Determination of Seawater Carbonate System Parameters: CO_2, TA, pH

Steffen Aßmann, Peer Fietzek

KONGSBERG

7th FerryBox Workshop in Heraklion, Crete

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Outline

- Background

- Determination of the Carbonate Parameters
  - Dissolved CO_2
  - Total Alkalinity
  - pH value

- Application Examples

Kongsberg Maritime Contros GmbH

Kongsberg Maritime Contros GmbH

Facts

- Founded in 2006 as CONTROS Systems & S
- Based in Kiel, Germany
- 100% purchased by Kongsberg Maritime in March 2015

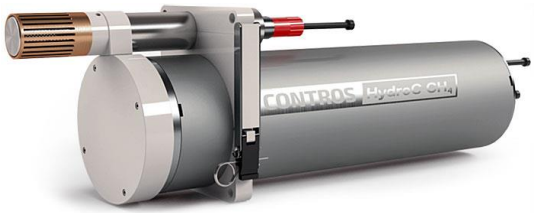
Team

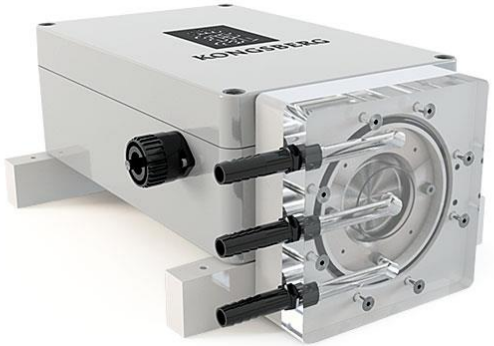
- KMCON approx. 16 employees
- Devision approx. 40 employees

Business fields

- Science: Environmental Monitoring
- Industry: Offshore Oil & Gas

Kongsberg Maritime Contros GmbH
Product Portfolio





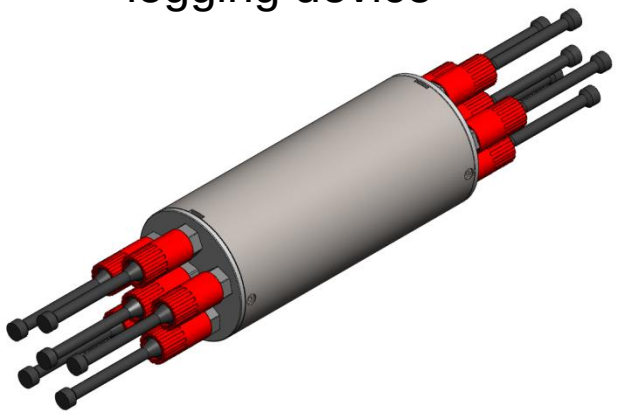
Kongsberg Maritime Contros GmbH
New Portfolio – Systems

Integrated environmental measuring solutions:

- Modular Subsea Monitoring-Network (MSM)
- K-Lander / K-Observer

System backbone *DPU:*

- Versatile data communication and logging device



CONTROS HydroC CO_2

Sensor for Dissolved CO_2 in Water

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CONTROS HydroC®CO_2

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**

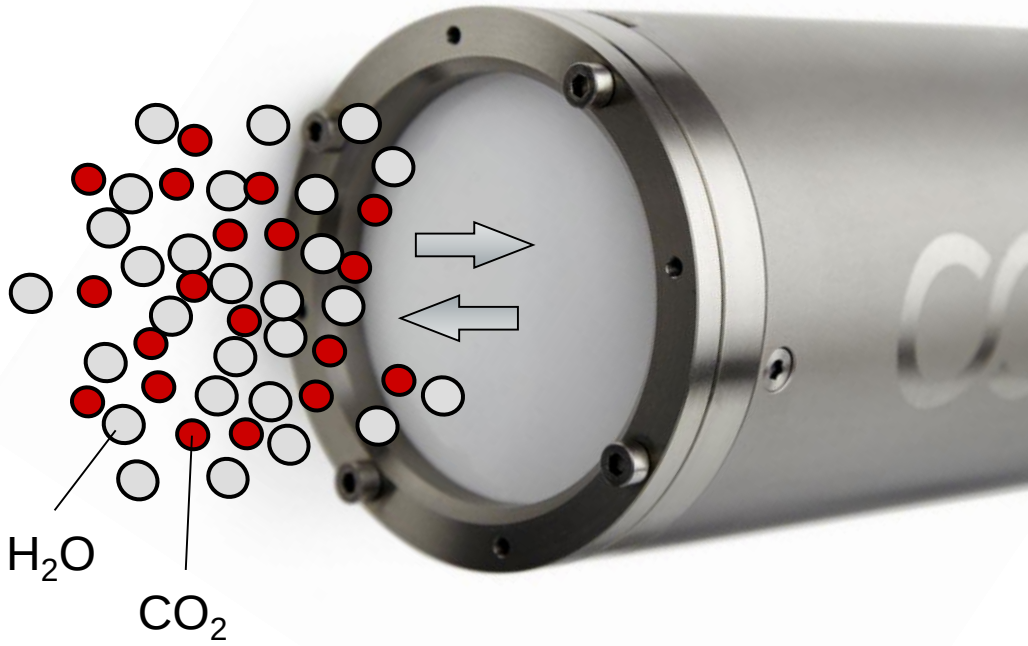
- Fast response time; first signal derived in under 7 seconds
  → **No worries about loosing a signal**

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

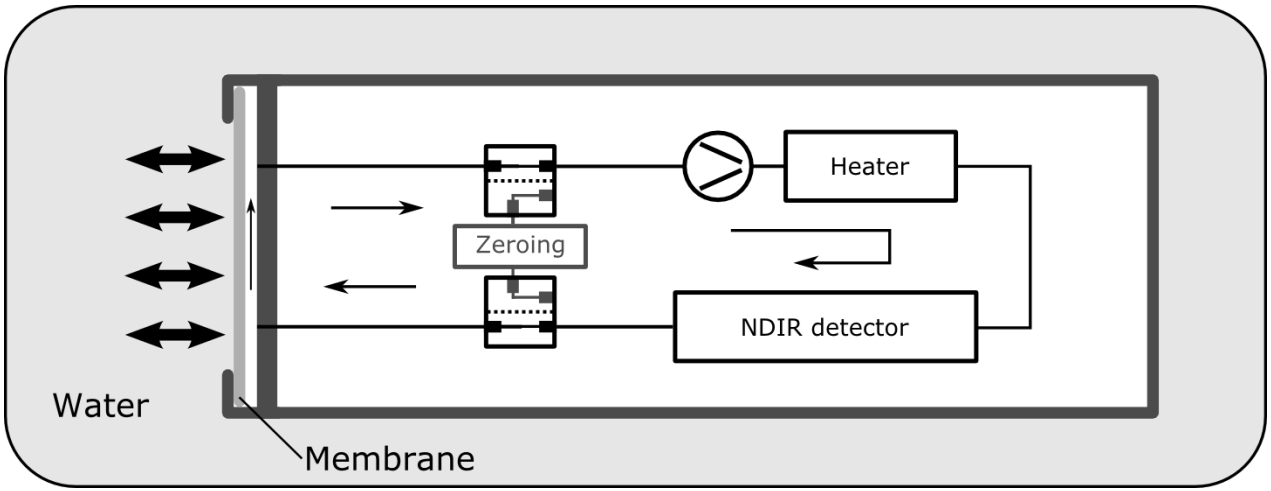
CONTROS HydroC®CO_2
Measurement Intervals and Principle

Warmup → Zero → Flush → Measure → Zero

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



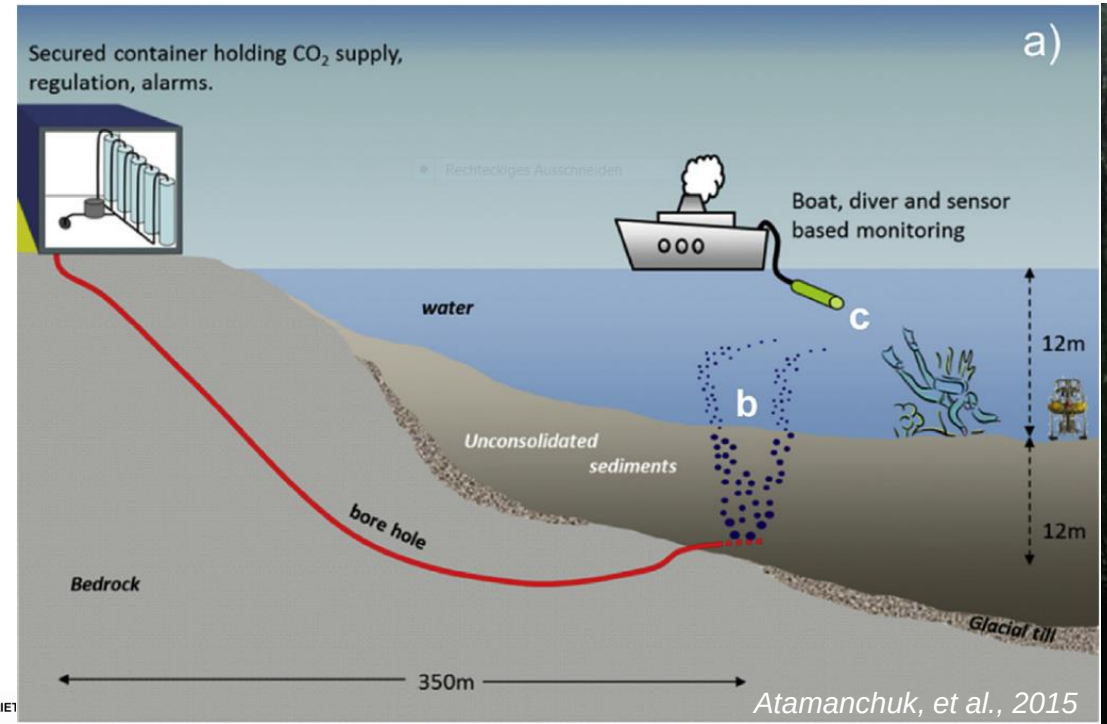
CONTROS HydroC®CO_2
Principle

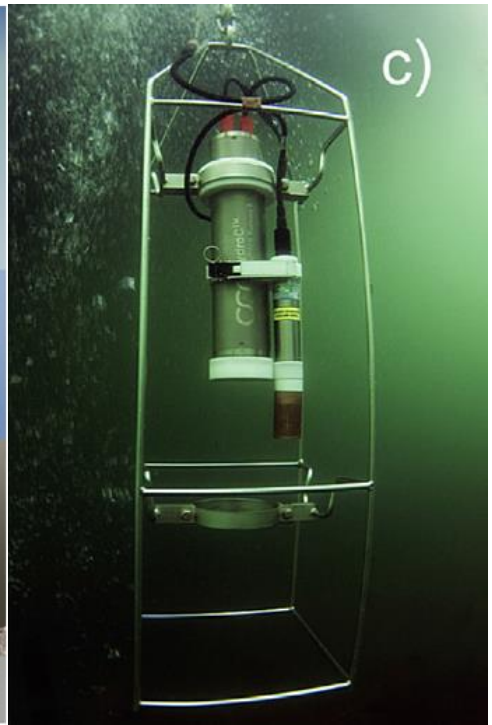


- Dissolved gasses and water vapour equilibrate through the membrane
- Gas concentration is measured by NDIR within a gas circuit; Zeroing included
- Internal data logger saves NDIR signals along with T, p and rH

Application Example
Shipborne Measurements at Gas Release Site

- CO_2-release experiment in Ardmucknish Bay, Scotland, 2012:
  - Release started with 90 kg CO_2/day; later 150 kg/day
  - Two weeks in total
- Sensor used in a CTD frame from a boat:
  - Vertical profiling and horizontal towing
  - At the release and at reference sites

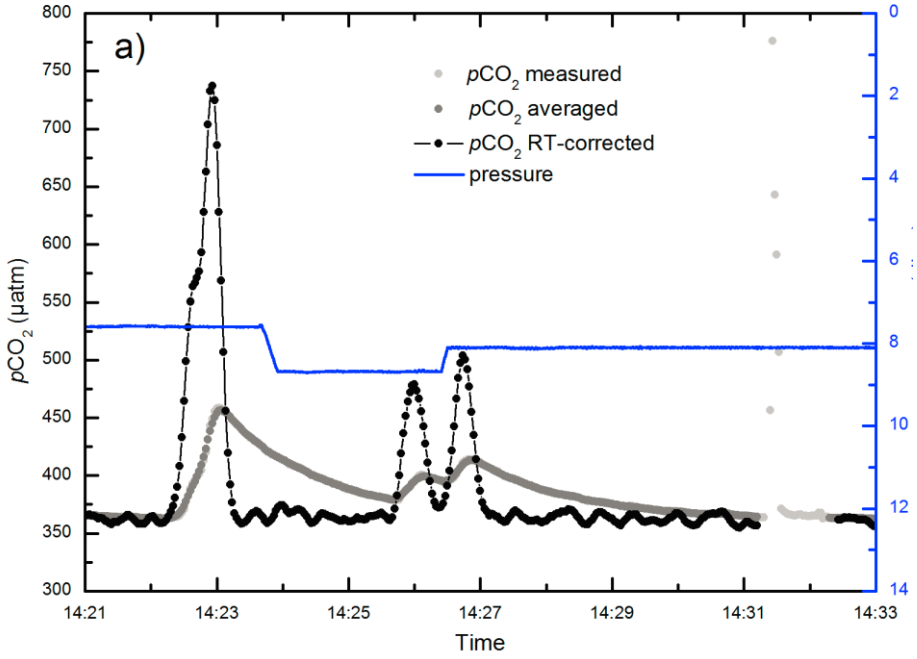




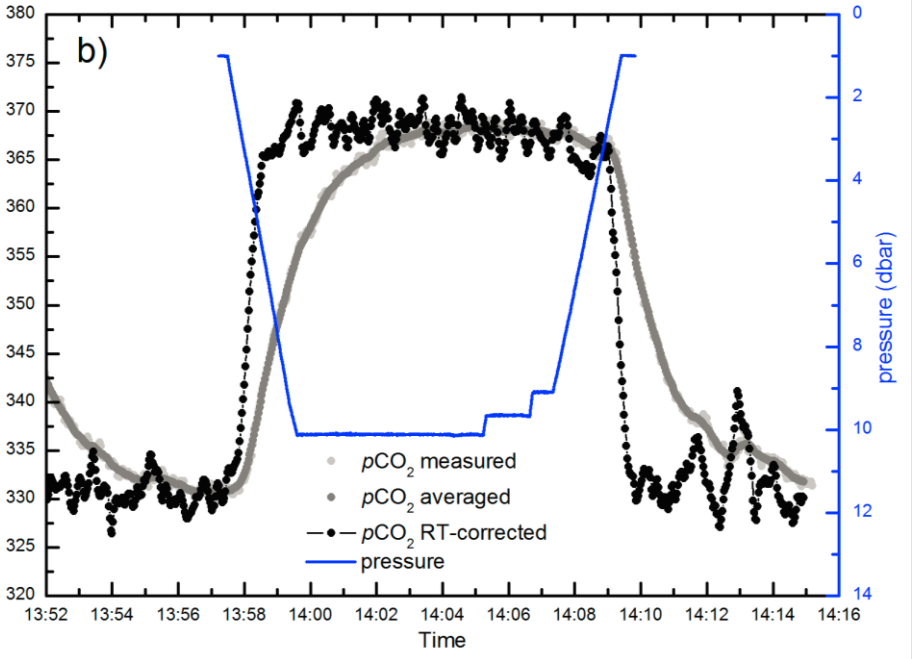
Atamanchuk, et al., 2015

Application Example
Shipborne Measurements at Gas Release Site

Horizontal towing through active area



Profiling after CO_2 release



- Gas bubble detection
- Event detection on a sub-minute scale and profiling capability through response time correction

Atamanchuk, et al., 2015

CONTROS HydroFIA TA

Analyzer for Total Alkalinity in Seawater

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CONTROS HydroFIA®TA

TA – Total Alkalinity

FIA – Flow Injection Analyses

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

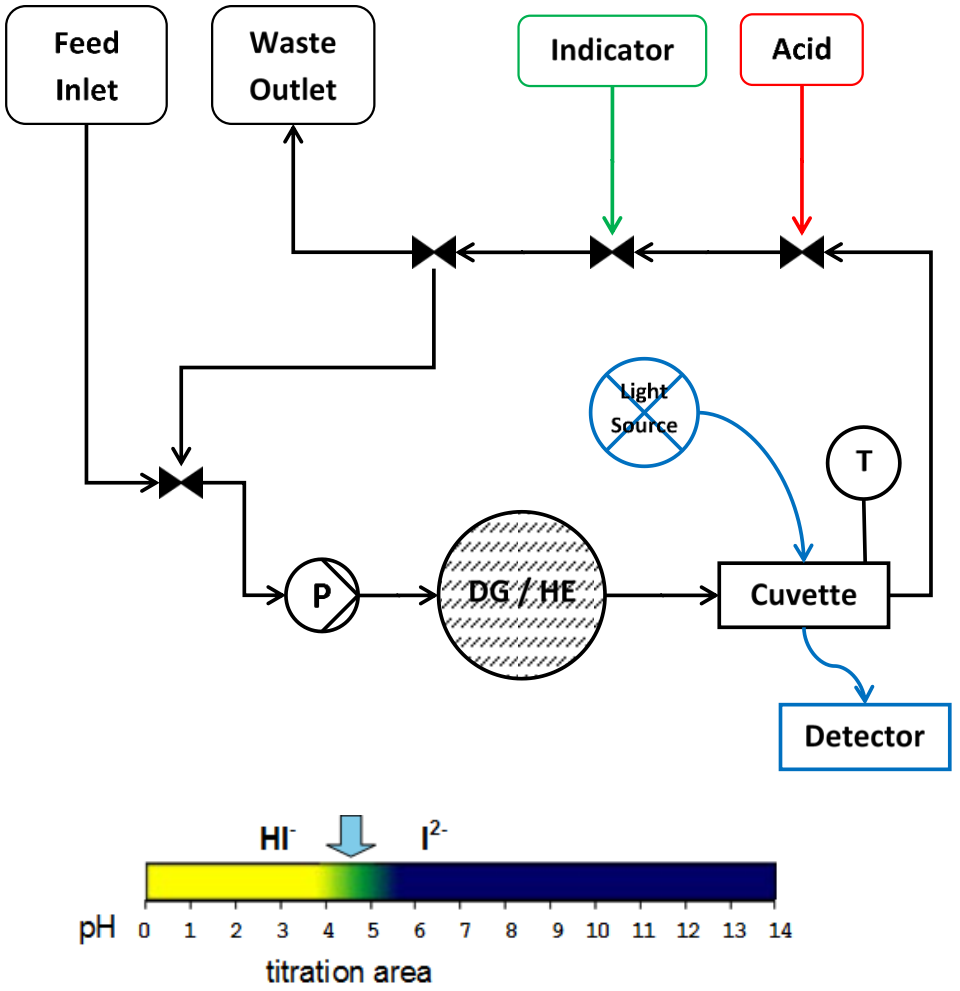
- Autonomous deployment longer than one month possible
  → **No more bottled samples**
  → **Save time and money**

- Low sample / chemicals consumption
  → **Decreased cost per meas.**

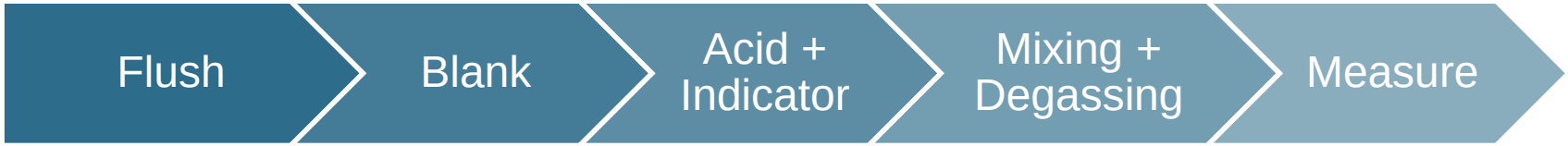
- Easy setup
  → **Replacing the sophisticated lab setup**

CONTROS HydroFIA®TA
Measurement Principle

- Sample is aspirated through the feed inlet
- Titration with hydrochloric acid (HCl) to a pH range of 3.0 to 4.5
- Addition of the acid-base indicator dye bromocresol green for spectrometric pH detection
- Calculation of TA using temperature and salinity of the sample water



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.
- **Indicator / 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
Development Activities

Project AtlantOS

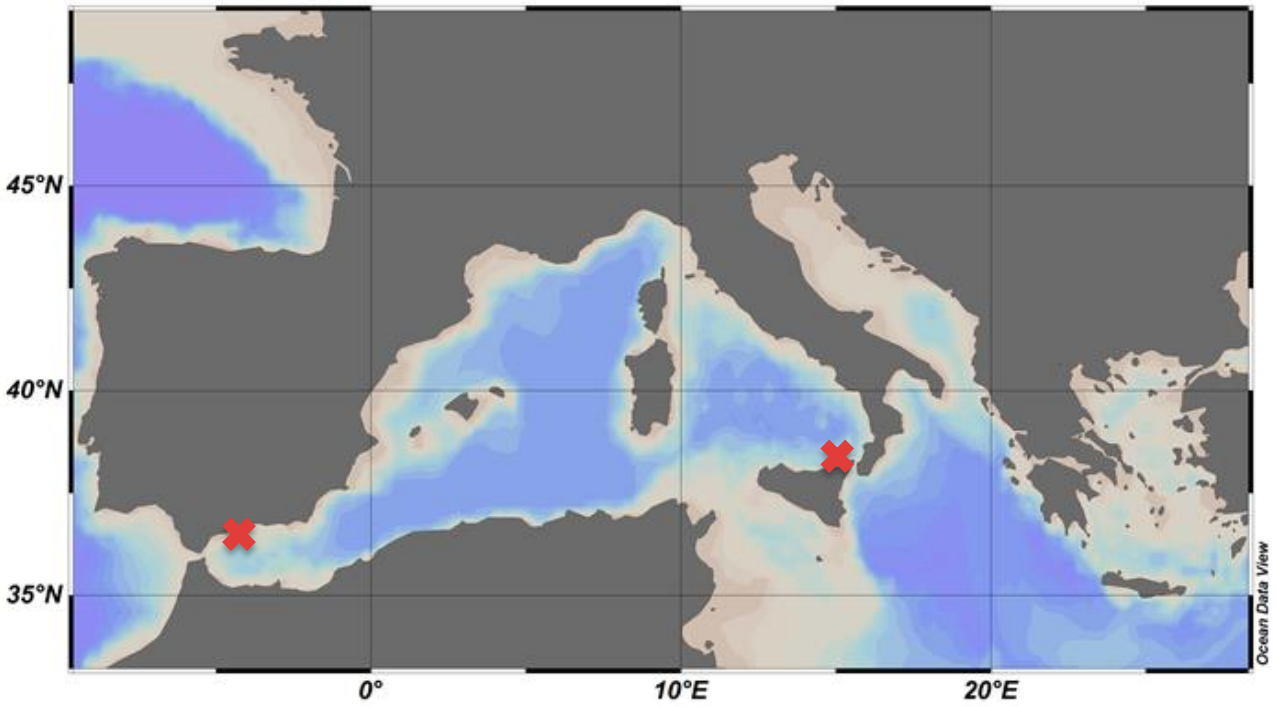
- A large scale EU Horizon 2020 research and innovation project contributing to the Trans-Atlantic Research Alliance and GEO.
- Budget: € 20.65m for 4 years (April 2015 – June 2019)
- Development of a Atlantic Observing Network
- Optimization of the HydroFIA TA for usage on VOS lines

Project **TAACT**

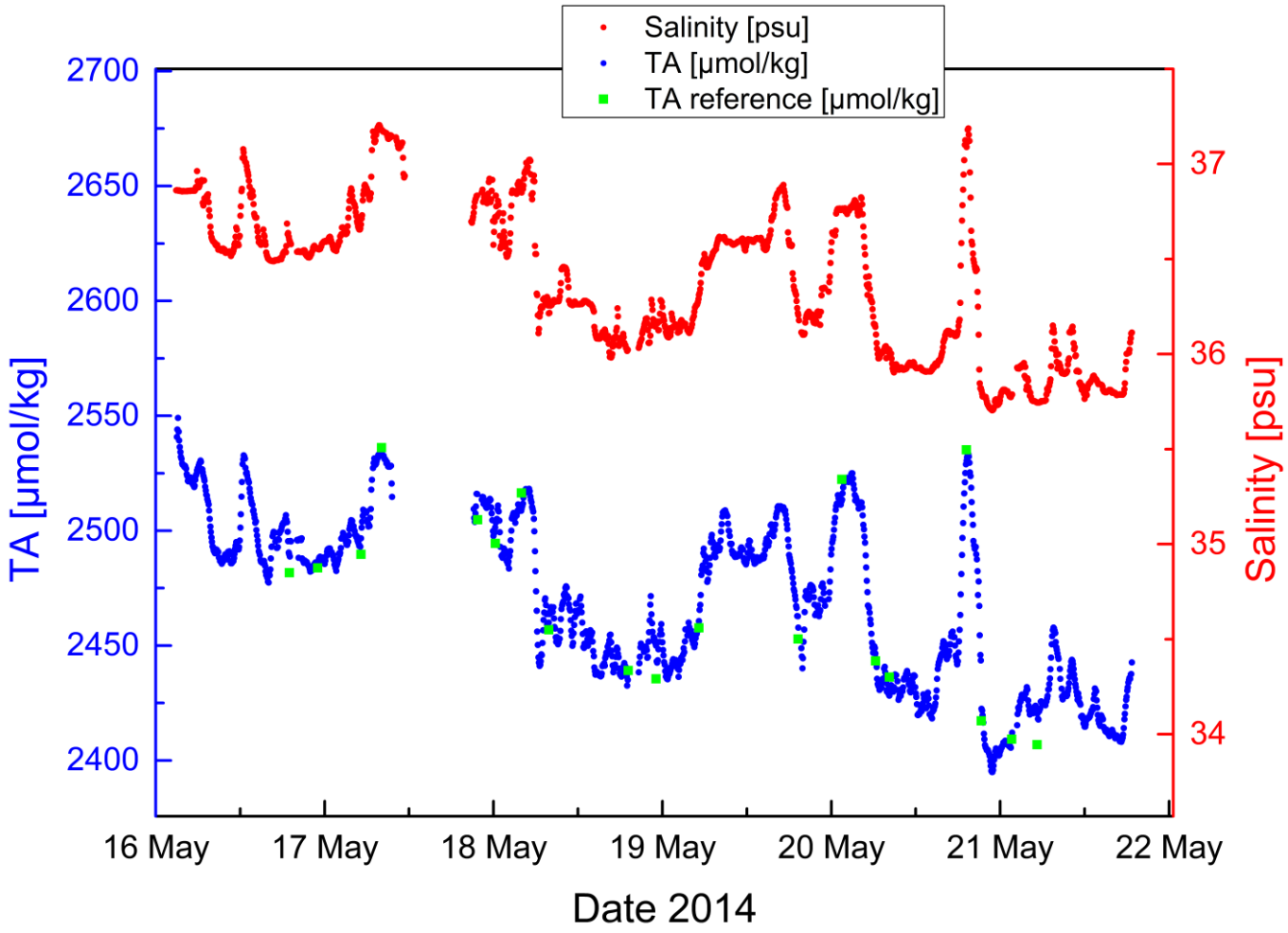
- Tracking Ocean Alkalinity Using New Carbon Measurement Technologies
- NOAA funding for 4 analyzers over 3 years (2015 – 2018)
- Establishing baseline data and autonomous techniques (i.a. CONTROS HydroFIA TA) for OA data collection that support offshore fisheries and climate applications

Application Example Mediterranean Sea

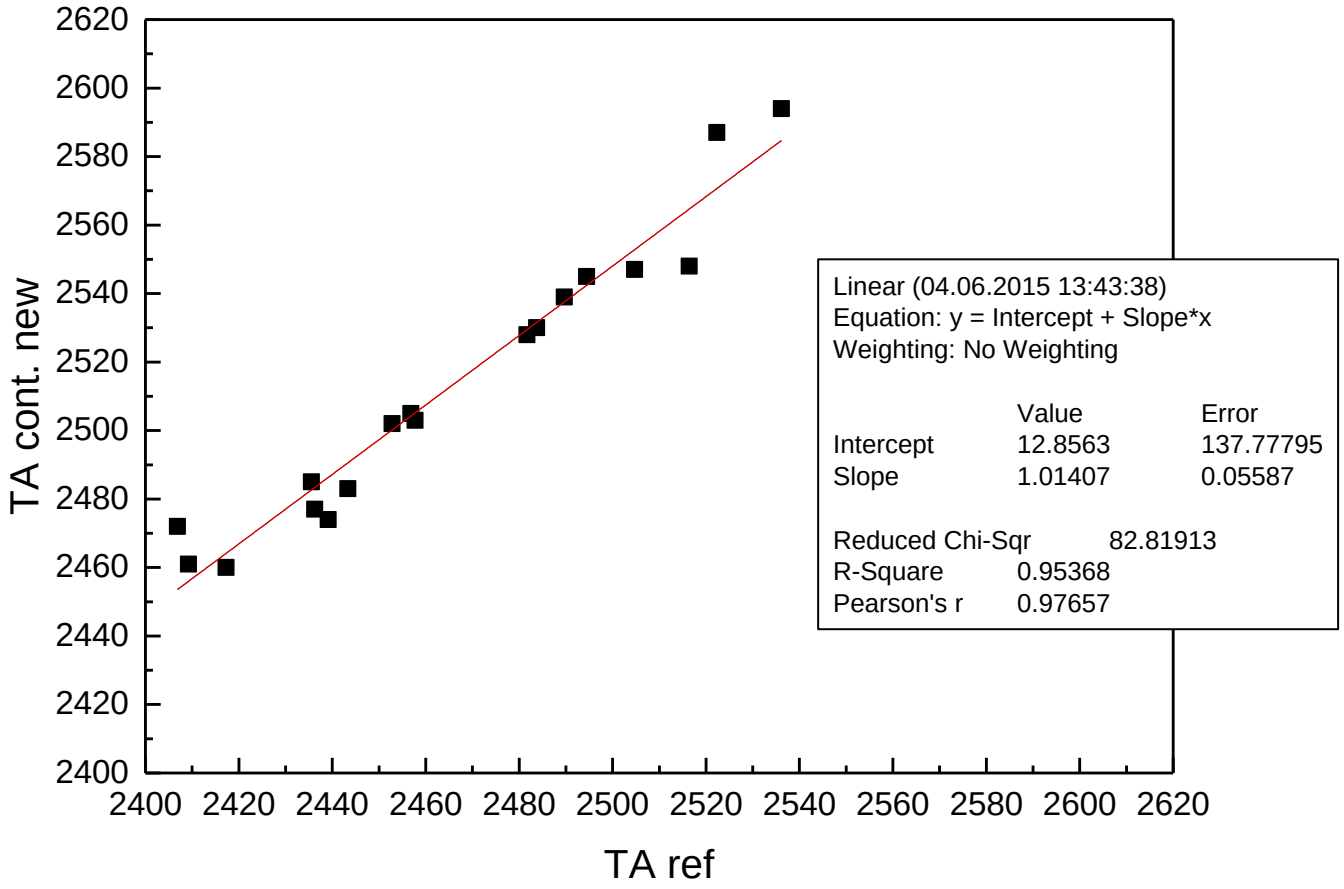
- Measurements in the Mediterranean Sea: Transit Panarea-Malaga
- Measurement Cycle: 5 minutes
- Period: 5 days
- ≈1500 values



HydroFIA TA vs Reference Samples



HydroFIA TA vs Reference Samples



CONTROS HydroFIA pH

Analyzer for pH in Seawater

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CONTROS HydroFIA®pH

pH – Proton Concentration

FIA – Flow Injection Analyses

- High quality continuous pH measurements
  → **Carbonate chemistry applicable**

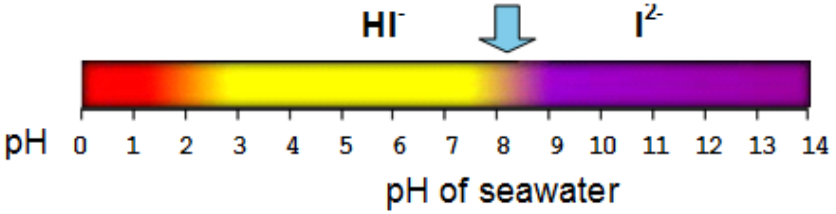
- Autonomous deployment longer than one month possible
  → **No more bottled samples**
  → **Save time and money**

- Low sample / chemicals consumption
  → **Decreased cost per meas.**

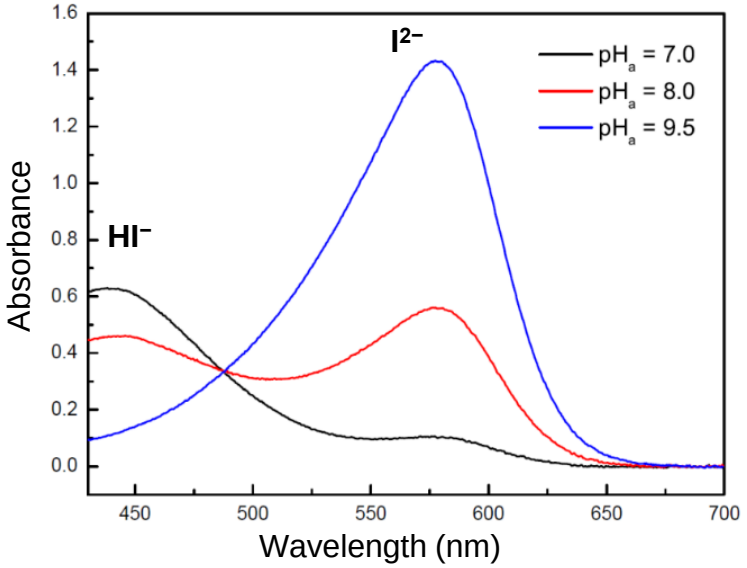
- Easy setup
  → **Replacing the sophisticated lab setup**

CONTROS HydroFIA®pH
Principle

- FIA system using an indicator dye *m*-Cresol purple



- Determination of the concentration of the indicator acid (HI^-) / base (I^{2-}) due to different absorption spectra using a CCD spectrometer

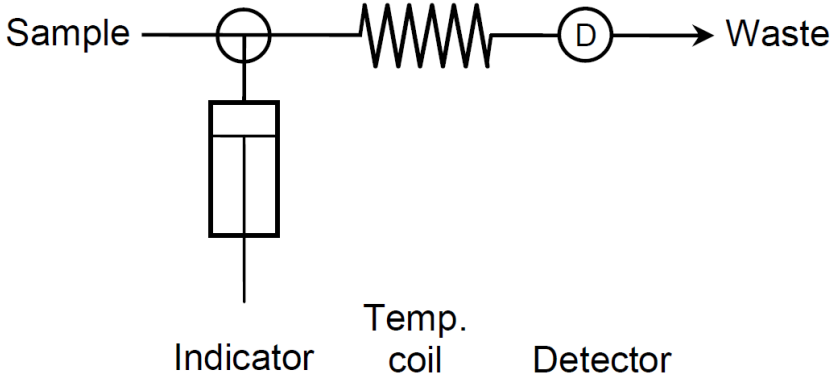


- Calculation of the pH value using Henderson–Hasselbach equation

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

CONTROS HydroFIA®pH
Measurement Intervals

- **Sample**
  Continuous sample stream.
- **Indicator**
  Injection of the indicator.
- **Temp. Control**
  Steadily controlled sample stream.
- **Measure**
  Spectrophotometric pH detection in the cuvette.

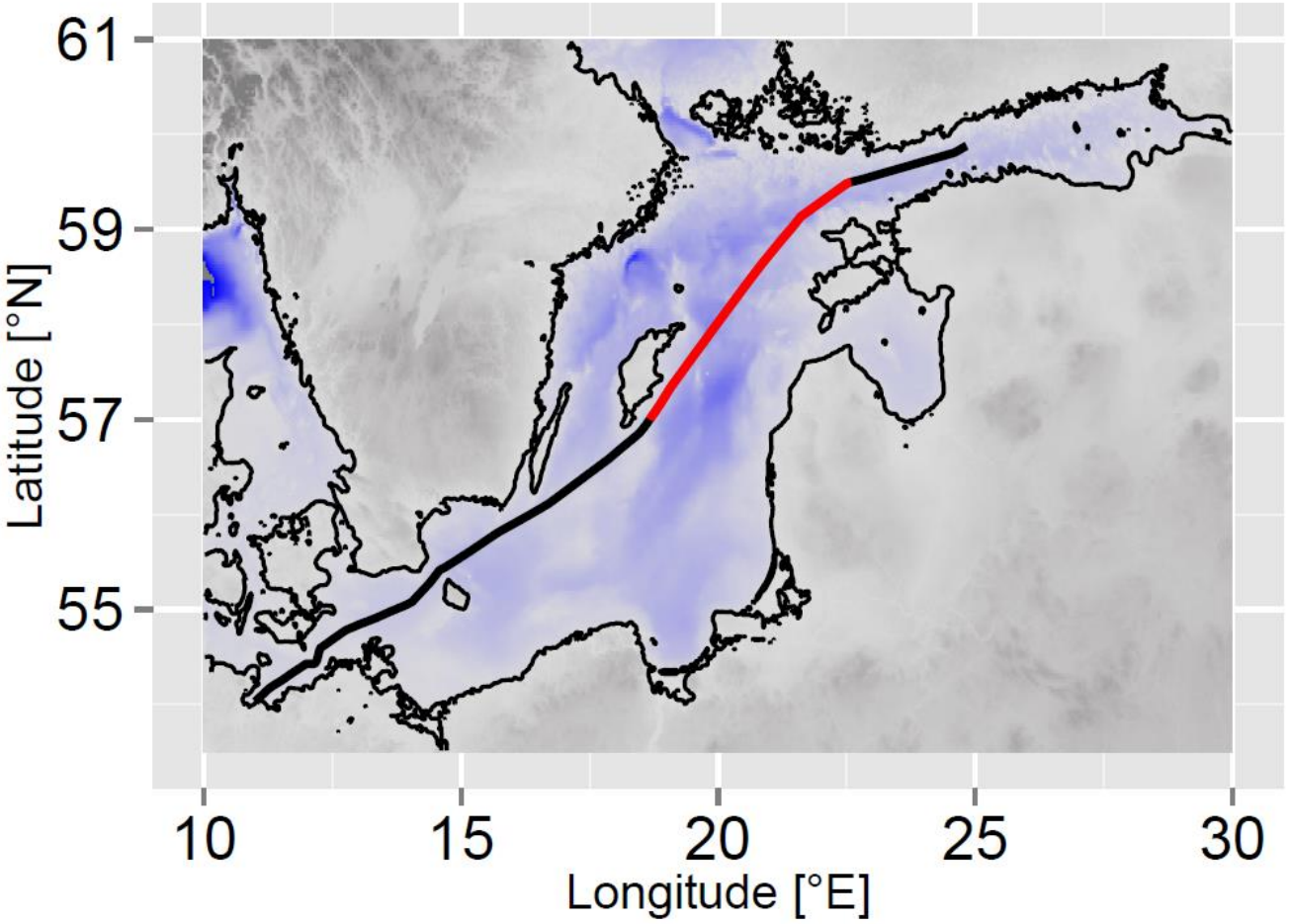


CONTROS HydroFIA®pH
Development Activities

Project **BONUS PINBAL**

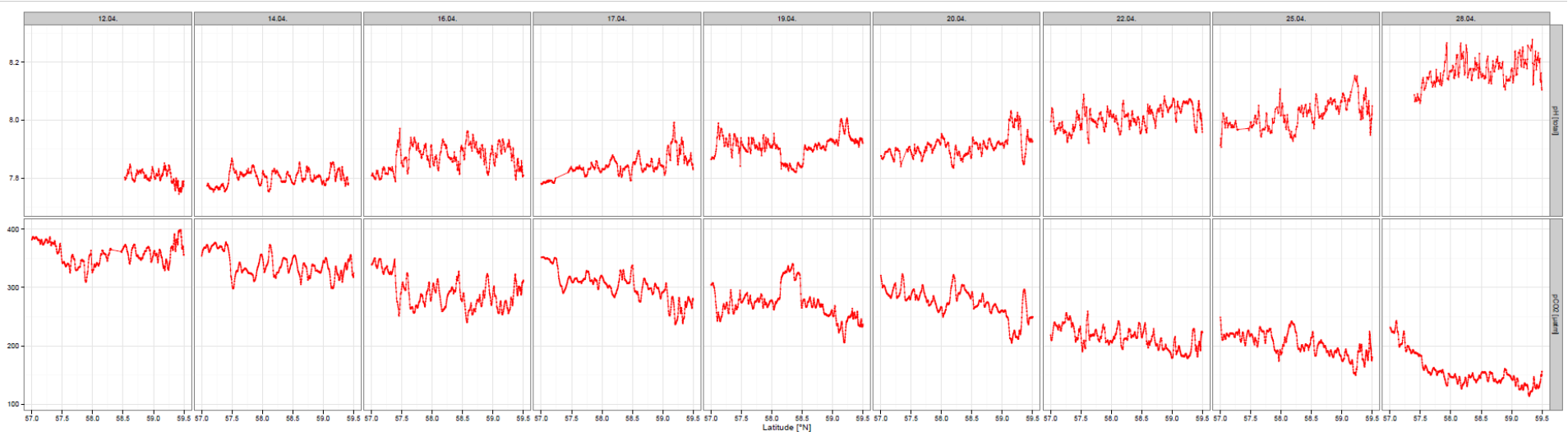
- Aiming at high accuracy pH measurements
- Characterization of the used indicator dye over a wide salinity range (approx. 0 – 40 psu)
- Evaluation of cross sensitivities (DOM, H_2S)
- Measurements at low pH seawater (wide pH working range)

Application Example
Finnmaid Ferry in the Baltic Sea

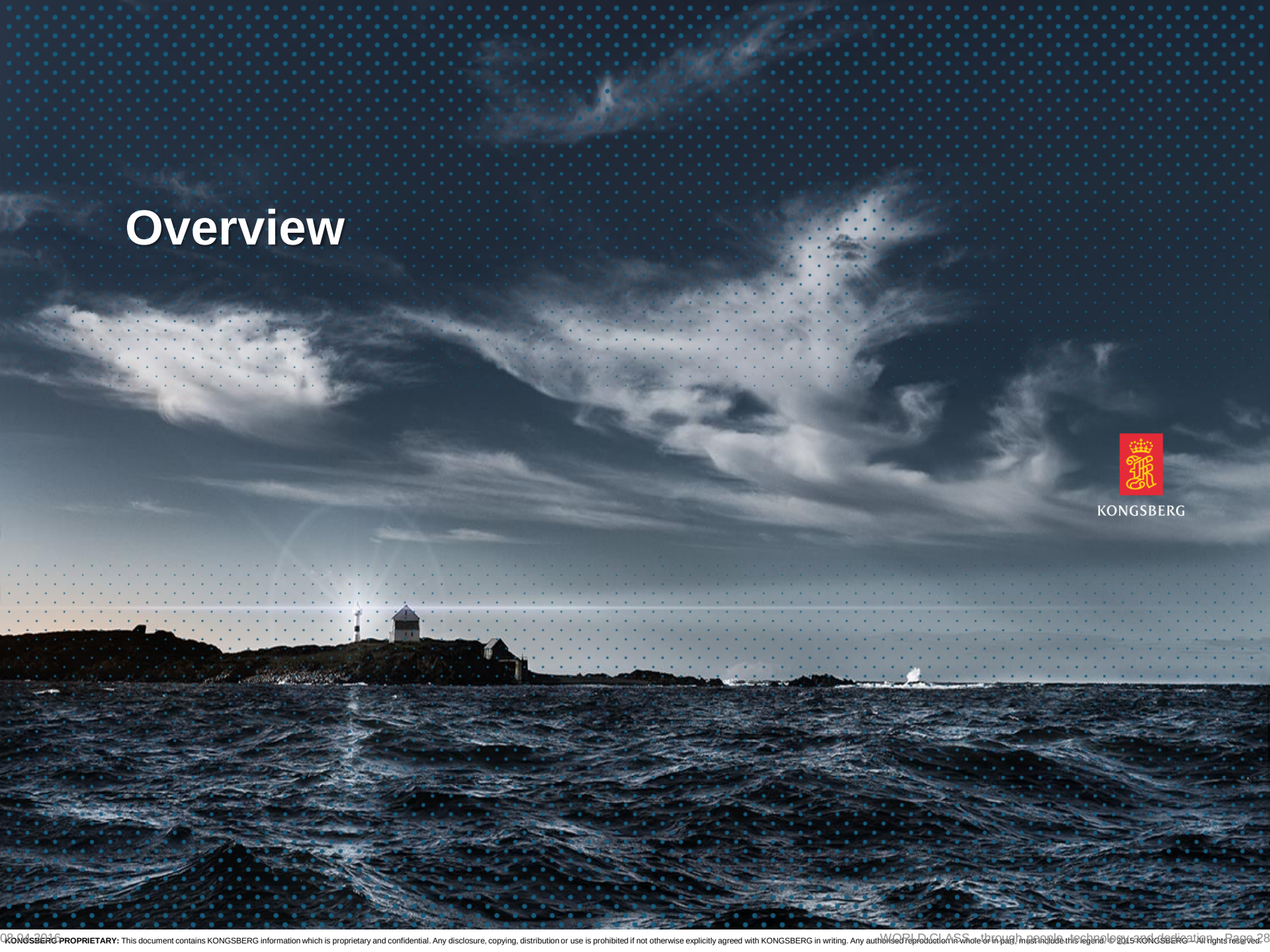


Application Example
Finnmaid Ferry in the Baltic Sea

- Monitoring the spring in the Baltic Sea
- Measurements of pCO_2 (HydroC CO_2) and pH (HydroFIA pH prototype)
- At low salinities of approx. 7 psu



Overview



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Specification Sheet

CONTROS	HydroC CO_2	HydroFIA TA	HydroFIA pH
Accuracy	± 1 %*	± 1 %	± 0.003^
Offset to Reference	± 0.6 µatm°	N/A#	± 0.01+
Precision	± 1 %	± 0.2 %	± 0.001
Meas. Interval	1 s	6.5 min	1 min
Meas. Range	200 – 1000 µatm	1400 – 2400 µmol/kg	7 – 9

* Applying pre- and post-deployment calibration

° Compared to a reference system from GO

Calibrated with reference → no initial offset

+ For impure indicator dye m-cresol purple

^ For the offset corrected pH of a standard

Thank You!

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Contact:
Dr. Steffen Aßmann
Kongsberg Maritime Contros GmbH
steffen.assmann@km.kongsberg.com