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# Performance of the *RINKO* FT optical dissolved oxygen sensors attached to Argo floats and other platforms

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RINKO FT, our newest dissolved oxygen (DO) sensor, was launched in 2015 as part of our RINKO® Series, and it helped us to overcome a well-known tradeoff between fast responsivity and stability of an oxygen sensing foil. The RINKO® Series is based on the optical (phosphorescence) principle which is now widely known as a remarkably fast response oxygen sensor with a high accuracy. The RINKO FT not only retains the fast response time identical to that of conventional RINKO® Series, but also has greater accuracy and stability by incorporating high-quality multipoint calibration and improved sensing method. As result, the RINKO FT enables fine scale DO measurements, contributing to the understanding of new aspects of physical and biochemical processes. The RINKO FT was primarily developed to target Argo float operations with a compact, lightweight design. However, its commonly used communication protocol widen the choice of platforms for installation (currently, this instrument is integrated in different platforms – see further in VI. Platforms in this document). We present a performance evaluation of the RINKO FT deployed in the laboratory and also in the field (using data from field observation and different Argo floats) down to 2000 m depth.

RINKO FT – *Optical dissolved oxygen sensor*

## I. *RINKO* FT

The most exciting feature of the RINKO® Series is its extremely fast responding time of the oxygen sensing foil (63% response time: less than 1 s in water at 1 atm and 25°C, as shown in Fig. 1). This feature allows for DO measurements with a high DO vertical distribution, helping to resolve small-scale distributions. In addition to that, a controlled excitation light emission (in order to slow down the deterioration of the oxygen sensing foil) together with a robust foil with increased gas permeability gives RINKO FT an outstanding long-term stability without undermining its fast responsivity.

The RINKO FT is calibrated with a modified Stern-Volmer equation, expressed in terms of phase-shift data (Uchida et al., 2010), achieving an absolute high accuracy of ±2% of the measured value or ±2 μmol $L^{-1}$. Coefficients are determined using a 16-point calibration (4 temperatures and 4 oxygen concentrations) at JFE Advantech Co., Ltd., facility as shown in Fig. 2. The four oxygen reference standards are produced by saturating the Primary Mixture (National Metrology Institute of Japan certified traceable gases) individually with each oxygen concentrations of approximately 4%, 10%, 17%, and 25%. These values correspond to an air saturation of approximately 20%, 50%, 80%, and 120%, respectively. The Winkler titration method is NOT applied to our multipoint calibration in order to minimize systematic and experimental errors, which in turn ensures high accuracy.

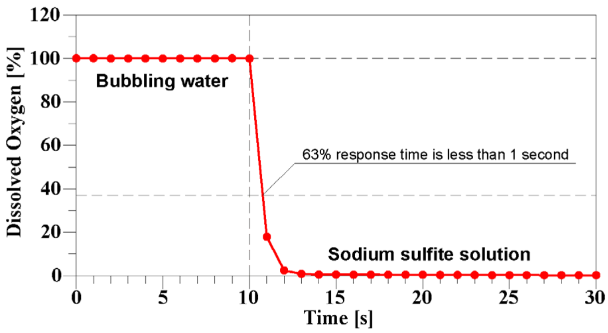


Fig. 1: Typical averaged response of the DO sensor in the time series at 25°C measured by RINKO-FT. Air saturated water (DO=100%) is prepared by bubbling for 30 minutes. Anoxic water (DO=0%) is prepared by dissolving sodium sulfite $Na_2SO_3$ in 1 L of distilled water.

After calibration, the RINKO FT is verified using oxygen reference water produced by saturating the Primary Mixture. The oxygen concentration of the traceable gas used in the verification is approximately 21%, which corresponds to air saturation around 100%. Our verification ensures that all residual errors of the measured DO values stay within 2% of measured value or ±2 μmol $L^{-1}$ (whichever is greater) at four arbitrary temperatures of approximately 1, 10, 20, and 30 °C (Fig.3).

In order to satisfy the demands of the observations done by Argo floats, RINKO FT is designed to satisfy the required accuracy for a number of years without the need for re-calibration. However, in case of long-term storage or even using in a recoverable platform we also provide a user-calibration kit as option with cable and GUI software (Fig. 4). The RINKO FT can be easily detached without disturbing the mounting-hole mechanism or the wiring of the platform in order to perform the user calibration.

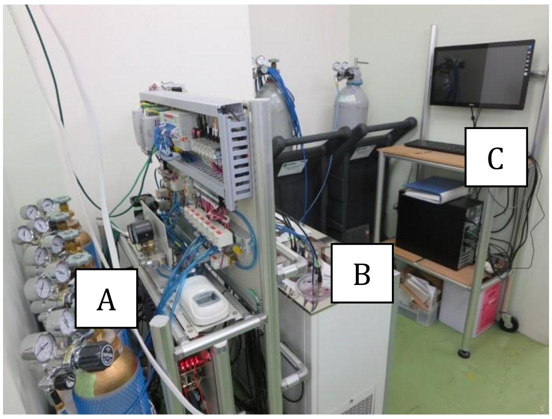


Fig. 2 Multipoint calibration system at JFE Advantech Co., Ltd. factory. A) 5 tanks of the highest grade traceable gases for calibration (4 tanks) and verification (1 tank). B) Isothermal bath. C) Control PC.

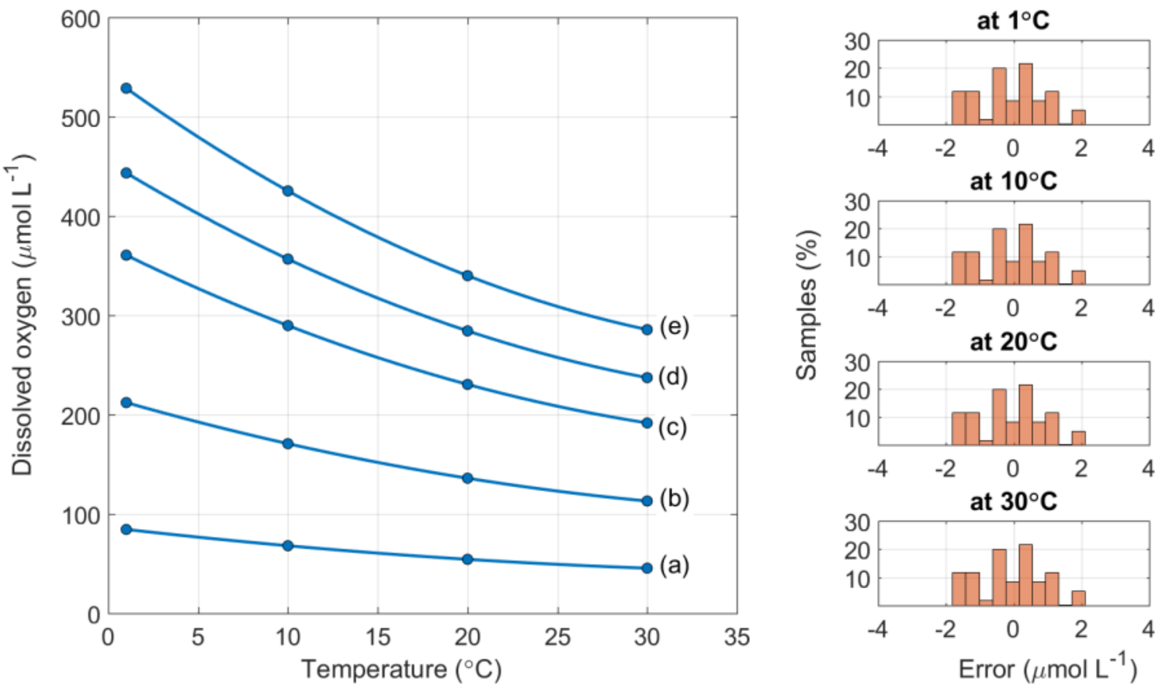


Fig. 3 RINKO FT calibration data in different DO saturation conditions, (a) 20%, (b) 50%, (c) 80% and (e) 120%, and verification points at 100% of saturation (d). All residual errors stay within 2% of measured value or 2 μmol $L^{-1}$ (whichever is greater) at four arbitrary temperature points of approximately 1, 10, 20 and 30 °C.

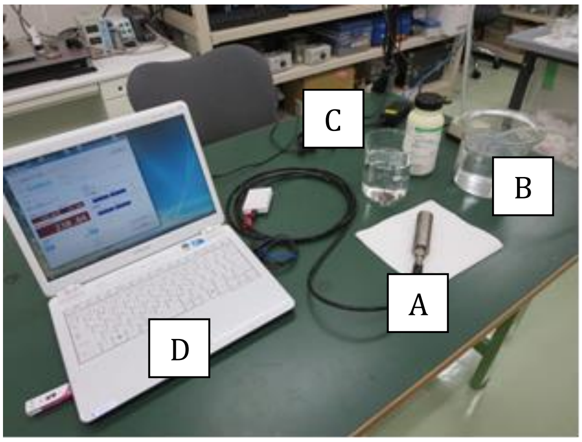


Fig. 4 Operation of the user calibration. It is possible to perform not only a simple two-point calibration (0% and 100% of saturation) but also any kind of calibration method. A) RINKO FT with USB cable (instrument is powered by USB port), B) Bubbling water (100% saturation calibration), C) Sodium sulfite solution (0% saturation calibration) and D) GUI software.

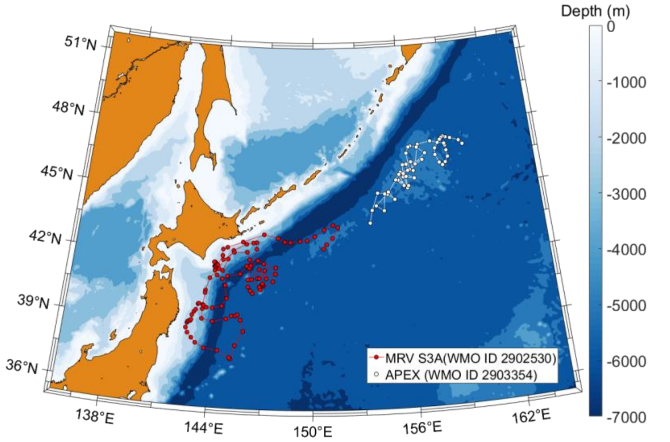


Fig. 5 Float trajectories (MRV float in red and APEX float in white). Both floats drifted in the North-western Pacific (off Hokkaido, Japan and Kuril Islands, Russia).

## II. PERFORMANCE

### (a) Argo floats

We present a performance evaluation of the RINKO FT on floats from BGC Argo program deployed by Japan Agency for Marine – Earth Science and Technology (JAMSTEC) in the northwestern Pacific Ocean since 2014.

We analyzed data from two floats, a MRV S3A and a Teledyne Marine's APEX floats publically available on Argo's Global Data Assembly Centers (GDACs). The MRV S3A recorded DO data every 2 dbar taking advantage of the fast responsivity of the RINKO FT. The trajectories of these floats are shown in Fig. 5 and float ID can be seen in Table 1. Note that we did not apply adjustments of any kind to the data labeled as "realtime QC mode data" available at the GDACs.

Fast response is essential to grasp a large DO variation at relatively small-scale vertical structure and the RINKO FT was able to identify DO minima/maxima thin layers, as well as sharp gradients as shown in Fig. 6 and Fig. 7.

Table 1 Observation period and WMO ID from the float data evaluated here.

| Period | WMO ID | Model | Observations |
|---|---|---|---|
| 07/2014 to 01/2016 | 2902530 | S3A (MRV) | – |
| 07/2018 to 08/2018 | 2903354 | APEX (Teledyne Marine) | still operational (03/18/2020) |

The first vertical profile of the RINKO FT DO data is plotted against the Winkler titration data sampled at the nearest site in Fig. 6, and shows that the DO concentrations from RINKO FT also agreed well with the Winkler DO concentrations. Such fine scale DO distribution that cannot be obtained by slow response sensors and/or water sampling. The RINKO FT oxygen sensing foil possesses a unique balance between fast responsivity and long-term stability. In general, a trade-off relationship exists between fast responsivity and stability of an oxygen sensing foil. In order to overcome such relationship, the sensing method of the RINKO FT has been improved by minimizing the LED emission time, decelerating the deterioration of the sensing foil. This improvement reduces considerably the time drift presented by RINKO FT as shown in Fig. 8, where we show DO time series from both floats at potential density ($\sigma_\theta$) of 27.60. During 2014, the drift was less than 1 µmol $kg^{-1}$ and less than 2 µmol $kg^{-1}$ in 2018.

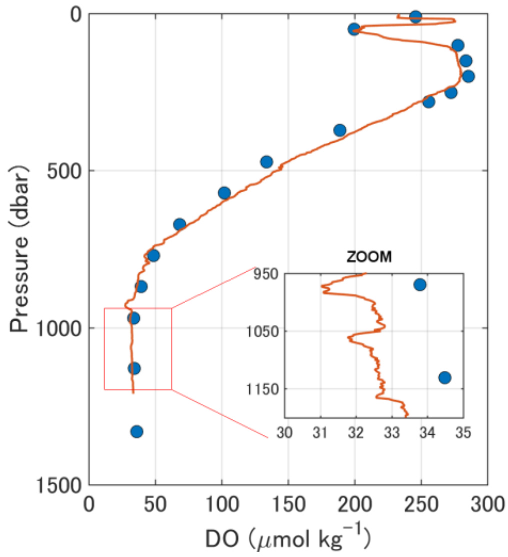


Fig. 6 First vertical DO profile obtained with the RINKO FT installed on the MRV S3A (WMO ID2902530) float (orange line) compared to DO data estimated by Winkler method from discrete water samples (blue circles).

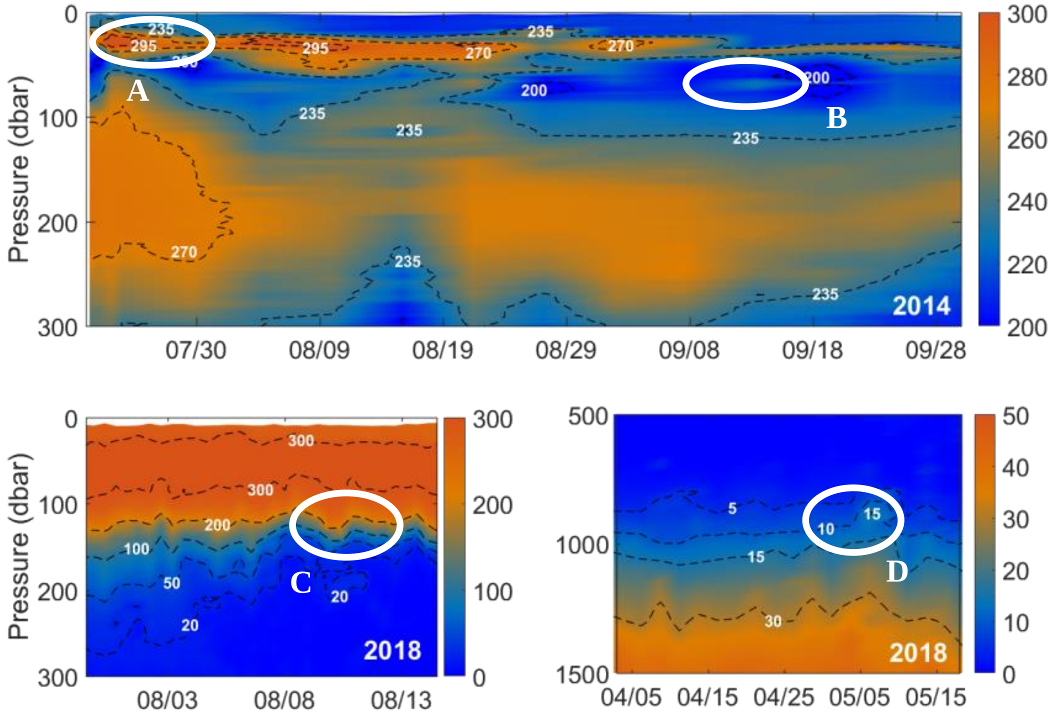


Fig. 7 In the upper panel, area A shows a local DO concentration maximum followed by local minimum highlighted in Area B. In the lower panels (left and right), a sharp DO gradient is identified between 100 and 200 dbar (Area C) and around 1000 dbar (Area D).

We did not observe any noticeable time dependent pressure effect on RINKO FT DO data from both floats down to 2000 m depth. The RINKO FT DO concentration varied within 2 μmol kg$^{-1}$ after several pressure cycles. This may be due to the fact RINKO® sensing foils do not seem to be affected by the time-dependent pressure effect at 1000 m, where these floats have their parking depth (Uchida, H. et al. 2018 - poster presentation at 6th Argo Science Workshop, Tokyo, Japan).

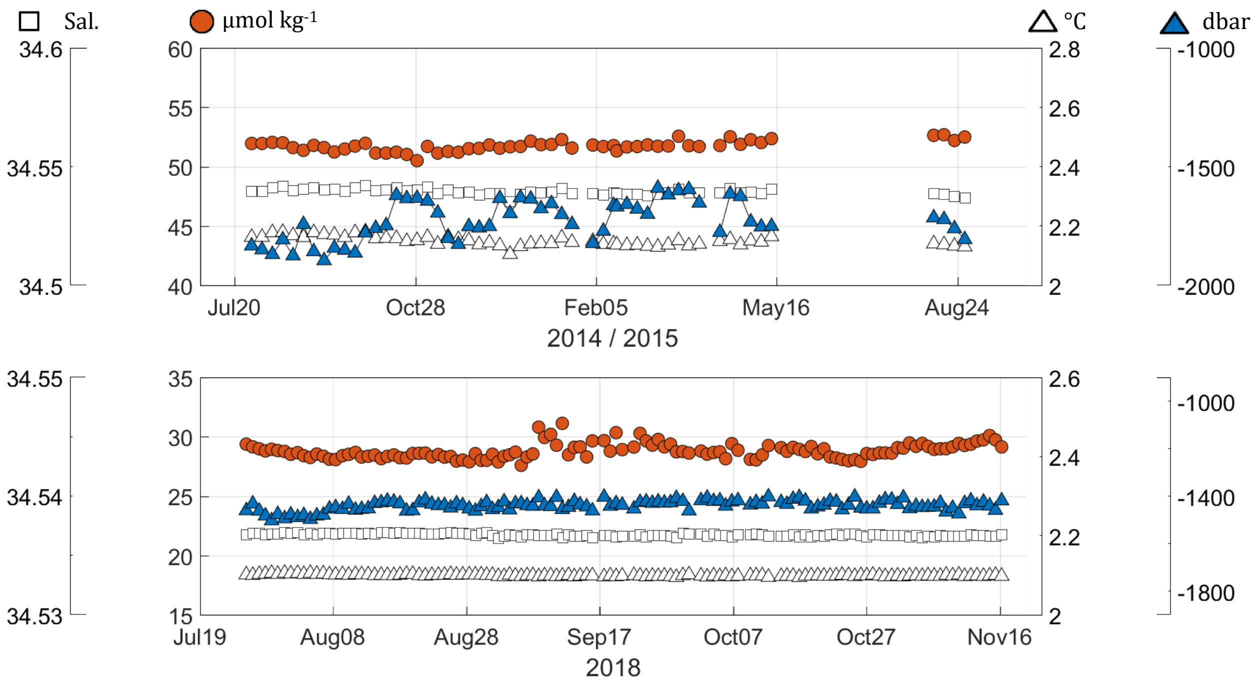


Fig. 8 Time series of pressure (blue triangle), salinity (white square), temperature (white triangles) and DO (orange circles) from the MRV S3A(WMO ID2902530) and APEX (WMO ID2903354) floats at $\sigma_\theta$ equal to 27.60.

### (b) Observation using a flow-through (underway) box

The RINKO FT was placed side by side with other instruments in a flow-through (underway) box during the field expedition M133 SACROSS onboard R/V METEOR between on December 17th 2016 and January 12th 2017, crossing a dynamic area in the Patagonian shelf and led by GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany. The underway box was continuously supplied with surface water pumped from 5.7 m depth and the measuring interval for the sensor was set to one minute. A bypass was used for obtaining discrete DO samples measured by the Winkler titration method, which are considered here as reference.

In Fig. 9, we show RINKO FT measurements compared to Winkler samples taken during the experiment. The RINKO FT presented a very good correlation with Winkler samples ($R^2$ of 0.99) and an absolute difference between both measurements averaging at 6.8 μmol $L^{-1}$. The offset presented by the instrument was consistent to what is expected if 2-point calibration is not performed before deployment (this experiment did not include RINKO FT 2-point calibration prior to the cruise).

On the lower right panels in Fig. 9, we show the difference between RINKO FT and the reference (Winkler samples). We did not find a significant dependence trend between the instrument's estimation and the total DO concentration (the linear regression has a very smooth slope).

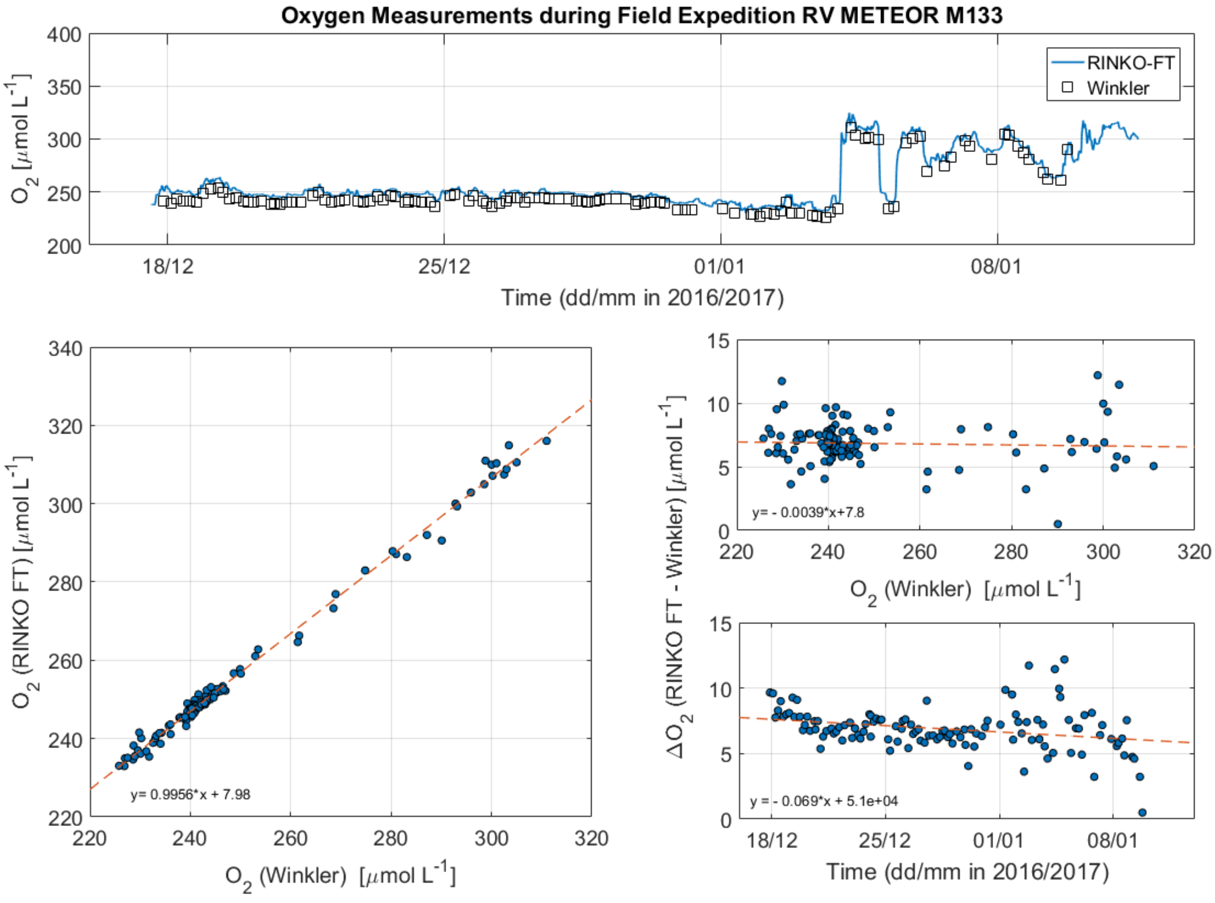


**Fig. 9** Measurements from RINKO FT (upper panel - blue line) and Winkler samples (upper panel black squares) time series. The correlation between RINKO FT and Winkler samples can be seen in the lower left panel. The dashed orange line is the linear fit between both quantities ($R^2$ equal to 0.99). The absolute difference between RINKO-FT and Winkler samples can be seen in the lower right panels against total DO concentration and against time.

## III. RINKO FT SPECIFICATIONS

### (a) Sensor specifications

| | | |
|---|---|---|
| **Measurement principle** | DO | Phosphorescence |
| | Temperature | Thermistor |
| **Range** | DO | Concentration: 0 – 425 μmol $L^{-1}$ (1)<br>Air saturation: 0 – 200% (calibration range: 0 – 120%) |
| | Temperature | -3 – 45 °C (calibration range: 0 – 35 °C) |
| **Resolution** | DO | 0.01 μmol $L^{-1}$ |
| | Temperature | 0.001 °C |
| **Initial accuracy** | DO | ±2% of measured value or ±2.0 μmol $L^{-1}$ (calibration range: 1 – 30 °C) |
| | Temperature | ±0.01 °C |
| **Repeatability** | DO | Sample-based drift:±5% of measured value or ±5.0 μmol $L^{-1}$ / 4,000,000 samples (2)<br>Pressure effect: ±2% of measured value or ±2.0 μmol $L^{-1}$ (3)<br>Temperature effect: ±2% of measured value or ±2.0 μmol $L^{-1}$ |
| **Response time (63%) (at 25 °C, typical)** | DO | < 1 s (in water) |
| | Temperature | < 1 s (in water) |

(1) Calculated from air saturation at 25 °C and 34 psu
(2) Accelerated degradation test
(3) Pressure hysteresis not considered

### (b) Instrument specifications

| **Model name** | **ARO-FT** | **AROD-FT** |
|---|---|---|
| **Sampling interval** | 1 s | 1 s |
| **Preheat time** | 5 s | 5 s |
| **Communication** | UART (3.3 V logic) or RS-232C | RS-232C |
| | Baud rate: 38400 bps, No parity, Handshake | Baud rate: 38400 bps, No parity, Handshake |
| **AD Converter** | 16 bit digital conversion | 16 bit digital conversion |
| **Power** | 6 – 26 VDC, 12 VDC recommended | 6 – 26 VDC, 12 VDC recommended |
| **Current drain** | Sampling: 30 mA, Sleep mode: < 0.1 mA (at 12 VDC, typical) | Sampling: 30 mA, Sleep mode: < 0.1 mA (at 12 VDC, typical) |
| **Material** | Housing: Titanium (grade 2)<br>Insulating attachment: POM | Housing: Titanium (Ti-6Al-4V) |
| **Connector** | 8-pin LEMO or MCBH-8MP | MCBH-8MP |
| **Weight** | In air: approx. 183 g (without attachment or cable)<br>In water: approx. 110 g (without attachment or cable) | In air: approx. 265 g<br>In water: approx. 175 g |
| **Depth rating** | 2000 m depth equivalent | 6700 m depth equivalent |

## IV. DIMENSIONS

Model ARO-FT with standard mounting attachment

Model AROD-FT with MCBH connector

Model ARO-FT with LEMO connector and 3 m of cable

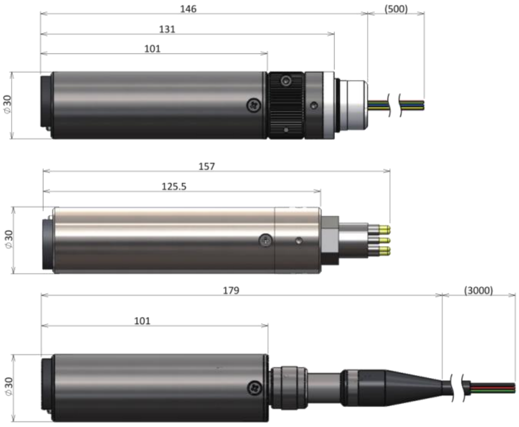


**Fig 10** Dimensions of RINKO FT models with different type of connectors. All dimensions are in mm.

## V. PLATFORMS

Currently, RINKO FT is integrated in a variety of platforms. Among them, our instrument can be used in APEX and APEX Deep floats from Teledyne Marine, SEAEXPLORER under-water glider from Alseamar-Alcen, and S3A floats from MRV (see Fig.11).

## VI. REMARKS ON THE RINKO FT's PERFORMANCE

RINKO FT was capable of providing high-accuracy data in two different instances. The instrument obtained a difference against the reference (Winkler samples) of approximately ±2 µmol $L^{-1}$ for the most of the analyzed data (Argo floats) and ±6.8 µmol $L^{-1}$ for the flow-through box (offset explained above). The instrument fast re-sponse allows for fine-scale DO gradient observations and can help the scientific community to understand new aspects of physical and biochemical processes.

As a next step, we will analyze the RINKO FT performance in the deep ocean using Deep Argo floats and laboratory experiments focusing on its response and accuracy regarding possible pressure effects on the sensor together with its time drift.

APEX float (Teledyne Marine)

S3A float (MRV)

Deep APEX float (Teledyne Marine)

SEAEXPLORER Glider (Alseamar-Alcen)

**Fig. 11** Different platforms that RINKO FT can be used.

### ACKNOWLEDGEMENTS

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