Determination of Seawater Carbonate System Parameters: CO$_2$, TA, pH

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Outline

• Background

• Determination of the Carbonate Parameters
  – Dissolved CO$_2$
  – Total Alkalinity
  – pH value

• Application Examples
Kongsberg Maritime Contros GmbH

Facts

- Founded in 2006 as CONTROS Systems & Solutions GmbH
- 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 CO₂

Sensor for Dissolved CO₂ in Water
CONTROS HydroC® CO₂

• 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

CO₂ – Carbon Dioxide
CONTROS HydroC®CO₂
Measurement Intervals and Principle

- **Warmup**
  Stable measuring conditions

- **Zero**
  Baseline determination for drift correction

- **Flush**
  Flagged response data / in-situ response time test

- **Measure**
  Measuring data
CONTROS HydroC®CO₂

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
CONTROS HydroFIA®TA

- 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

TA – Total Alkalinity
FIA – Flow Injection Analyses
**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

![Graph showing TA and Salinity over time from 16 May to 22 May 2014. The graph compares TA [μmol/kg], Salinity [psu], and TA reference [μmol/kg].]
HydroFIA TA vs Reference Samples

Linear (04.06.2015 13:43:38)
Equation: y = Intercept + Slope*x
Weighting: No Weighting

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
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<tbody>
<tr>
<td>Intercept</td>
<td>12.8563</td>
<td>137.77795</td>
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<tr>
<td>Slope</td>
<td>1.01407</td>
<td>0.05587</td>
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<tr>
<td>Reduced Chi-Sqr</td>
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<td></td>
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<tr>
<td>R-Square</td>
<td>0.95368</td>
<td></td>
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<tr>
<td>Pearson's r</td>
<td>0.97657</td>
<td></td>
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</table>
CONTROS HydroFIA pH
Analyzer for pH in Seawater
CONTROS HydroFIA®pH

• 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

pH – Proton Concentration
FIA – Flow Injection Analyses
CONTROS HydroFIA® pH Principle

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

- Determination of the concentration of the indicator acid (HI⁻) / base (I²⁻) due to different absorption spectra using a CCD spectrometer

- Calculation of the pH value using Henderson–Hasselbach equation

\[
\text{pH} = pK_a + \log_{10} \left( \frac{[I^{2-}]}{[HI^-]} \right)
\]
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, H₂S)
- 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
## Specification Sheet

<table>
<thead>
<tr>
<th>CONTROS</th>
<th>HydroC CO₂</th>
<th>HydroFIA TA</th>
<th>HydroFIA pH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Accuracy</strong></td>
<td>± 1 %*</td>
<td>± 1 %</td>
<td>± 0.003^</td>
</tr>
<tr>
<td><strong>Offset to Reference</strong></td>
<td>± 0.6 µatm°</td>
<td>N/A#</td>
<td>± 0.01+</td>
</tr>
<tr>
<td><strong>Precision</strong></td>
<td>± 1 %</td>
<td>± 0.2 %</td>
<td>± 0.001</td>
</tr>
<tr>
<td><strong>Meas. Interval</strong></td>
<td>1 s</td>
<td>6.5 min</td>
<td>1 min</td>
</tr>
<tr>
<td><strong>Meas. Range</strong></td>
<td>200 – 1000 µatm</td>
<td>1400 – 2400 µmol/kg</td>
<td>7 – 9</td>
</tr>
</tbody>
</table>

* Applying pre- and post-deployment calibration  
° Compared to a reference system from GO  
# Calibrated with reference → no initial offset  
^ For the offset corrected pH of a standard  
+ For impure indicator dye m-cresol purple
Thank You!

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