r^2 = 0,9869$

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Response test
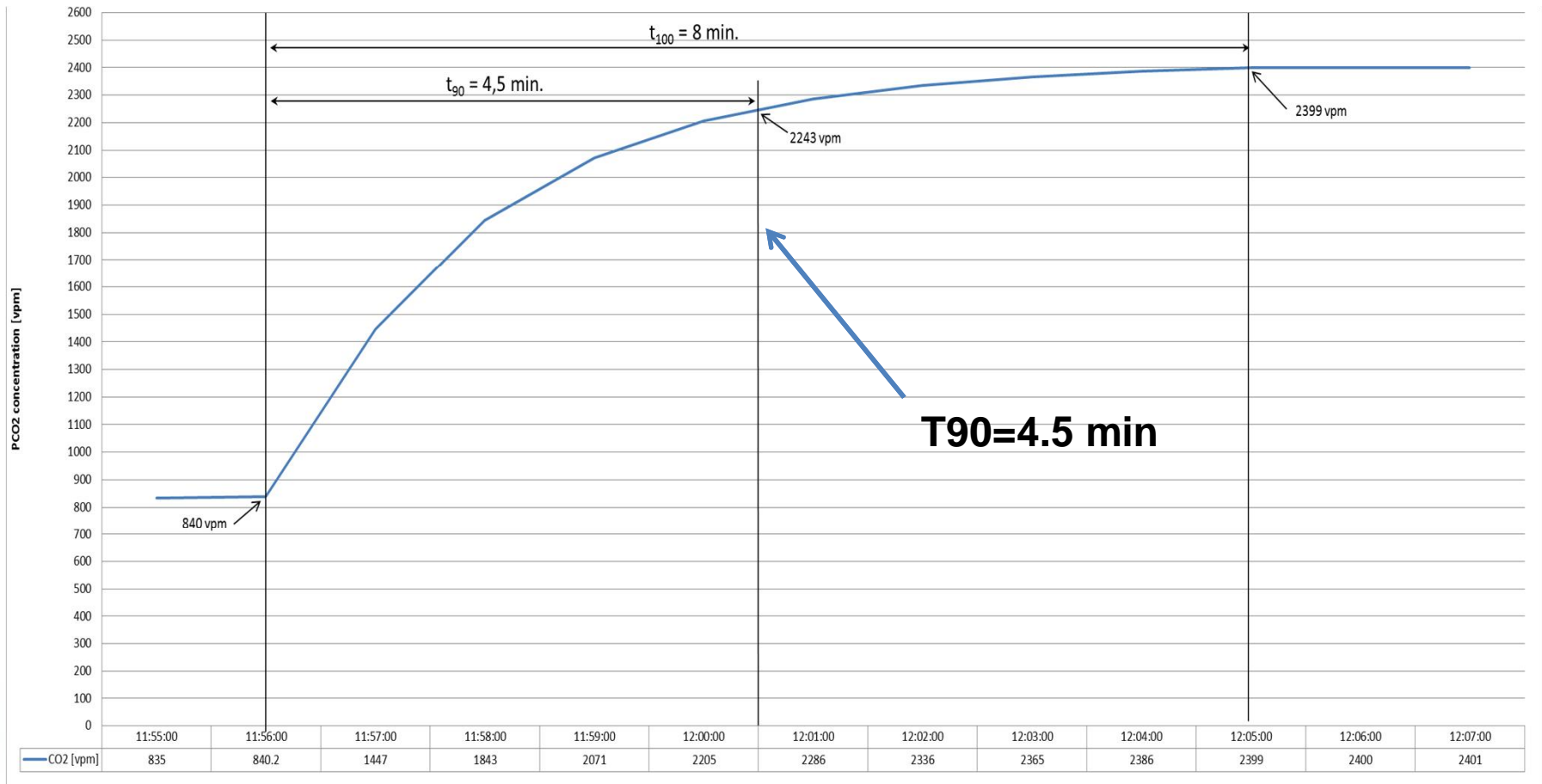
- Preliminary test show typically < 5 min
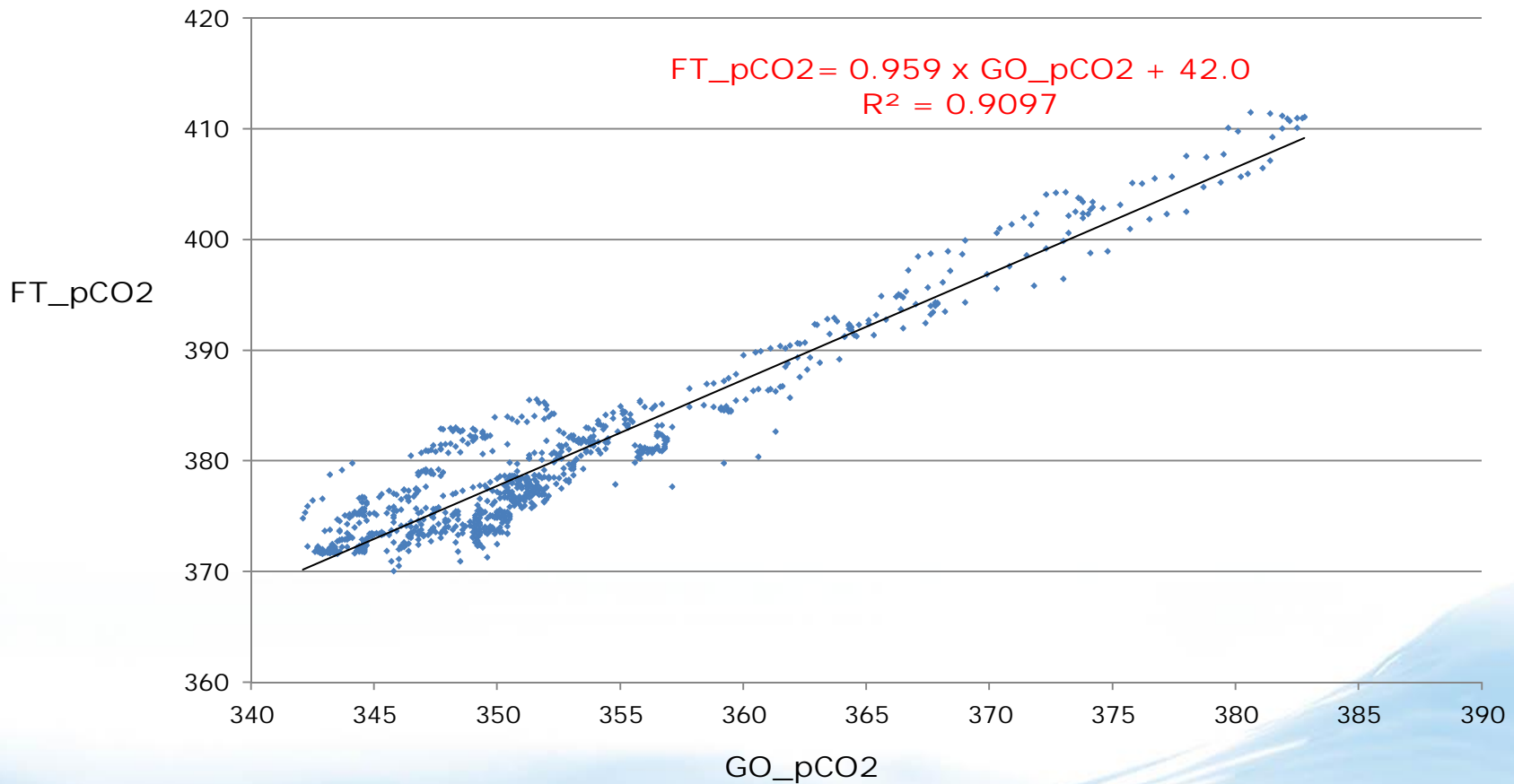
Field test comparing with the GO-systems (GEOMAR)

Field tests between GO_pCO₂ and Franatech
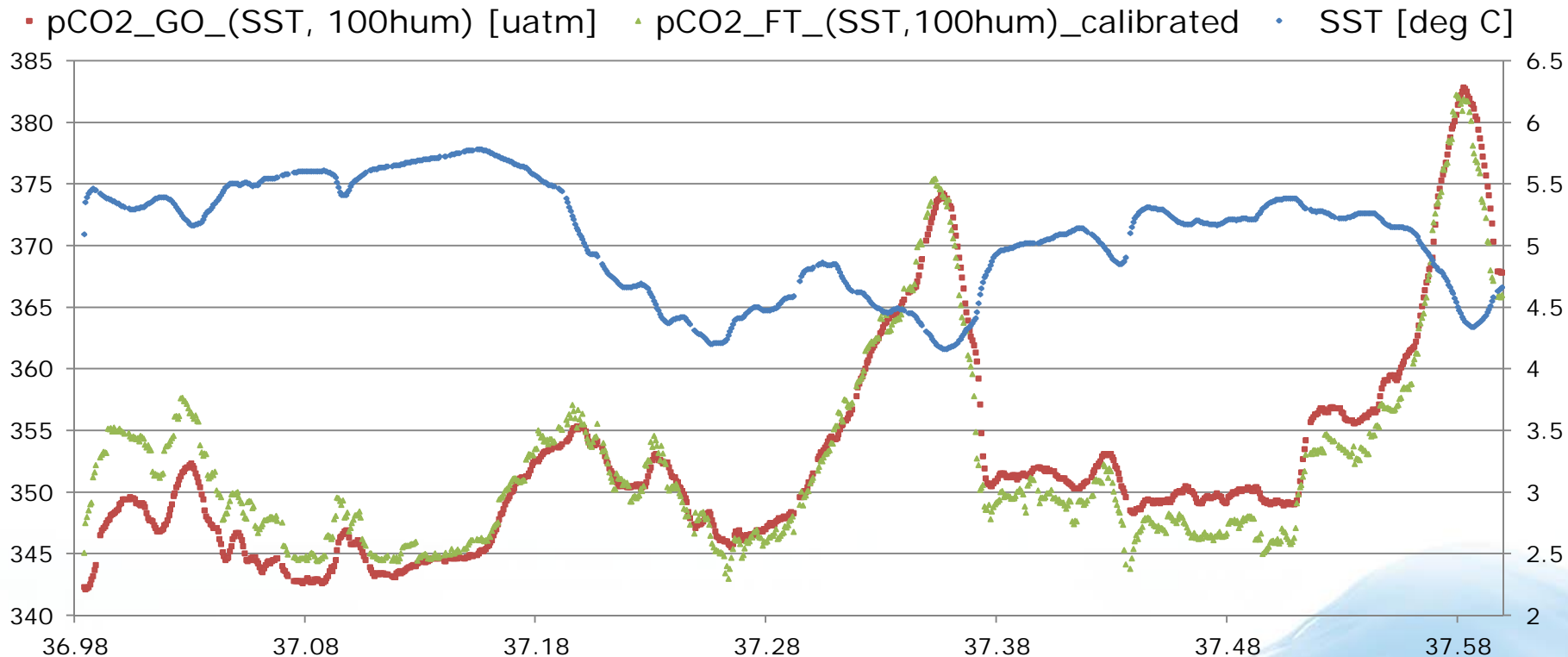

- +/- 2 % accuracy of the calibration gasses

Comparisions of GO_ pCO2 and FT_pCO2 in a short term test (24 h)

FT_pCO2= 0.959 x GO_pCO2 + 42.0
R^2 = 0.9097

FT_pCO2

GO_pCO2

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FT_pCO2 vs GO_pCO2 after applying a new calibration

Calibrations issues

- Calibration with high precision gas to have the best absolute accuracy
- Wet or dry gas calibration
- Compensation for water vapor
- Calculations from dry to wet
- Compensation for pressure differences

Needs for a standard operation procedure (SOP) for membrane systems in Ferrybox installations!
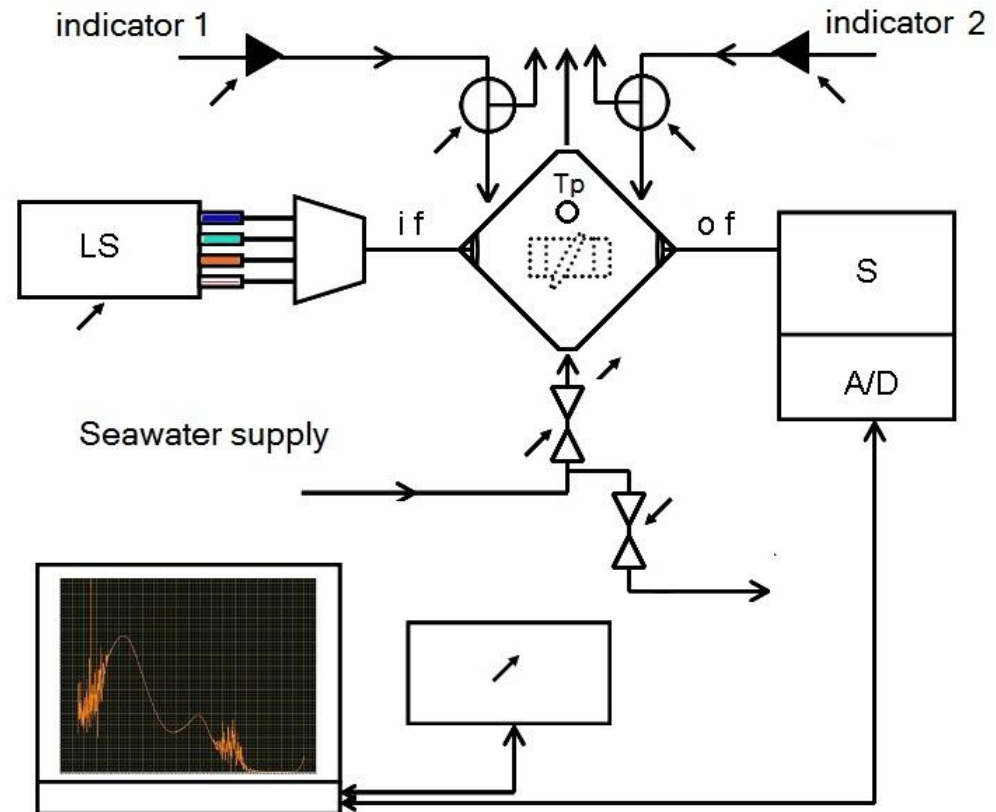
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Development of a miniaturized *in situ* detection system for pH and carbonate
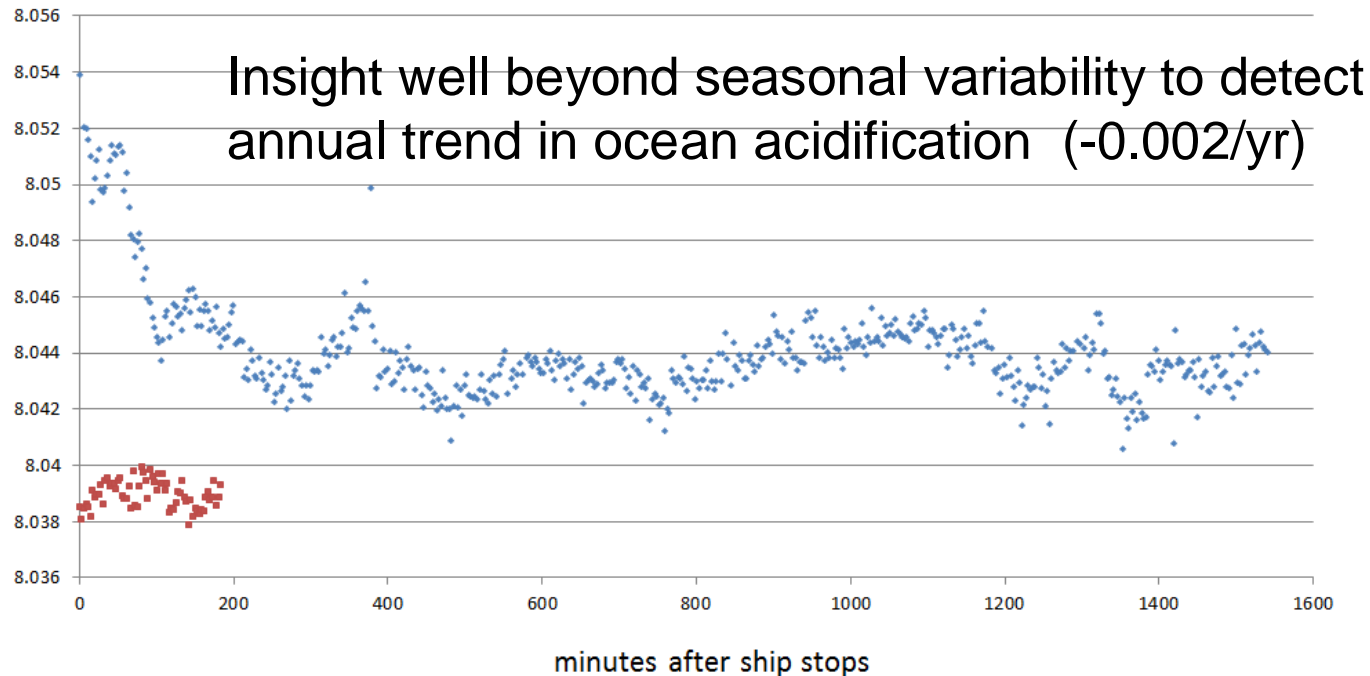
Spectrophotometric pH detection
- calibration free
- precision: $< 10^{-3}$ pH
- accuracy [2]: $\pm 2.5 \times 10^{-3}$ pH
- drift : within precision
- sampling interval: 20 s
- ideal solution onboard VOS
- underway/discrete

Further improvement:
- direct UV carbonate detection within a pCO_2 detection manifold for complete carbonate system speciation

Test of the miniaturized pH detection system prototype on a research vessel cruise April 2012


Insight well beyond seasonal variability to detect annual trend in ocean acidification (-0.002/yr)

minutes after ship stops

Meteor 87/1, station coord.: -11, 61.5   ▪ t0   ▪ … one month later

Short term precision (1h): 0.0005
Medium/long term precision (1 day/1 month): 0.001/ to be assessed
(better than CRM or combined $Ct/At/pCO_2$ could provide)

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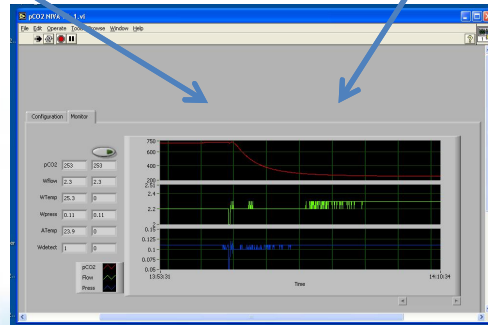
Combined approach pH and pCO2 into the Ferrybox
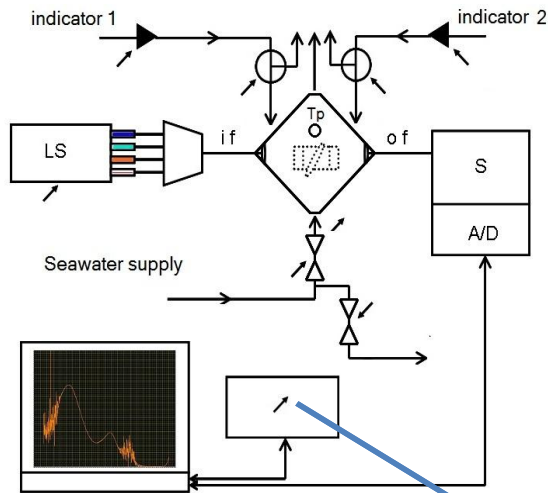
Physically implemented into the pCO2 will be tested!

pH and carbonate

pCO2

Combined in a common labview Software with data from the Ferrybox like SST, pressure e.g..

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Future work

- Combine pH and pCO2 into one system
- Deployment for long term tests on three ship routes (seasons, years)
  - Kattegat/Skagerrak (low saline water, high Chl-a)
  - Coastal areas (Fjords, Rivers mouth)
  - Barents Sea (cold waters/Arctic)
- Long term technical experience
- Long term calibrations experience (NOAA-gas)
- Establish the overall precision and accuracy
  - Comparison and implementation in the monitoring program
  - Hopefully implementation into the monitoring programs?
- Comparisons with other systems (Jerico-activity?)
  - GO-System, other membrane systems and other detectors

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