# KONGSBERG MARITIME CONTROS GMBH

## WE DETECT TO PROTECT

Steffen Aßmann

ICOS OTC Workshop, Bergen, 08.03.2018

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# KONGSBERG MARITIME CONTROS GMBH

**LOCATION**

Based in Kiel, Germany

**TEAM**

KM Contros approx. 16 employees
KM AS approx. 4000 world wide

**BUSINESS FIELDS**

Sensors, analyzers and monitoring systems for the industrial and scientific sector.

**INFRASTRUCTURE**

Calibration, chemical and electronic labs, production, temperature stabilized pressure tank

# KONGSBERG MARITIME CONTROS GMBH

CONTROS
Systems & Solutions GmbH

CONTROS

Founded 2006
Spin-off from Helmholtz Centre Geesthacht

Initial product: $CH_4$ sensor targeting the Oil & Gas market

Patents in place and applications pending

2013: KM and CONTROS entered a cooperation agreement → modular sensor packages into KM solutions for subsea monitoring. As part of this agreement & KM took a 10% shareholding in CONTROS

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2015: Successful collaboration over 15 more months
→ complete company acquisition

# CONTROS® SENSORS

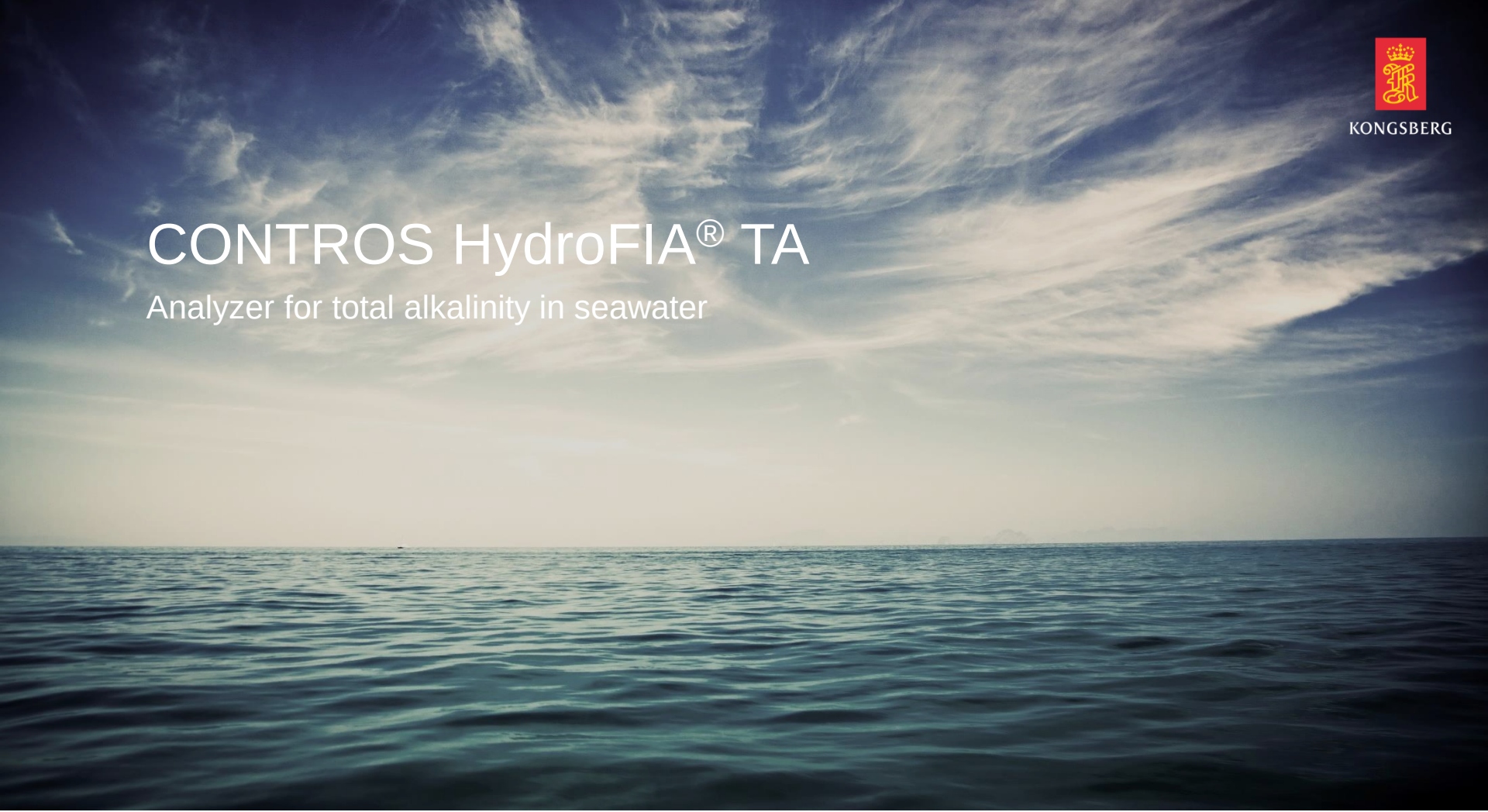
**HydroC $CH_4$**
3000 meters
High accuracy
Long-term deployment

**HydroC $CO_2$**
6000 meters
High accuracy
Long-term deployment

**HydroC $CO_2$ FT and $CH_4$ FT**
High accuracy
Fast response time
User-friendly
Long-term maintenance-interval of 12 months

**HydroFlash $O_2$**
6000 meters
High accuracy
Very fast response time
Long-term deployment

**HydroFIA TA & pH**
Analyzer for total alkalinity and pH in seawater for autonomous long-term installations



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# CONTROS HydroFIA® TA

## Analyzer for total alkalinity in seawater

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# CONTROS HydroFIA® TA
## Benefits

**TA** – Total Alkalinity

**FIA** – Flow Injection Analyses

- **Worlds first commercially available autonomous TA analyzer**

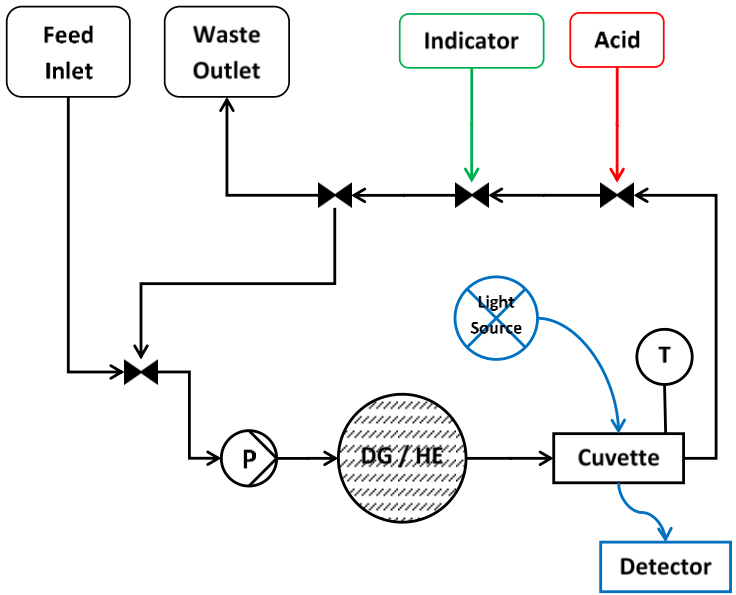
- Autonomous deployment longer than one month possible
  → **No more bottled samples**
  → **Save time and money**

- Low sample / chemicals consumption
  → **Decreased cost per measurement**

- Easy setup
  → **Replacing the sophisticated lab setup**

# CONTROS HydroFIA® TA
## Principle

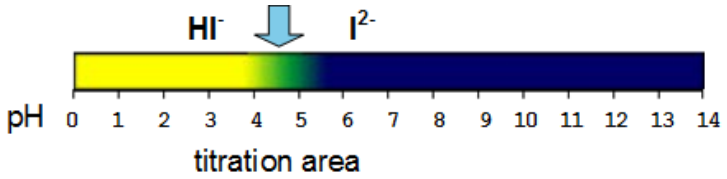
- Sample is aspirated through the feed inlet into a closed sample loop.
- One-Point-Titration with hydrochloric acid (HCl) to a pH range of 3.0 to 4.5 and removal of the formed $CO_2$.
- Addition of the acid-base indicator dye Bromocresol green for spectrometric pH detection.
- Calculation of TA using temperature, salinity, mass of the sample water and accurately known amount of added acid.

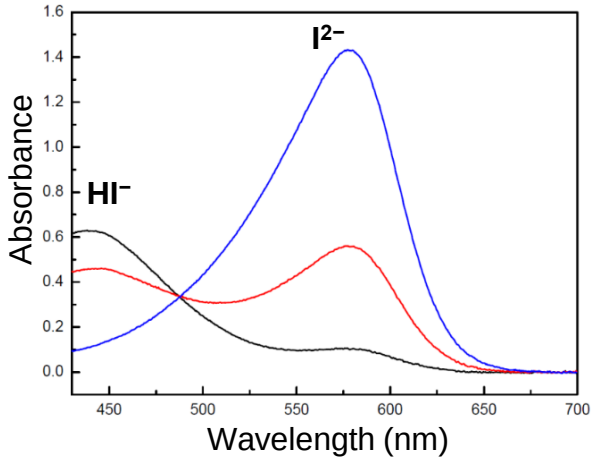


# CONTROS HydroFIA® TA
## Principle

- Usage of proven optical pH detection method based on absorption measurement.
- Determination of the concentration of the indicator acid ($HI^-$) / base ($I^{2-}$) due to different absorption spectra using a CCD spectrometer
- Calculation of the pH value using modified Henderson–Hasselbach equation

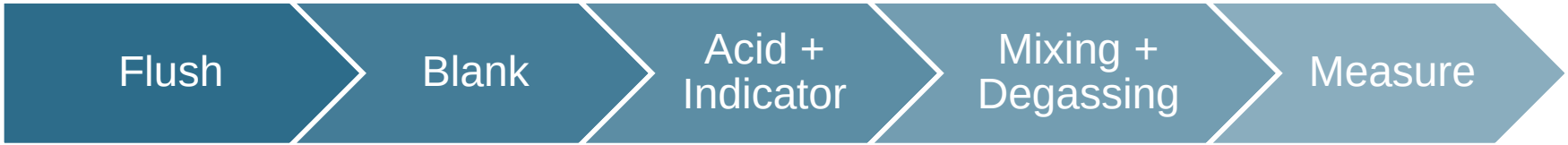
$$pH = pK_a + \log_{10}\frac{[I^{2-}]}{[HI^-]}$$



# CONTROS HydroFIA® TA

## Measurement Intervals



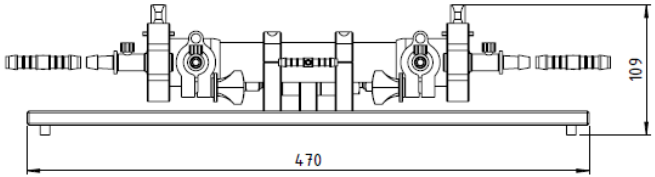

- **Flush** — Full replacement of the sample solution; water intake closed and subsequent sample treatment.
- **Blank** — Recording the blank spectrum of the sample.
- **Ind. / Acid Injection** — Injection of the hydrochloric acid and indicator dye into the sample loop.
- **Degassing / Mixing** — Full removal of the $CO_2$; Looping of acidified, indicator-added sample until complete removal of DIC.
- **Measure** — Spectrophotometric pH detection.

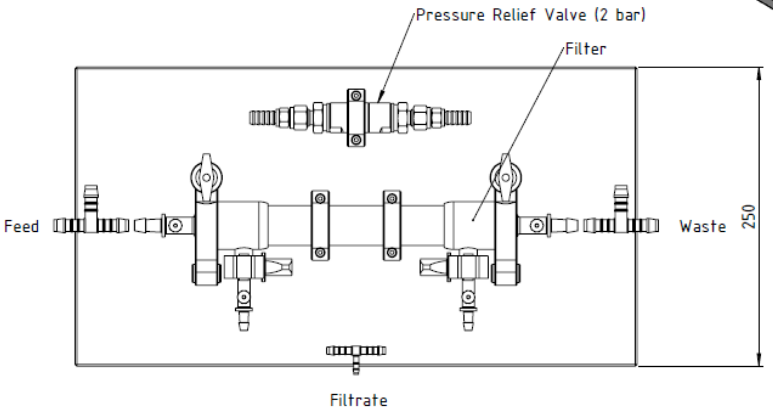
# CONTROS HydroFIA® TA
## Cartridges

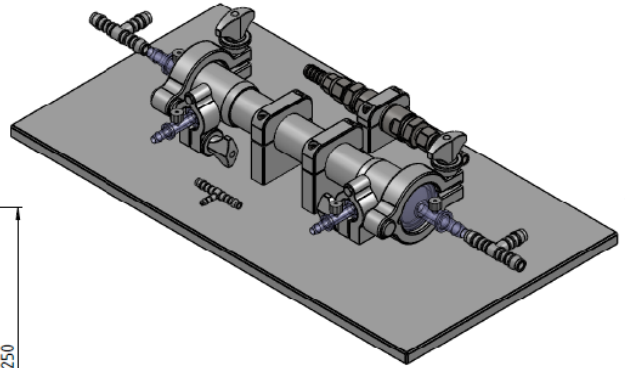
- Chemicals are provided in cartridges
  - Separate indicator and acid
- User friendly and robust design.
- Usage of gas-tight bags to avoid the introduction of a head space during operation/consumption of the chemicals.
- No gas exchange with surrounding air.
- No degradation of the substances due to light.
- One cartridge set lasts for 2500 measurements

# CONTROS HydroFIA® TA
## Cross-Flow Filter

- Important for particle loaded waters to avoid clogging
- 0.2 µm pore size filter removes stray light particles in the visible light spectrum
- Reduction of bio-fouling



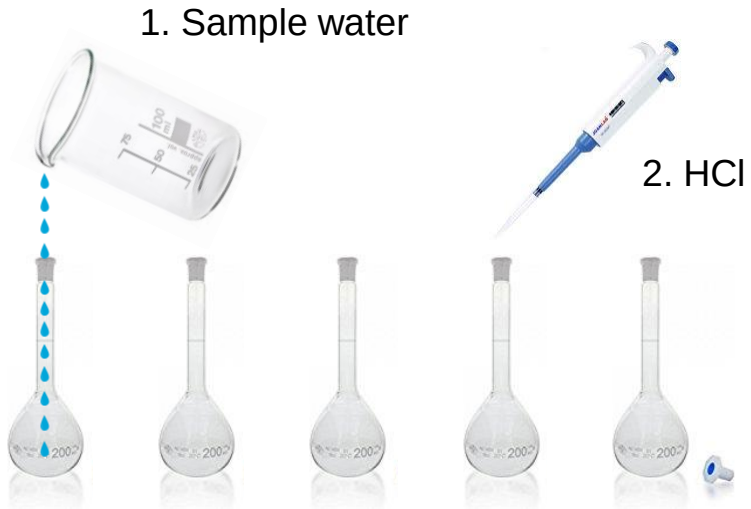



# CONTROS HydroFIA® TA
## Calibration

- Measurement principle is an absolute method after Dickson et al., 2007 and Li et al., 2013
  → no relative calibration needed

- One-point calibration
  → internal sample volume determination

- Verification of the method in the lab
  - Titration of high alkalinity real sample water
  - Covering ±200 µmol/kg of the desired working range
  - Extended working range possible with limited accuracy
  - Automated measurement of the titrated aliquots
  - No correction of the found signal

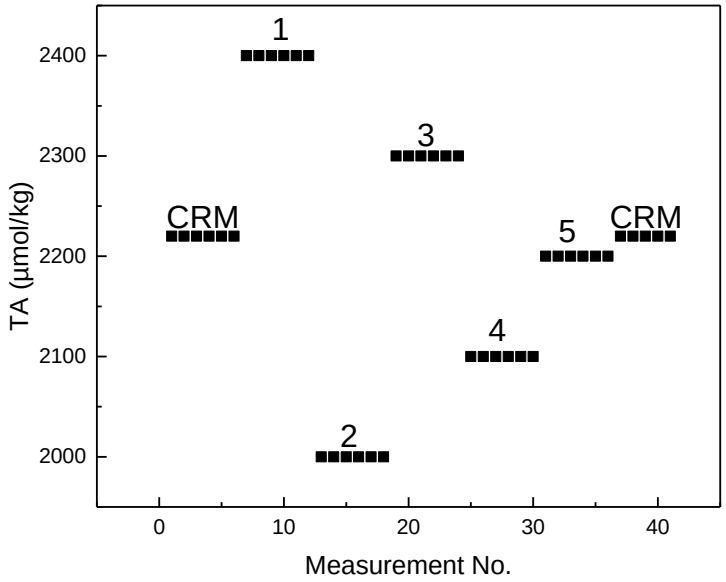


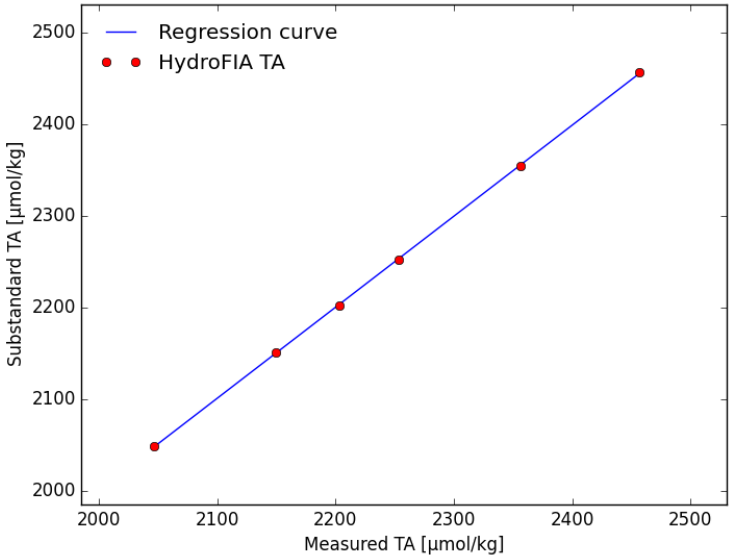

Li, Q., Wang, F., Wang, Z.A., Yuan, D., Dai, M., Chen, J., Dai, J., Hoering, K., 2013. An Automated Spectrophotometric Analyzer for Rapid Single-point Titration of Seawater Total Alkalinity. Environ. Sci. Technol. doi:10.1021/es402421a

Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to Best Practices for Ocean CO2 Measurements. PICES Special Publication 3.

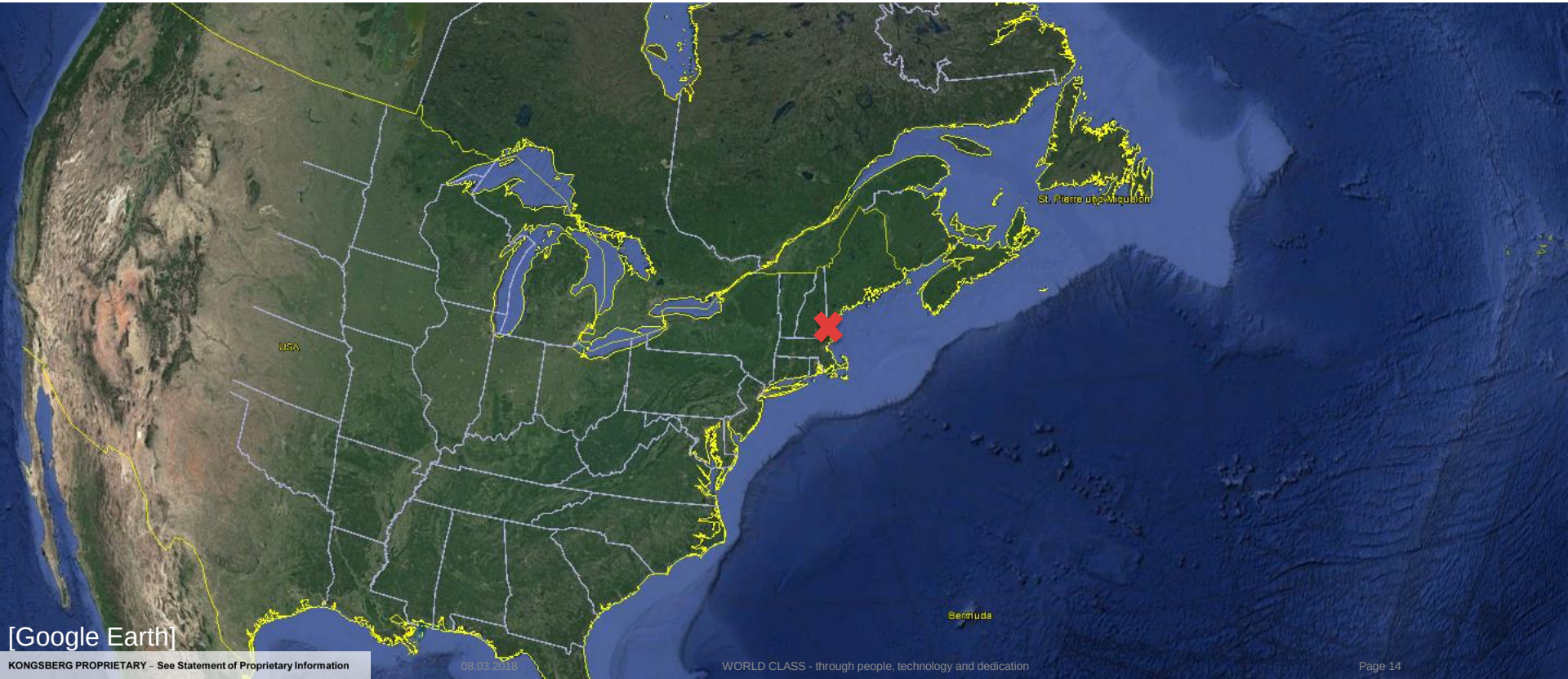
# CONTROS HydroFIA® TA
## Calibration

5 Steps verification | Linear relationship | $R^2 > 0.999$ | RMSE < 2 µmol/kg



# CONTROS HydroFIA® TA
## Example Data



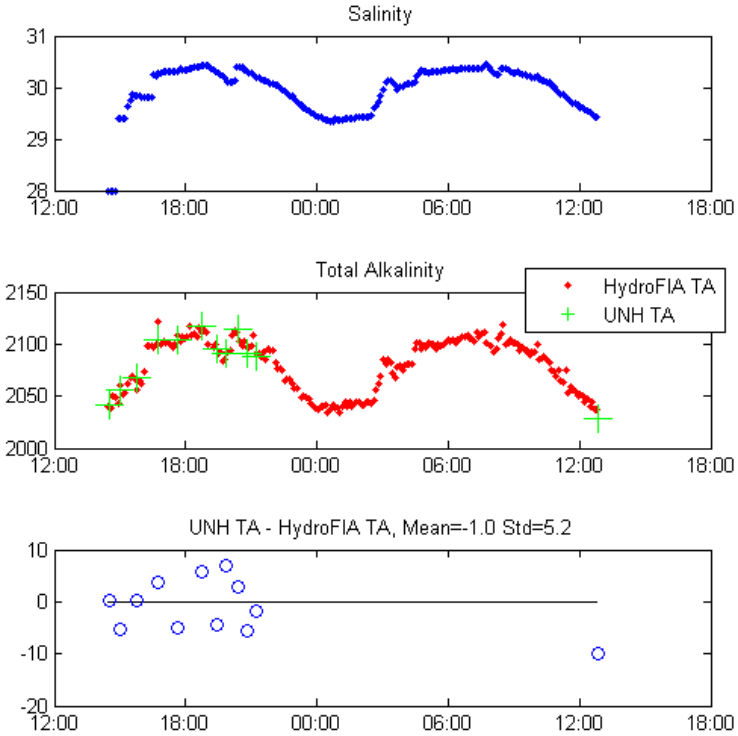

[Google Earth]

# CONTROS HydroFIA® TA
## Example Data

| | |
|---|---|
| Ref. offset | - 1.0 µmol/kg‡ |
| Precision | ± 2.0 µmol/kg |
| Accuracy | ± 5.2 µmol/kg# |
| Meas. frequency | 10 min |
| Range | 2000–2400 µmol/kg |

‡ Compared to bottled reference samples measured in the lab

# Found for 24 h field test with reference samples



# CONTROS HydroFIA® TA
## Requirements Ship Installation

- 15 VDC power source (or 220 VAC)
- Benchtop system, no mounting bars available yet
- RS-232 connection for remote control / live data or **provision of salinity**
- Ethernet for further system checkups and raw data access
- Steady water supply of clean water (usage of cross-flow filter recommended)
- If needed, separate water tank for colored waste water of the analyzer

# CONTROS HydroFIA® TA
## Deployment

- **BEFORE**
  - Proper cleaning of the analyzer with DI water or 0.1 M HCl
  - Measure seawater sample until stable condition are reached
  - Calibration with CRM (5 repetitive measurements recommended)
- **DURING**
  - Start continuous measurements
  - Regular (sub-) standard measurements (once a day) for potential drift correction
- **AFTER**
  - CRM measurement at deployment end
  - Final cleaning with (0.1 M HCl and afterwards with) DI water before shut down of the instrument
  - Maintenance by manufacturer every year

# CONTROS HydroFIA® TA
## Summary

- **Continuous** and **automated** measurement of total alkalinity in seawater.
- Easy **calibration doable by operator**.
- Calibration and measurements tested and further developed in **R&D projects**.
- **User-friendly** through comprehensive, easy-to-use and continuously improved **firmware** as well as application-oriented features (e.g. addition of second inlet for regular standard measurements).
- Chemicals are provided in **cartridges** for easy operation and maintenance.

# CONTROS HydroFIA® TA
## User Feedback

- UDP commands for remote control
- PP canister tapes with gas tight metallic tape to store substandard and reducing the evaporation of water
- In web interface adjust concentrations or cartridge volume for custom made solutions
- Warning flag for low indicator concentration
- Checklist for deployment in manual or as separate sheet
- Sensor for pressure or water flow to detect missing water flow and thus shutting down the system to avoid damage
- Eyelets for save installations on ship

# CONTROS HydroC® $CO_2$

## Sensor for dissolved carbon dioxide

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# CONTROS HydroC® $CO_2$
## Benefits

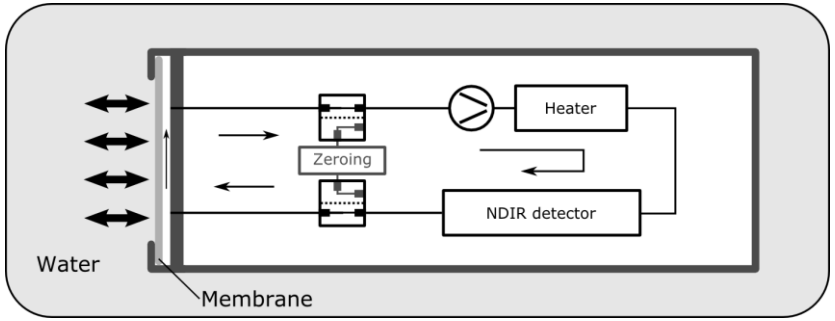
| | |
|---|---|
| **C** | – Carbon |
| **$CO_2$** | – Carbon Dioxide |

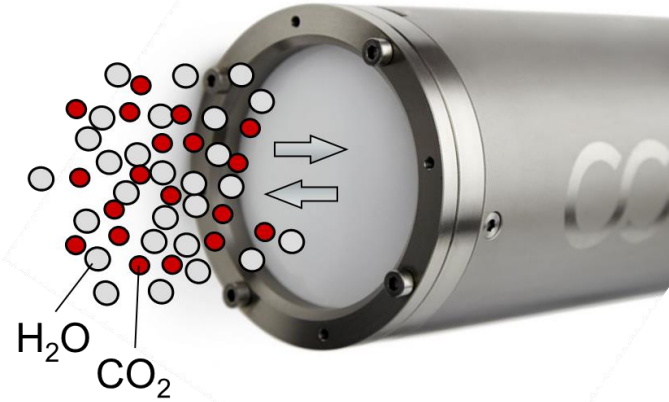
- Very robust and versatile; can be used in water depths up to 6000 m
- Easy integration with almost every oceanographic measurement system and platform
  → **Use it wherever you want**

- Fast response time; first signal derived on a sub-minute scale
  → **No worries about loosing a signal**

- Long-term quality tracing of the measured signal
  → **Built in quality control parameters**

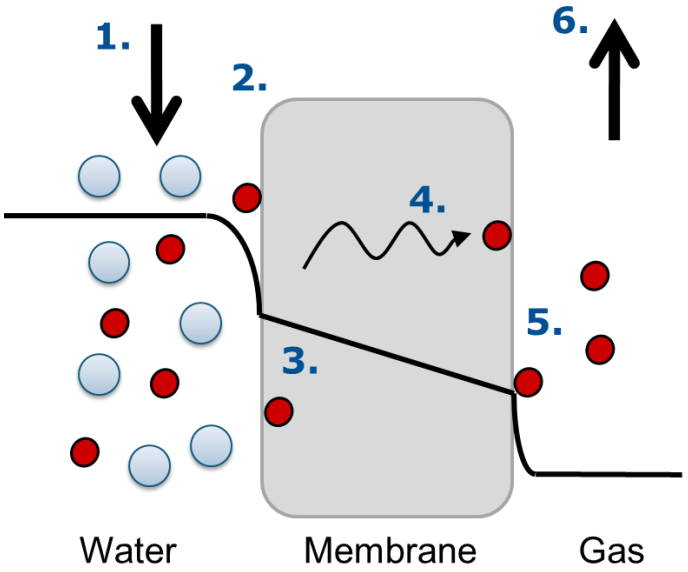
# CONTROS HydroC® $CO_2$
## Principle




- Dissolved gasses and water vapour equilibrate through the membrane
- Gas concentration is measured by NDIR within a gas circuit; Zeroing included
- Internal data logger saves NDIR signals along with $T, p$ and $r_H$

# CONTROS HydroC® $CO_2$
## Membrane Equilibrator

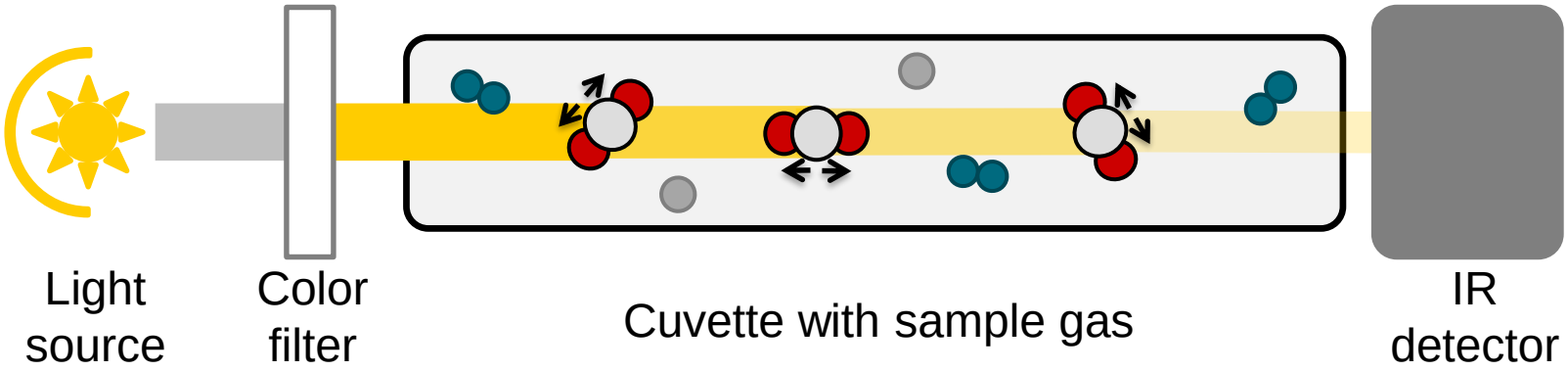



1. Transport by diffusion (in water)
2. Adsorption at surface
3. (Desorption or) absorption
   → Dissolution process
4. Diffusion driven by $\Delta[G]$
5. Desorption into gas phase
6. Transport by diffusion (in gas)

# CONTROS HydroC® $CO_2$

## NDIR Detector

- Broad band light source
- Filter for wavelength selection
- Small, robust, proven

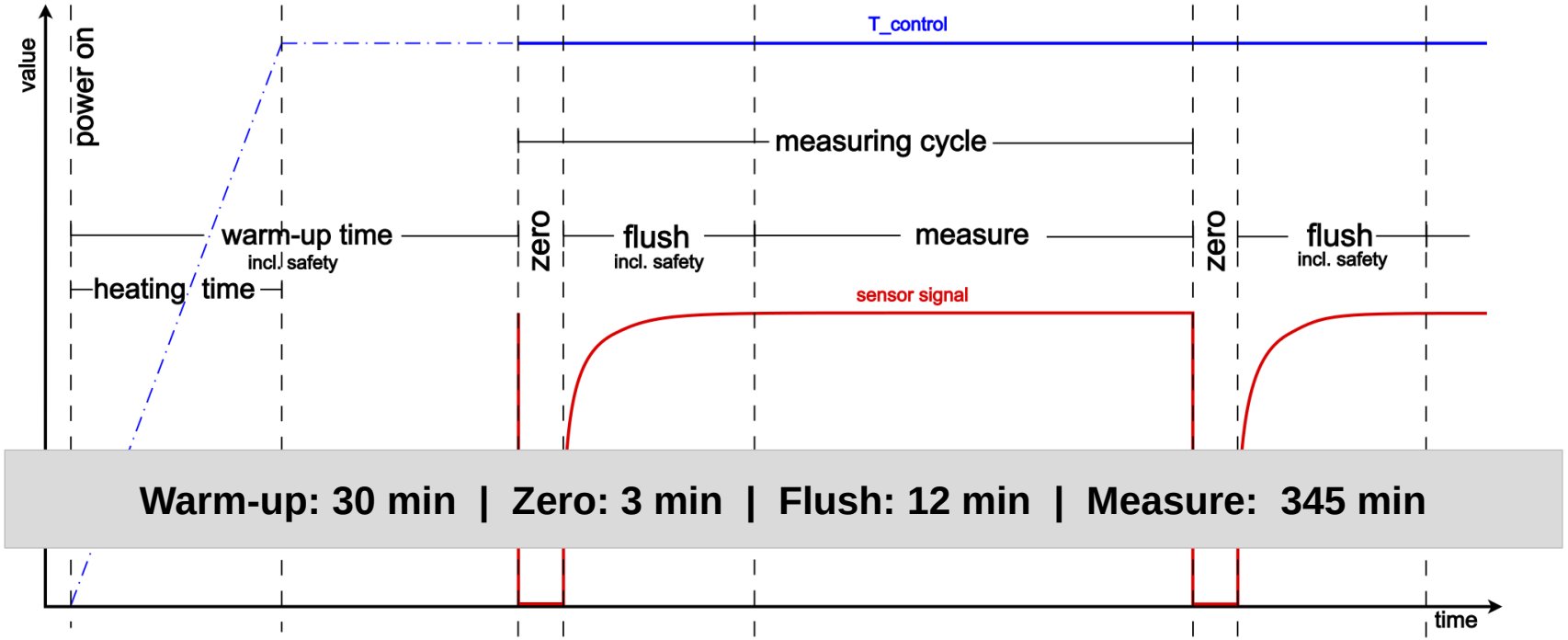


# CONTROS HydroC® $CO_2$
## Measurement Intervals

- **Warmup** Stable measuring conditions
- **Zero** Baseline determination for drift correction
- **Flush** Flagged response data / in-situ response time test
- **Measure** Measuring data

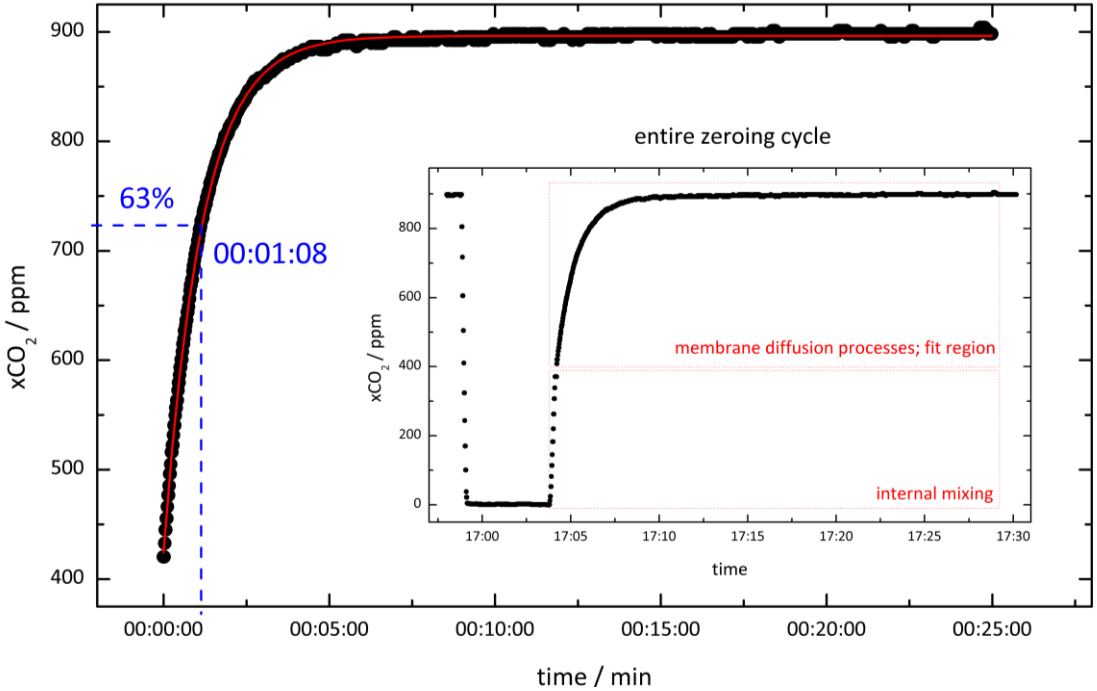
# CONTROS HydroC® $CO_2$

## Measurement Intervals – Continuous




**Warm-up: 30 min | Zero: 3 min | Flush: 12 min | Measure: 345 min**

# CONTROS HydroC® $CO_2$
## Response Time



# CONTROS HydroC® $CO_2$
## Antifouling Strategy

- Membrane is kept in the **dark.**
- **Water flow** limits the on-growth on the center of the membrane.
- **Membrane surface** properties and its elasticity make the membrane less prone to fouling than e.g. hard metal components.
- Extensive usage of **copper components** inhibit biological on-growth at key positions within the gas stream and minimize spreading of fouling along the water path:

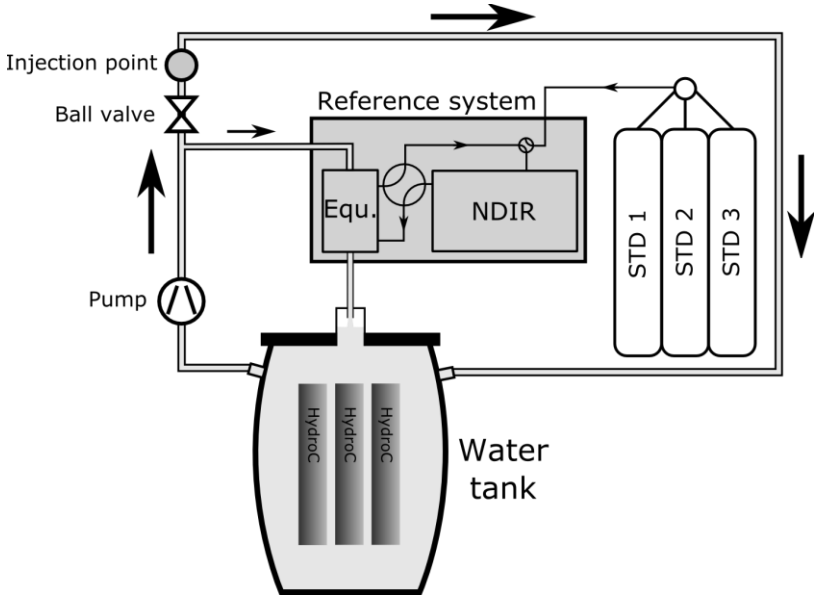
Fouling has no direct effect on the measurement as the membrane is not used as a sensing component within a HydroC, but solely as a phase boundary between water and internal headspace.

→ Regular response time determination as a measure for membrane status.

# CONTROS HydroC® $CO_2$
## Calibration

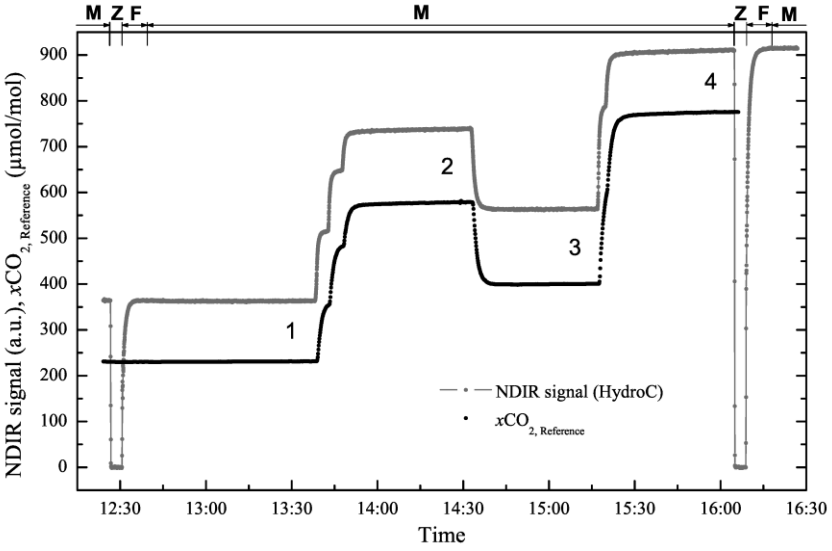
- Regular re-calibration with high quality gas standards
  → Direct liquid – gas equilibrators

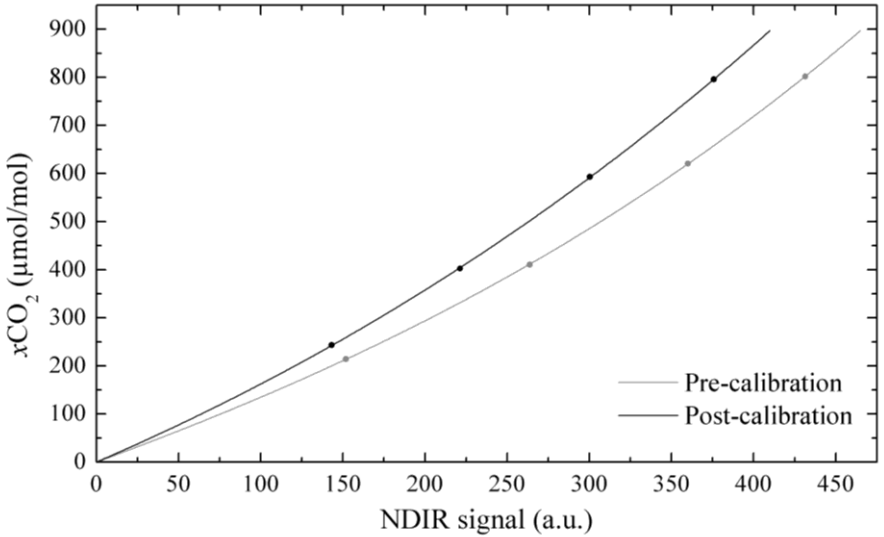
- Occasional referencing
  → Membrane liquid – gas equilibrators
  – Comprehensive pre-deployment calibration
  – Comprehensive post-deployment calibration
    (no sensor is drift free)
  – In-situ measurement quality parameter (e.g. zeroing)



# CONTROS HydroC® $CO_2$
## Calibration

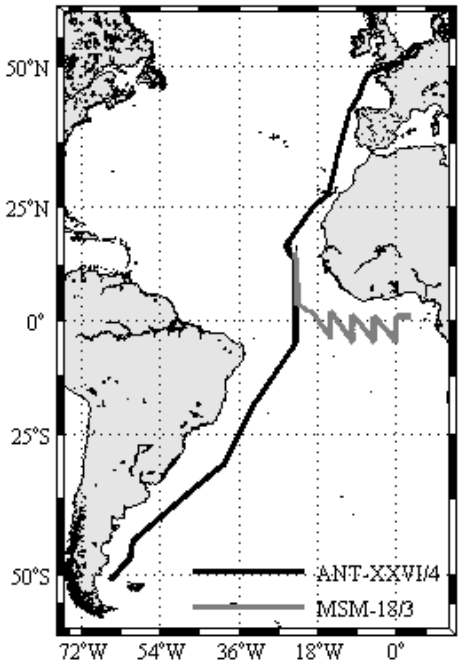
4 Steps | Polynomial rank 3 with forced zero crossing | $R^2 > 0.999$ | RMSE < 1 ppm

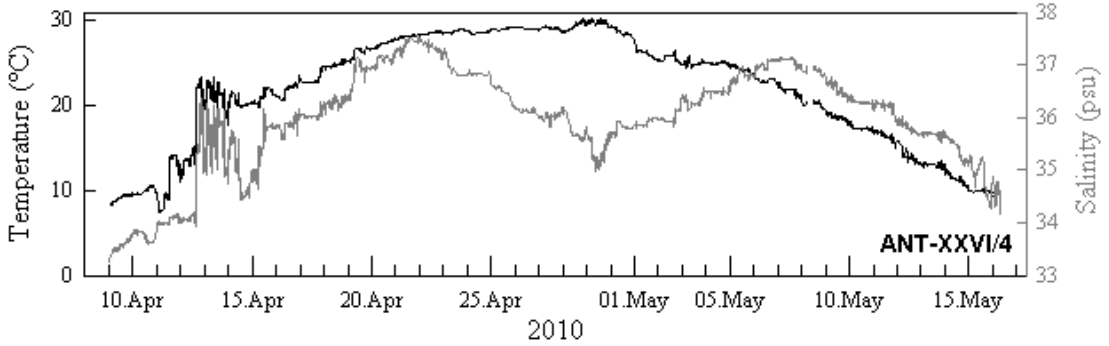


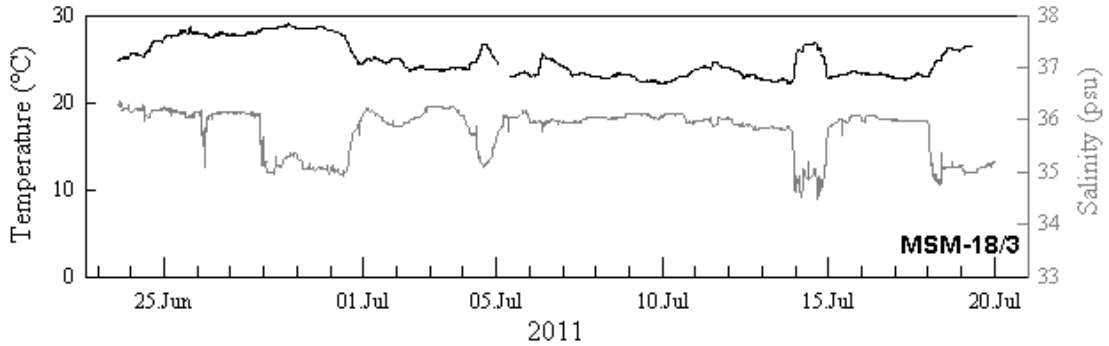



# CONTROS HydroC® $CO_2$

## Example Data



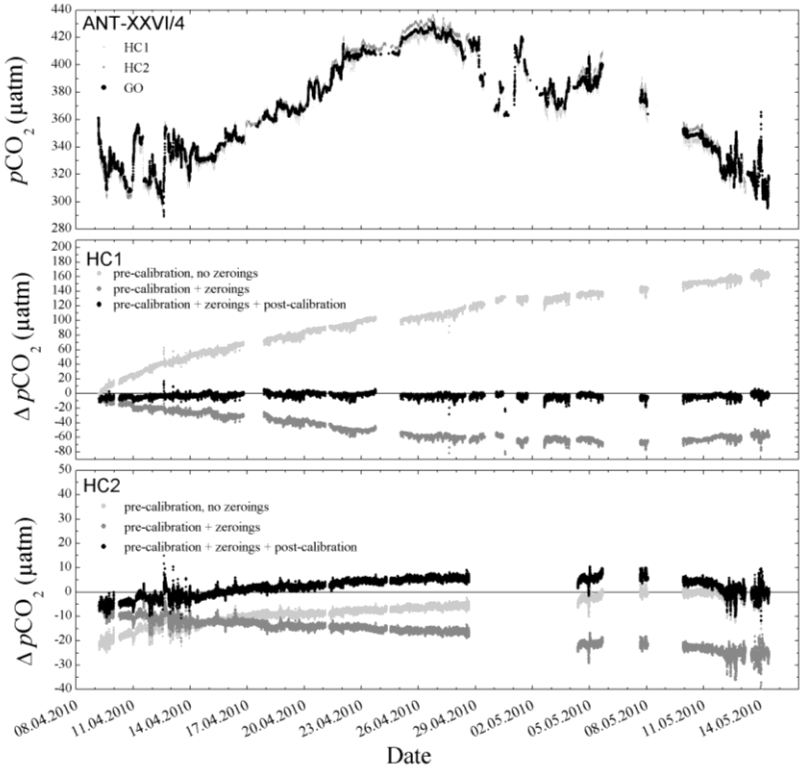
# CONTROS HydroC® $CO_2$

## Example Data

| | |
|---|---|
| **Ref. offset** | - 0.6 µatm° |
| **Precision** | ± 3 µatm |
| **Accuracy** | ± 3.7 µatm▽ |
| **Meas. frequency** | 1 s |
| **Range** | 200 – 1000 µatm |

° Compared to a reference system from GO

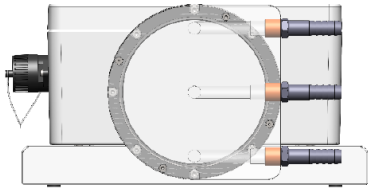
▽ Applying pre- and post-deployment calibration over one month deployment

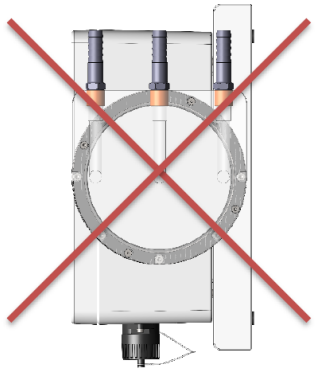



Fietzek, P., Fiedler, B., Steinhoff, T., Körtzinger, A., 2014. In situ quality assessment of a novel underwater pCO2 sensor based on membrane equilibration and NDIR spectrometry. J. Atmos. Ocean. Technol. 31, 181–196. doi:10.1175/JTECH-D-13-00083.1

# CONTROS HydroC® $CO_2$
## Requirements Ship Installation

- 11 ot 24 VDC power source (or 220 VAC)
- Mounting bars available for attachment on e.g. sidewall
- RS-232 connection for live data
- Data logging optional if no live data recording available
- Steady water supply of approx. 5 to 7 L/min





# CONTROS HydroC® $CO_2$
## Deployment

- **BEFORE**
  - Pre-calibration
  - Mission planning using CONTROS DETECT software
  - Sensor mounting and flush with seawater
- **DURING**
  - Steady water supply and continuously running system
  - Regular baseline measurements (zeroing → every 12 hours) for potential baseline drift correction
- **AFTER**
  - Cleaning the sensor with fresh water
  - Post-calibration for correction of the potential span drift
  - Maintenance every year for exchange of wear parts (e.g. pumps and valves)

# CONTROS HydroC® $CO_2$
## Summary

- **Continuous** and **direct measurements** of dissolved gas parameters.
- Small, individually **in-water calibrated**, **fast** and including drift correction means.
- **High quality production**, calibration and measurements incl. **peer-reviewed publications**.
- **User-friendly** through comprehensive, easy-to-use and continuously improved **software** as well as application-oriented features (logger, sleep-mode, etc.).
- Strong **customer support**.
- **Reliability** and ruggedness is proven during many missions and on various platforms.
- In the new compact version **temperature measurement** in the equilibrator head is included as well as new **TOUGH membrane**.

# CONTROS HydroC® $CO_2$
## User Feedback

- Implement standard gas inlet in front of the membrane
- Provide software for drift correction
- Provide data as raw data, uncorrected as it is currently
- Offer data processing as a service

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# WORLD CLASS

THROUGH PEOPLE, TECHNOLOGY AND DEDICATION

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