Dissolved Methane Gas Sensors for operation on Autonomous and Remote Underwater Vehicles (AUVs/ROVs)

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1. Purpose

The objective of this document is to list and evaluate all available dissolved methane gas sensors to help end users identify which sensor(s) meet their specific needs. This review only includes sensors that are in commercial production.

2. Introduction

Advancement in understanding our world's oceans has gone hand in hand with innovations in technology. The development of dissolved methane sensors verses the historic method of collecting discrete water samples followed by gas-chromatography analysis has greatly improved our understanding of dissolved methane in aqueous environments. Electronic methane sensors over traditional methods have improved the temporal-spatial resolution, and quality of the data collected on methane in aqueous environments (Boulart et al., 2010). Methane sensors are able to operate independent of ship based platforms by being integrated to autonomous or remotely operated underwater vehicles (AUVs/ROVs), as well as on fixed moorings and in subsea floor spaces. Modern methane sensors are able to log data over long periods of time (hours to years), and are able to measure methane concentrations at relatively rapid intervals (seconds to minutes) (Wynn et al., 2014). Lastly, the data product can be obtained in real-time, or at least very near. These are the main traits modern methane sensors possess and are what makes this technology an irreplaceable improvement over historic methodologies (e.g., water sample/gas chromatography).

While the oil and gas industry routinely utilizes methane sensors to monitor subsea pipelines, and wells via fixed mooring, vertical profiles, and ROV/AUV platforms. There is a diverse array of research areas where the application of these sensors is ideal. Marine geological features such as anoxic sediments, cold vents, and submarine volcanic activity all actively source methane gas to the ocean. While these sources are widely recognized, they are still not well quantified (Sauter et al., 2006). Methane gas is an important molecule to quantify accurately as it is a significant contributor (~20%) to the greenhouse-gas effect. Because the ocean is a significant source of methane gas, its study is important for accounting the global methane gas budget (Boulart et al., 2010).

Developments in remote and autonomous underwater systems are revolutionizing the scientific community's ability to monitor, access, and study the depths of the marine environment. Untethered vehicles are at the frontier, accessing the most remote and hostile of marine environments (e.g., deep hydrothermal vents, under ice sheets in polar regions) that were virtually inaccessible in the past, and still remains a challenging task today. While vehicles allow access to new environments, developments in instrumentation which can mount to a vehicle are vital to improve the spatiotemporal resolution of the data they collect (Wynn et al., 2014).

Relative to surface ships, AUVs can collect much more detailed data by flying at low altitudes over larger areas of seafloor. The deeper the study site, and the more hazardous the location only magnifies this difference. Sensors outfitted to autonomous vehicles need to meet sensitivity and sample rate needs to be able to resolve subtle changes in seawater chemistry (Wynn et al., 2014).

Autonomous Underwater Vehicles (AUVs) are highly relevant to geological oceanographic research which target to study the interface between the seafloor and water column. At this interface, high resolution data is essential for understanding the processes which occur there (Wynn et al., 2014). Methane gas in this environment is a common parameter and a vital proxy for locating fluid escape features on the seafloor such as fault features, hydrothermal activity, and anthropogenic influences like leaking gas lines. These features have shown to be best understood from data collected using AUVs equipped with sensor suites that include a dissolved methane sensor (Sauter et al., 2006).

Measurement of dissolved gasses in aqueous environments cannot be accomplished through the direct application of air monitoring techniques to a liquid environment. To quantify dissolved gases in water, the gas must first go through a gas extraction step. This is accomplished by using semi-permeable materials, which are often applied in the form of a membrane through which gases are able to permeate (Boulart et al., 2010). Membranes used in dissolved methane sensors are constructed of silicon rubbers such as polydimethysiloxane (PDMS). These silicone materials in membrane form are characterized as having high gas permeability, and low molecular selectivity due to the materials significant amount of free volume (free volume (Vf): the interstitial space, or volume fraction, between molecules comprising a material) (Benounis et al., 2008). This technique though causes artifacts in the data due to the fact that membrane performance is dynamically influenced by all environmental factors, particularly temperature and pressure (Benounis et al., 2005).

Some sensors and membrane materials consume methane as a part of their operation. In this scenario, the diffusivity of the membrane will decrease over time resulting in a greater concentration differential across the membrane at equilibrium. This decreases the sensitivity of the sensor which is housed in the gas detection chamber of the instrument. Variations in the flow of water through the system also affects the sensors sensitivity as convective transport of the analyte alters the concentration of the analyte that is at the surface of the membrane. Decreased diffusivity in non-consumptive sensors does not have a long-term effect on calibration, but it does however reduce the temporal responsiveness of the sensor. Additionally, low temperatures alter the free volume of PDMS membranes by decreasing the amount of free volume. This effect on the membrane reduces the materials permeability which is compounded by the effect low temperatures have in decreasing the mobility and solubility of gas molecules (Boulart et al., 2010).

Today membranes used on underwater methane sensors are much improved from the past. Anomalies that are produced in data, and sensor drift over time are dealt with in a number of ways specific to the manufacturer and sensor model. Sensor drift is primarily a problem with the lower cost semiconductor sensors. To mitigate these problems, routine factory re-calibrations are necessary over set time intervals, or after environmental or physical trauma occurs to the sensors components. Calibrations specific to the temperature and pressure (depth) of the environment being sampled is also vital for obtaining accurate measurements. Improved detection methods (optical) are some of the most notable areas developed for minimizing inaccuracies in the data collected by these sensors. Sensors that utilize optics as their detection method are able to automatically compensate for anomalies in their methane detection.

3. Commercially Available Instruments

Despite technological advancements, all the commercially available methane sensors reviewed in this document still use a semi-permeable membrane. The membrane material is usually silicone based (e.g., polydimethysiloxane), and is used to transfer dissolved gases into the sensors detection chamber. This separation is important for even the top line optical sensors because of waters rapid absorption of the IR spectrum (Boulart et al., 2010). The methane sensors in this document were evaluated based on a variety of characteristics such as their price, size, weight, power consumption, detection ranges, temperature ranges, sampling speed, and maintenance needs.

3.1. Franatech

Franatech is a German based company that produces an advanced and diverse selection of underwater methane sensors relative to the other manufactures reviewed. In 1999, Franatech released the METS methane sensor which was touted as being the first commercially available sensor for observing dissolved methane in aqueous environments. Over the years, METS has under gone multiple revisions with several models being developed for specialized applications. The full range of METS sensors are: (1) Classic METS; (2)IR-METS; (3) W-METS; and (4) K-METS. The K-METS was discontinued several years ago. At the top of their methane sensor product line is the Laser Methane Sensor (Franatech 2018). All information is obtained from the manufacturer, Franatech.

3.1.1. Laser Methane Sensor

The Franatech Laser Methane Sensor (laser based sniffer), now in its 3rd generation, is the newest and most technologically advanced dissolved methane sensor that is commercially available for deep ocean applications. It is routinely utilized by several organizations and companies, including oil companies. For purchase, the unit costs $85,071 and rental is $10,775 per month. This is the most expensive and best performing dissolved methane sensor commercially available (Table 1).

Methane concentrations detectable by the Laser sensor range from 2 – 10,000 ppmv. Accuracy of the sensor is $\pm$2 ppmv at ranges less than 100 ppmv, and $\pm$2 % of reading above >100 ppmv. Franatech's laser methane sensor is contained in a 412 x 110 mm titanium housing that is depth rated to a maximum of 4000 meters (Figure 1). This sensor is also calibration and maintenance free, warms up in 60 – 120 seconds, and is initialized after 5 minutes in the water.

This dissolved methane sensor has the fastest reaction time of all the sensors reviewed (Reaction time is 5 seconds; T90 is 10 seconds; and T99 is 120 seconds). Power supply is between 11-30 VDC, which is within the same power range as all the other sensors reviewed. The 3rd generation, when equipped with its own pump (SBE5M), has a power consumption of 7 W. There are two bulkhead connectors on one end of the pressure housing; (1) eight-pin connector to power the sensor, and (2) a two-pin connector to drive the mechanical pump (Figure 2).

Mobile platform applications are well suited for this sensor due to its compact size and fast accurate sample rate (T90= 10s). The 3rd generation is smaller than previous generations and has been successfully deployed on a various AUV an ROV systems including a Teledyne Slocum glider, OUTLAND 2000 AUV, and a bottom lander (Figure 3).

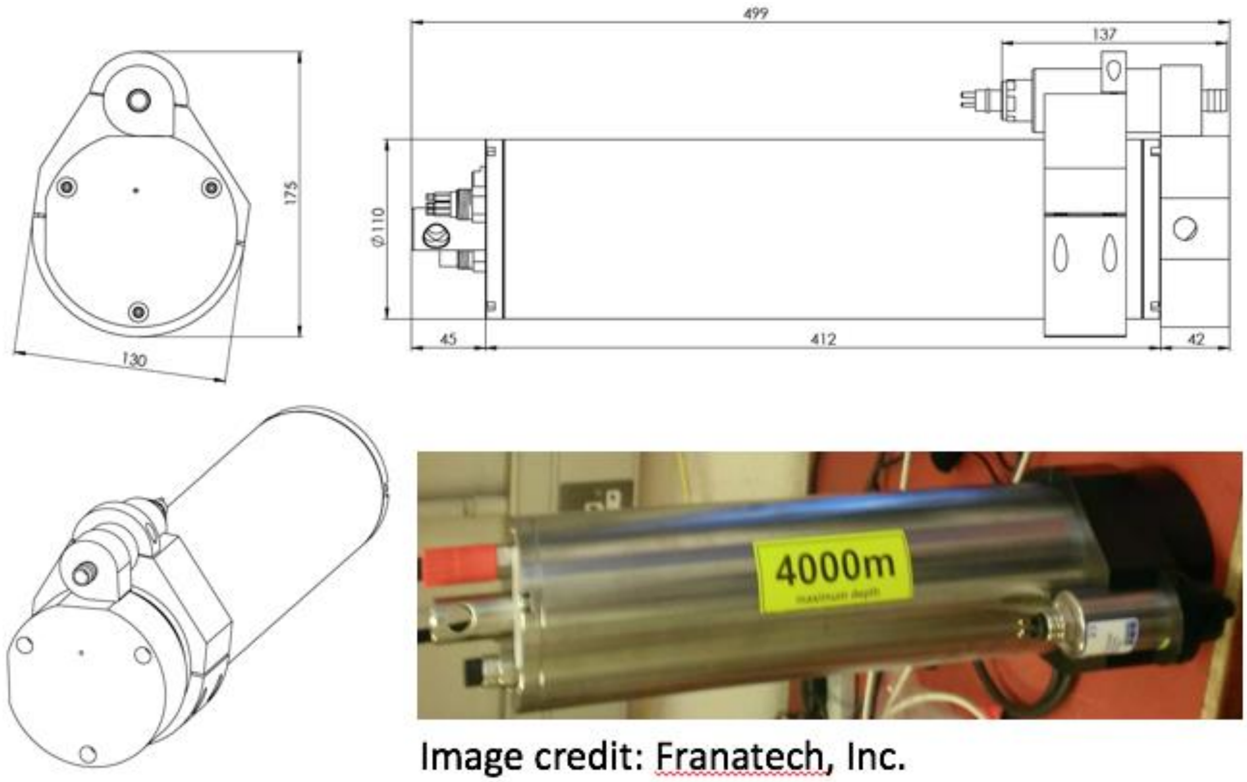


Figure 1: Franatech 3rd generation Laser Methane Sensor dimensions.

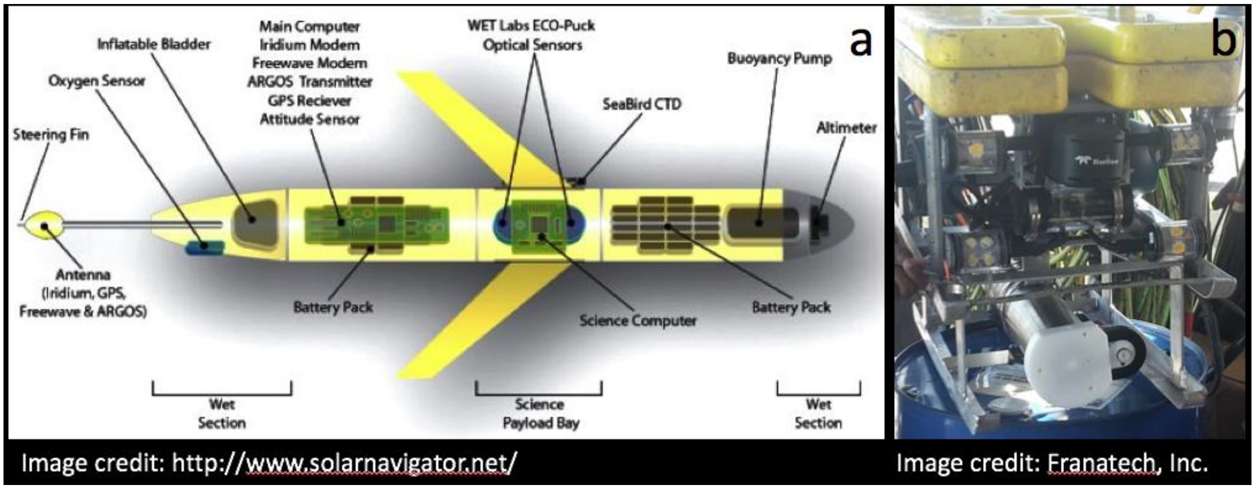
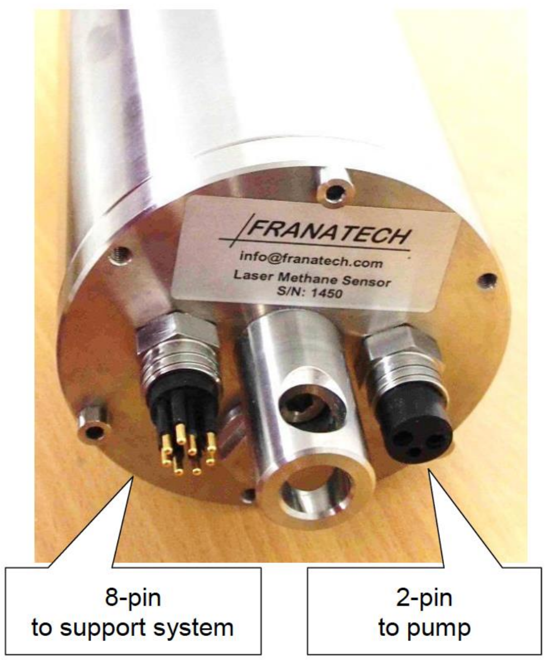


Figure 2: (a) Teledyne Slocum Glider; (b) OUTLAND 2000 AUV.



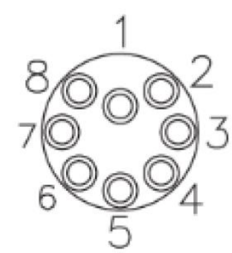
Pin #	Configuration	Description
1	+11..30 V DC	 Male Face View
2	GND	
3	NC	
4	NC	
5	NC	
6	RS232 GND	
7	RS232 RX	
8	RS232 TX	
1	GND	 Female Face View
2	+12 V DC	

Figure 3: Connector pin-out for the Franatech Laser Methane Sensor.

3.1.2. METS

The Franatech METS methane sensor is available in several different models (Table 1). Instead of using a laser to detect dissolved methane concentrations, the METS uses a silicone tin oxide membrane and a semiconductor in the detection chamber. The Classic METS has an oxygen correction for its data output. All versions of the METS sensor are available in two pressure housing; titanium (3500m depth rating), and stainless steel (2000m depth rating). Over the Laser sensor, the METS is much more affordable at $11,115 per unit. That is $340 less than the monthly rental fee for the Laser Methane Sensor.

The METS sensor has a T90 ranging between 1-30 minutes. The T90 is dependent upon the version of sensor and the deployment conditions. Required power supply is 9-36 VDC, which is within the same power supply range as all the sensors reviewed. The connector pin-out for the METS sensor is a single 8-pin wet matable plug (Figure 4).

Calibration of the METS sensor is accomplished using the manufacturers universal calibration formula format that comes standard. Special formats compatible with different CTD manufacturers can be requested. Because environmental temperature ranges influence the diffusivity of methane gas across the sensors gas permeable membrane, temperature needs to be accounted for in the calibration. Typical temperature range for the METS sensor is 2-20°C, and optional 10-30°C. Temperature ranges different from these can be specially requested.

The Classic, IR, and W METS are the same dimensions (Housing 163mm x 49mm; with connectors 200mm x 49mm), while the K-METS, which is discontinued, has a longer pressure housing (Housing 313mm x 49mm; with connectors 350mm x 49mm) (Table 1).

3.1.3. Classic METS

The Classic METS is the platform from which the other METS models are built upon (Figure 5). The sensor has been updated through several revisions since its introduction in 1999. Similar to the Laser Methane Sensor, the Classic METS is useful in high resolution applications and is suitable for mobile platforms including ROVs, AUVs, and Gliders.

Several standard detection ranges are optional (50 nM/L – 10 μM/L), sensitive (10 nM/L – 1 μM/L; operated in flow through mode), and high range (1-100 μM/L). Two temperature ranges are offered to help optimize detection accuracy and power consumption (Table 1). Made to order customized concentration and temperature ranges to meet special needs of the user are also possible.

Applications of the Classic METS are wide ranging. The sensor is regularly purchased by Kongsberg Maritime as a part of the HUGIN AUVs routine payload. ENI Oil Company routinely uses the sensor on the Saab Seaeye Sabertooth AUV for routine offshore work on pipelines and seeps surveys. In one of its applications, ENI operated the Classic METS for 270 near consecutive days to inspect ~650km of pipelines, and were able to successfully detect leaks for immediate repair (Figure 6).

3.1.4. IR-METS

The IR-METS is still in production but uses a slower sampling older METS platform. Depending on the options selected, concentration ranges are from ~10 up to saturation (Table 1). It was made as a more cost effective sensor for long-term fix point sampling applications (e.g. long-term monitoring of leachate water).

3.1.5. W-METS

The W-METS was developed for use in supersaturated aqueous environments. The detection range is 2 – 150 mM/L. Applications include methane hydrate synthesis, offshore deep-well monitoring, and in one case, work in Lake Kivu in Africa.

3.1.6. K-METS

This version of the METS methane sensor was developed for mobile platform applications and has been discontinued for several years. Despite no longer being in production, used sensors may potentially be available. The K-METS is specifically designed for water column profiling, ROVs, and AUVs (100 nM/L – 10 µM/L, or 2 – 150 mM/L) (Table 1). The overall length of the K-METS is longer than the Classic METS sensors (Figure 7).

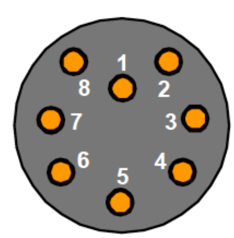
pin #	configuration	description
1	positive supply 9 – 36 VDC	
2	GND	
3	signal methane 0-5 V	
4	NC	
5	signal temperature 0-5V	
6	GND	**male face view**
7	TxD(RS232)	
8	RxD(RS232)	

Figure 4: METS sensor connector pin-out.

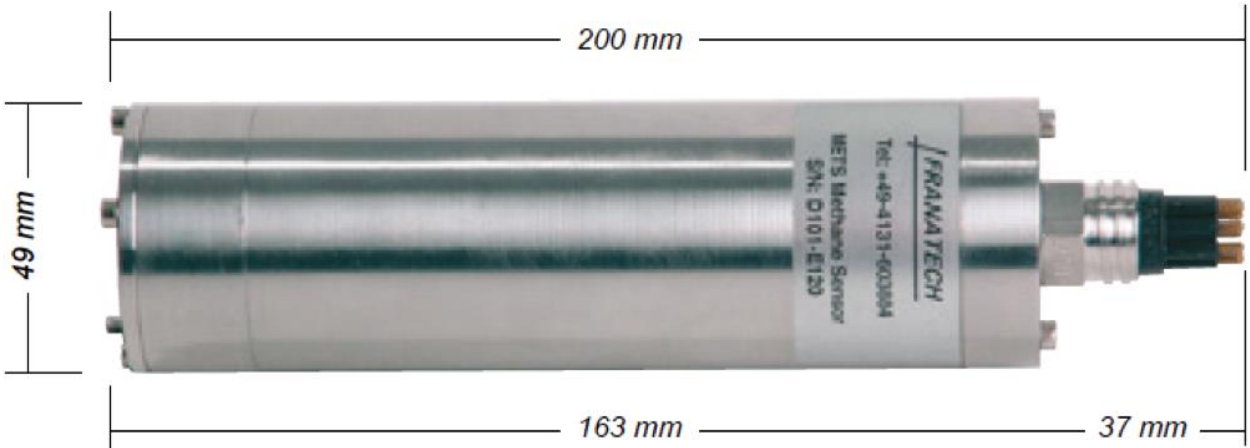


Image credit: Franatech, Inc.

Figure 5: Classic, IR, and W METS.

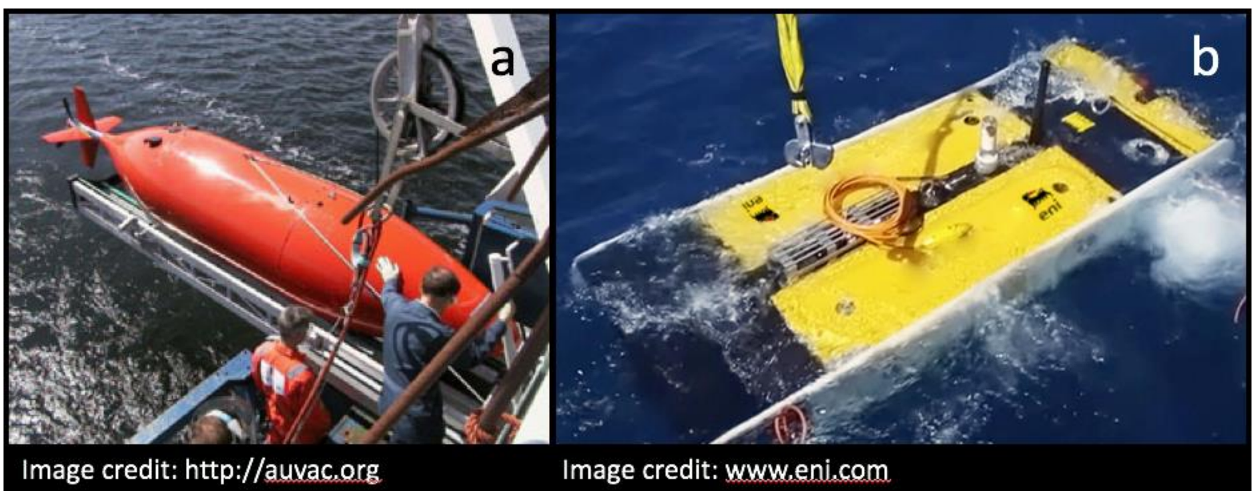


Figure 6: (a) Kongsberg HUGIN AUVAC; (b) Saab Seaeye Sabertooth AUV.

Image credit: Franatech, Inc.

Figure 7: K-METS (discontinued).

3.2. Pro-Oceanus

3.2.1. Mini CH4

Manufactured by Pro-Oceanus is the Mini CH_4 methane gas sensor. This is the only sensor offered by the Nova Scotia based company for detection of dissolved methane gas in aqueous environments (Figure 8). The Mini CH4 was designed for long-term deployments of continuous in-situ data collection on dissolved methane concentrations. Unique to this sensor over the other sensors reviewed are the two optional pressure housings (acetal plastic and titanium) which drastically affect cost. Whether the sensor is digital or analog also affects price. The acetal plastic housing is rated to 600m and costs $7,600 for digital, and $6,400 for analog. Titanium pressure housings are rated to 4000m and costs $12,700 for digital, and $12,000 for analog (Table 1). All information is obtained from the manufacturer, Pro-Oceanus.

The Mini CH4 operates through diffusion of dissolved gases from water through a supported oil resistant semi-permeable silicone membrane. After crossing the membrane, dissolved gases enter the gas headspace where concentrations are measured using a nondispersive infrared detector (NDIR). Over the delicate semi-permeable membrane, a copper mesh hovers to prevent biofouling of the gas exchange surface. The membrane and copper antifouling shield are replaceable. For pumped flow through, a cap fits with two ports, one for inflow, and the other for outflow (Figure 9). Optional pumps are SBE 5P pump at 2000 RPM and the SBE 5T pump at 3000 RPM. The pumped head flow rates should not exceed 3 L/min.

Customized Mini CH_4 units that are uniquely designed and/or modified are available for order from Pro-Oceanus. Modifications can include larger battery pack capacity, variable concentration ranges, changes to the logging program, pressure housing material, thickness of the membrane, bulkhead connector design, and more as cited by Pro-Ocean. Standard is an Impulse MCBH-4-pin wet-mateable bulkhead connector to power and communicate with the system. Internal logger/ controller is optional. The Mini CH4 as standard is offered in two outputs, 0-5V or 4-20mA, and can be either digital or analog.

3.2.2. Analog Mini CH4

The analog version of the Mini CH4 has a single 4-pin male impulse connector at the end of its bulkhead (MCBH(WB)-4-MP-SS): (1) Ground; (2) Signal+ Out TDGP; (3) Signal+ Out pCH4; (4) V+ In (Figure 10). Total Dissolved Gas Pressure (TDGP) is measurable with this sensor and can be recorded simultaneously with CH4. The dependence of the gas pressure within the NDIR chamber is vital for accurate readings of CH4. TDGP muse be known to determine the ratio of gas molecules being measured versus the total number of molecules. The analog version of the Mini CH4 sensor does not make this correction internally. Therefore, correcting CH4 concentration signal for deviations in the TDGP is accomplished using the TDGP measured from the sensor. TDGP can in this case be used to correct the raw CH4 output. Output in V or mA can be converted to a measured value using the factory supplied calibration curve fits for both

CH4 and TDGP. Analog Mini CH4 sensors are factory calibrated at 20 °C and an atmospheric pressure of 1000 mbar.

$$\frac{CH4\ raw}{TDGP} = \frac{xCH4\ corrected}{Pcal}$$

From the above equation, *CH4 raw* is the CH4 reading from the sensor and the *TDGP* is the pressure reading from the sensor while *xCH4* is the pressure corrected CH4 value in ppm. *Pcal* is the true pressure during calibration and is stated on the supplied data sheet with the sensor.

Calibration must be completed in house by Pro-Oceanus as the calibration procedure requires 4-6 calibration gas standards and a proprietary curve fit function. To ensure the best accuracy, multiple calibrations are made. Recalibration of the instrument is recommended every 12-18. Over the course of a year, sensor drift is normally less than 3% of the maximum measuring range.

3.2.3. Digital Mini CH4

A digital version is offered for real-time data acquisition, programmable sampling intervals, and includes internal logging to a Micro-SD memory card. Internal battery packs in the digital version make the instrument fully autonomous. The optional internal battery housing provides 4.8 am-hour at 6 VDC using one battery pack and a charger. This autonomous battery power option adds an additional $800 cost to the instrument. The visible difference between the battery and non-battery powered digital Mini CH4 is that the battery version has two bulkhead connectors, and a longer pressure housing (Figure 11). The 4-pin male impulse bulkhead connector is identical to the analog model (MCBH(WB)-4-MP-SS: (1) Ground; (2) Signal+ Out TDGP; (3) Signal+ Out pCH4; (4) V+ In). The second female connector is the on/off switch for the battery which is operated by shorted and non-shorted dummy plugs. While the instrument is designed to utilize either an external power supply of 5-30 VDC, or internal battery power. It is important to note that the Mini CH4 digital methane sensor is not designed to use both at the same time.

The digital Mini CH4 unit can be programed to operate in (1) continuous mode, (2) timed mode, or (3) command mode. Continuous mode requires that the Mini CH4 be connected to an external computer operating on a windows platform. Timed mode is used when the logger is configured for autonomous operation. Command mode is the same as timed mode with the exception that the user has control over the timing of the sample in command mode. It is important to note that a sample takes at minimum 4 minutes to complete from warm-up through to final equilibration of the instrument.

Figure 8: Pro-Oceanus Mini CH4 Methane Sensor in acetal plastic housing (600m).

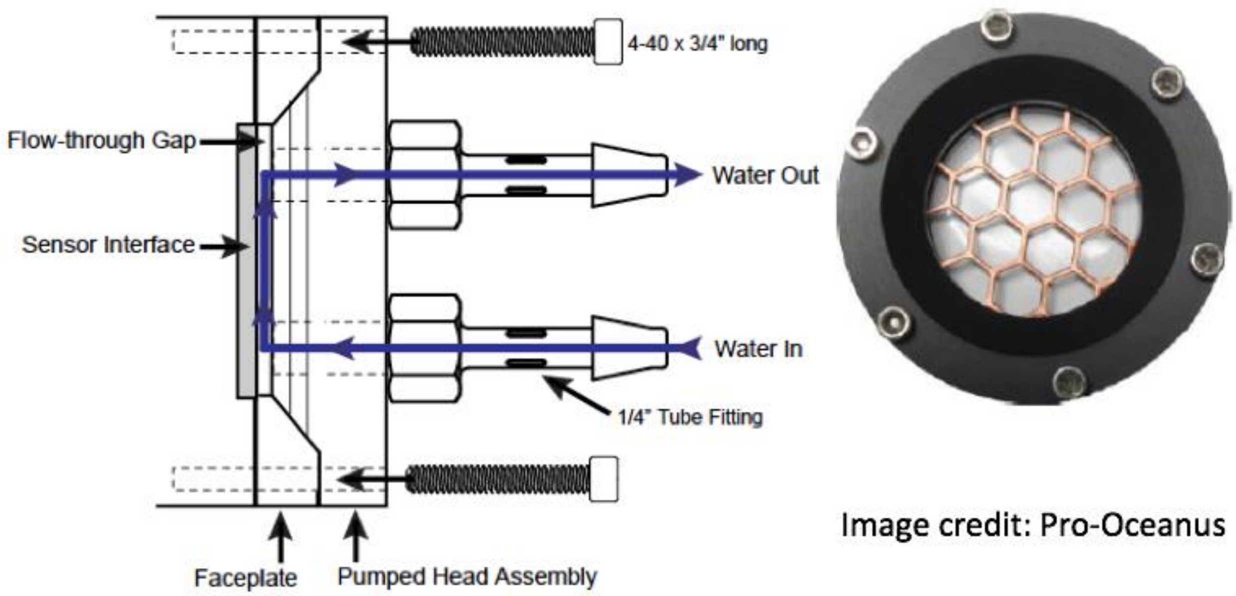


Figure 9: Pro-Oceanus flow through pump head (left), and antifouling shield over the sensors membrane (right).

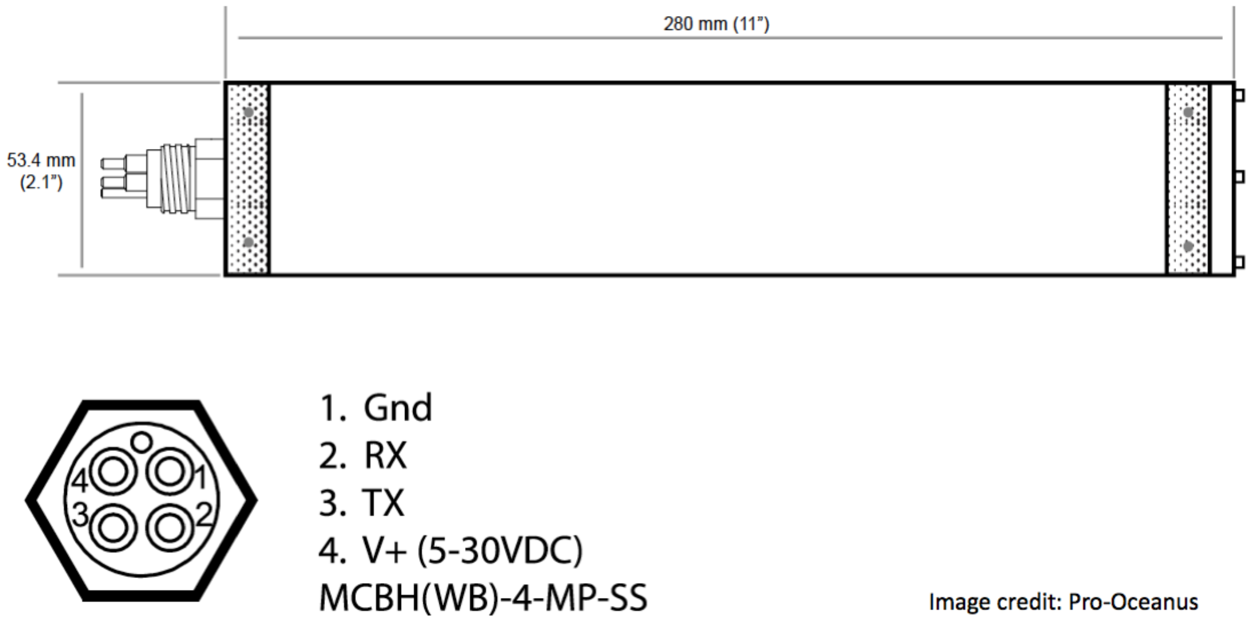


Figure 10: Pro-Oceanus standard pressure housing and bulkhead connector for the analog and non-battery powered digital Mini CH4 Methane Sensor.

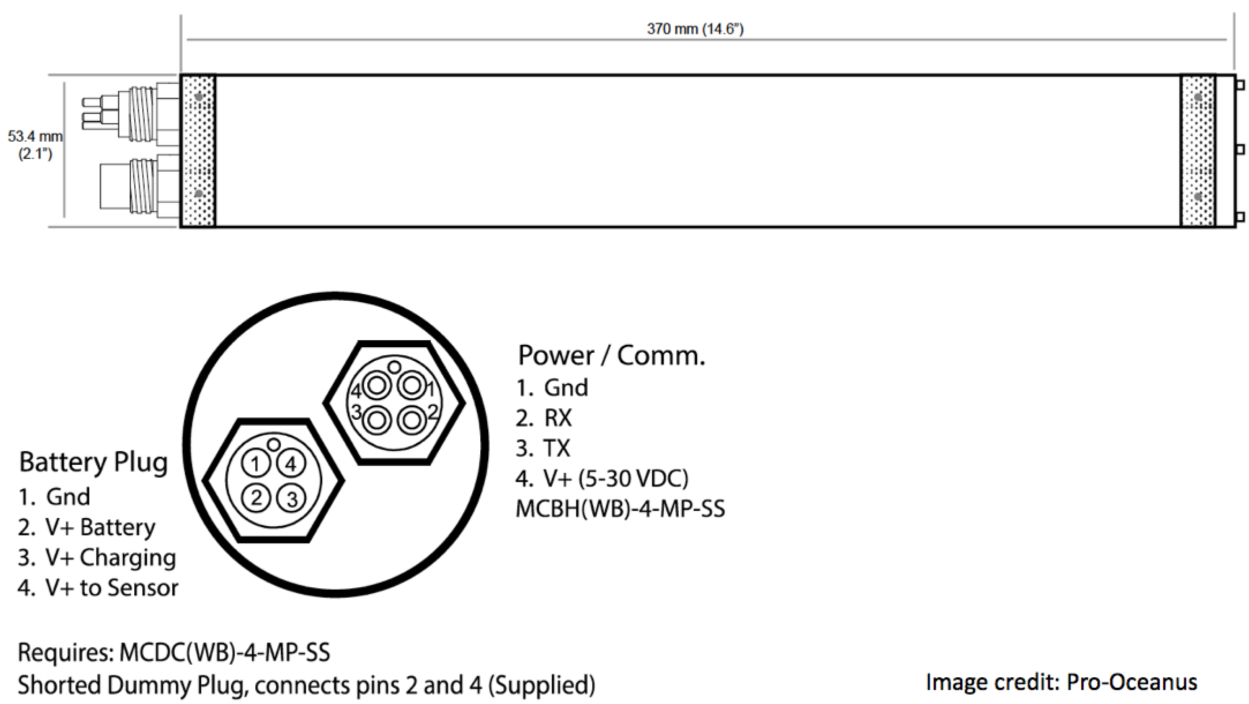


Figure 11: Pro-Oceanus extended pressure housing for the autonomous digital Mini CH4 sensor with an additional on/off plug for the battery.

3.3. Kongsberg/Hydroid

Kongsberg Underwater Technology, Inc. is international company based in Germany which offers their CONTROS product line in the United States. Presently, they are one team with Hydroid. The CONTROS HydroC CH4 and MELDS are the two sensors the company offers for observing dissolved methane in aqueous environments (Table 1). The MELDS leak detection system integrates with a CH4 sensor and other sensors into a single package. All information is obtained from the manufacturer, Kongsberg/Hydroid.

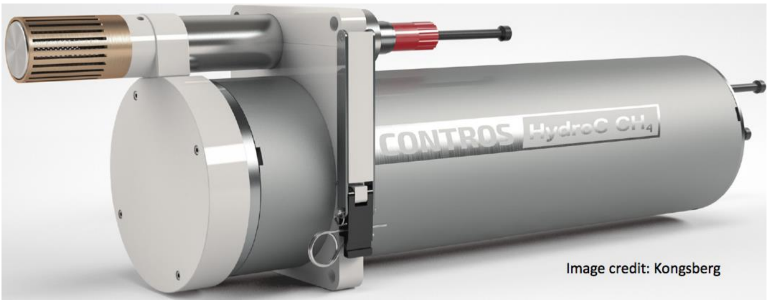
3.3.1 CONTROS HydroC CH4

The CONTROS HydroC CH4 is a top of the line sensor, and is the second most expensive sensor reviewed in this document at $42,000 per unit (Figure 12). This sensor uses a non-consuming semi-permeable thin film membrane through which dissolved gasses pass over into an internal gas circuit leading to the detection chamber where a tunable diode laser absorption sensor (TDLAS) is contained. Concentration depended laser light intensities are then converted into an output signal. The conversion to the output signal is accomplished by applying calibration coefficients stored in the instruments firmware, and data from additional sensors in the gas circuit.

This sensor features high accuracy and low detection limit of background concentration with a measuring range of 0.6 – 40,000 matm. The accuracy of the sensor is $\pm$2 µatm or $\pm$3 %, whichever is greater. The sensor has a maximum temperature range of -2 – 30 °C. The sensor has optimal long-term stability, and because of the narrow line-width the TDLAS is highly accurate and ideal for methane selectivity. This selectivity means that the sensor measures methane and no other hydrocarbons. Methane measurements are non-consuming. Using a titanium pressure housing the sensor is depth rated up to 3000m (Table 1).

Kongsberg calibrates each sensor individually and the calibration quality is assessed in calibration tanks. Because the sensors detector tunes the TDLAS to CH4 absorbing and non-absorbing wavelengths for each measurement, potential drifts are compensated for providing long term stability in readings. Due to the technology utilized, the sensor has high accuracy, low detection limit of background concentration, a large measurement range, and ideal methane selectivity that is non-consuming of CH4. When combined with the CONTROS DETECT software data visualization, parameter settings, data download, and sleep mode functions can be accessed in real-time.

This sensor is suitable for mobile platforms such as AUVs and ROVs, as well as profiling and fix or mooring applications. For REMUS, the sensor has not yet been integrated to the platform. The manufacturer suggests that the sensor could be integrated to a REMUS 600 and certainly the 6000. The REMUS 100 is too small to incorporate the sensors payload size.



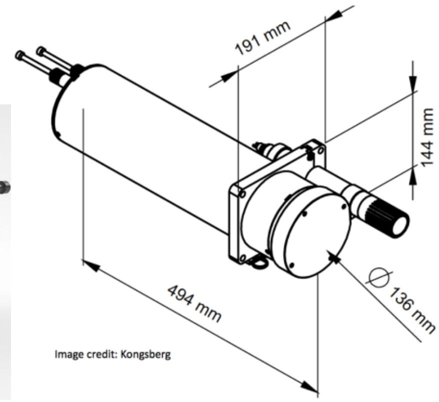


Figure 12: Kongsberg/Hydroid CONTROS HydroC CH4 Methane Sensor.

3.3.2. CONTROS MELDS

The Mobile Early Leak Detection System (MELDS) is a CH4 sensor combined with other CONTROS sensors such as the CONTROS CO2 sensor, Polycyclic Aromatic Hydrocarbon (PAH) sensor, and Conductivity, Temperature and Depth (CTD) sensor (Figure 13). MELDS was designed with easy ROV/AUV integration in mind. The system is modular with the ability to pair with 3rd party sensors measuring C02, O2, Redox, pH, etc. The purpose of the sensor is to detect hydrocarbon leaks in oil and gas industry that are not yet visible and are very early stage. The system has an integrated flow through system with a power pump to allow for vehicle manipulator directed measurements such as wipe tests on flanges for example.

MELDS is able to be paired with their DETECT software suite for graphical data visualization of raw or auto-processed data. This software is able to provide graphical display and interface to ROV operators. It supports standard oceanographic sensors to fully cover detection of any anomalies. Leak detection can also be automated using this same software.

Figure 13: Kongsberg/Hydroid CONTROS MELDS sensor suite.

Table 1: Data chart detailing all commercially available dissolved methane sensors.

Name	Brand	Production	Application	Platform	Cost	Measurement /environment	Membrane	Detector	Depth Rating	Concentration range	T 90	Operating Temperature	Power Supply	Power Consumption	Housing Material	Weight	Dimensions
Laser	Franatech (GER)	3rd Generation	Sniffer High resolution	Mobile Gilders AUV/ROV Profiling/Mooring	75,000 EUR 85,071 USD **Rent per Month** 9,500 EUR 10,775 USD	Gas Phase/ water column	silicone	laser	4000 m	2 - 10,000 ppmv **(Accuracy)** +2 ppmv (<100 ppmv) or +2 % of reading	10 s	-2 to 30 degC	11 - 30 VDC	7W with own pump (SBE5M)	Titanium (ti)	**Air** 14 kg **Fresh Water** 8 kg	L x D (mm) 412 x 110
Classic METS	Franatech (GER)	Latest Generation	high resolution	Mobile Gliders AUV/ROV Profiling/Mooring	9,800 EUR 11,115 USD	Gas Phase/ water column	Silicone & tin oxide	semiconductor	3500 m (ti) 2000 m (ss)	**(standard)** 50 nanomol/l - 10 micromo/l **(sensitive)** 10 nanomol/l - 1 micromol/l **(high range)** 1 - 100 micromol/l	1 - 30 min (depending on version and deployment conditions)	**(standard)** -2 - 20 degC **(optional)** 10 - 30 degC	9 - 36 VDC	40 to 120 mA @ 12 VDC	Titanium (ti) or Stainless Steel (ss)	**Titanium** 0.8 kg (in air) 0.5 kg (in water) **Stainless Steel** 1.3 kg (in air)	L x D (mm) 163 x 49
IR-METS	Franatech (GER)	Still in production	Fix or profiling (slower sample rate)	Profiling/Mooring	unknown	Gas Phase/ water column	Silicone & tin oxide	semiconductor	3500 m (ti) 2000 m (ss)	**(standard)** 100 micromol/l - 2 millimol/l (w/ SBE-5M pump) 10 micromol/l - 2 millimol/l	1 - 30 min (depending on version and deployment conditions)	**(standard)** 2 - 20 degC **(optional)** 10 - 30 degC	9 - 36 VDC	40 to 120 mA @ 12 VDC	Titanium (ti) or Stainless Steel (ss)	**Titanium** 0.8 kg (in air) 0.5 kg (in water) **Stainless Steel** 1.3 kg (in air)	L x D (mm) 163 x 49
W-METS	Franatech (GER)	Special Design	High resolution Super saturated waters	Profiling/Mooring	unknown	Gas Phase/ water column	Silicone & tin oxide	semiconductor	3500 m (ti) 2000 m (ss)	2 -150 millimol/l	1 - 30 min (depending on version and deployment conditions)	**(standard)** 2 - 20 degC **(optional)** 10 - 30 degC	9 - 36 VDC	40 to 120 mA @ 12 VDC	Titanium (ti) or Stainless Steel (ss)	**Titanium** 0.8 kg (in air) 0.5 kg (in water) **Stainless Steel** 1.3 kg (in air)	L x D (mm) 163 x 49
K-METS	Franatech (GER)	Discontinued for ~3 years	High resolution	Mobile AUV/ROV/DSV Profiling/Mooring	unknown	Gas Phase/ water column	Silicone & tin oxide	semiconductor	3500 m (ti) 2000 m (ss)	**(standard)** 100 nanomol/l - 10 micromol/l **(optional)** 2 - 50 millimol/l	1 - 30 min (depending on version and deployment conditions)	**(standard)** 2 - 20 degC **(optional)** 10 - 30 degC	9 - 36 VDC	40 to 120 mA @ 12 VDC	Titanium (ti) or Stainless Steel (ss)	**Titanium** 1.4 kg (in air) **Stainless Steel** 2.2 kg (in air)	L x D (mm) 313 x 49
Mini CH4 (analog)	Pro-Oceanus (USA)	In production (generation unknown)	Longterm deployments	Profiling/Mooring	**Titanium Analog** 12,000 USD **Acetal Analog** 6,400 USD	Gas Phase/ water column	silicone	Nondispersive infrared detectior (NDIR)	**Acetal Plastic** 600 m **Titanium** 4000 m	**Standard Range** 0 - 2000 ppm pCH4 **Optional Ranges** 0 - 1000 ppm 0 - 4000 ppm 0 - 1 % (0 - 10,000 ppm) 0 - 10 % 0 - 100 %	8 min (with water pumped head)	-2 to 40 degC	12 - 24 VDC	55 mA @ 12 VDC	Acetal Plastic (ap) or Titanium (ti)	**Air** 0.53 kg **Water** -0.06 kg	L x D (mm) 494 x 191
Mini CH4 (digital)	Pro-Oceanus (USA)	In production (generation unknown)	Longterm deployments	Profiling/Mooring	**Titanium Digital** 12,700 USD **Acetal Digital** 7,600 USD	Gas Phase/ water column	Silicone	Nondispersive infrared detector (NDIR)	**Acetal Plastic** 600 m **Titanium** 4000 m	0 - 300 microgram/l (0 -1 % pCH_4) 0 - 3 milligram/l (0 - 10 % pCH4) 0 - 30 milligram/l (0 - 100 % pCH4) TDGP (0 - 2000 mbar)	8 min (with water pumped head)	-2 -to +30 degC -2 to +20 degC -2 to +8 degC	5 - 30 VDC	0.45 W (35 mA @ 12 VDC) 30 microAmp Sleep Current	Acetal Plastic (ap) or Titanium (ti)	**Air** 0.53 kg **Water** -0.06 kg	L x D (mm) 494 x 191
CONTROS HydroC CH4	Kongsberg/ Hydroid (GER/USA)	In production (generation unknown)	High resolution	Mobile AUV/ROV Profiling/Mooring	42,000 USD	Gas Phase/ water column	non-consuming thin film	Tunable Diode Laser Absorption (TDLAS)	3000 m	0.6 - 40,000 microatm **(Accuracy)** ±2 microatm or ±3 % (whichever is greater)	unknown	-2 to +30 degC -2 to +20 degC -2 to +8 degC	12 - 30 V	690 mA @ 12 V and additonal 8 W with SBE-5T external pump	Titanium (ti)	**Air** 12.5 kg **Water** 5.5 kg	L x D (mm) 494 x 136 (w/o connector) 528 x 136 (with connector
CONTROS MELDS	Kongsberg/ Hydroid (GER/USA)	In production (generation unknown)	high resolution Leak detection Sensor integration	Mobile AUV/ROV Profiling/Mooring	unknown	Gas Phase/ water column plus CTD	non-consuming thin film	Tunable Diode Laser Absorption (TDLAS)	3000 m	CH4: 0.01 - 50 micromol/l PAH: 0 - 500 micrograms/l Cond: 0 - 60 mS/cm ± 0.001 mS/cm Press: 0 - 4000 dbar ± 1dbar Temp: -4 to +40 degC ± 0.1 degC	unknown	-2 to + 40 degC (arctic and other ranges avaliable)	12 - 24 VDC	18 W @ 12 VDC (max. 36 W on start-up)	Titanium (ti)	**Air** 12.3 kg **Sea Water** 9.2 kg	L x D x H (mm) 520 x 170 x 200

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Works Cited

Benounis, M., N. Jaffrenzie-Renault, J. P. Dutasta, K. Cherif, and A. Abdelghani. 2005. Study of a new evanescent wave optical fibre sensor for methane detection based on crytophane molecules. Proceedings of the 7th European Conference on Optical Chemical Sensors and Biosensor – EUROPT(R)ODE VII **107**: 32.

Benounis, M., T. Aka-Ngnui, N. Jaffrezie, and J. P. Dutasta. 2008. NIR and optical fibre sensor for gases detection produced by transformation oil degradation. Sens. Actuators A **141**: 76-83.

Boulart, C., D. P Connelly, M. C. Mowlem. 2010. Sensors and technologies for in situ dissolved methane measurements and their evaluation using Technology Readiness Levels. Trends in Analytical Chemistry **29**: 186-195.

CONTROS HydroC CH4 Methane Sensor (**Kongsberg/Hydroid, United States/Germany**).

CONTROS MELDS, Mobile Early Leak Detection System (**Kongsberg/Hydroid, United States/Germany**).

Laser Methane Sensor (**Franatech, Lüneburg, Germany**).

METS (Classic, IR, W, and K) Methane Sensor (**Franatech, Lüneburg, Germany**).

Mini CH4 Methane Sensor (**Pro-Oceanus, Nova Scotia, Canada**).

Sauter, E. J., S. I. Muyakshin, J. Charlou, M. Schluter, A. Boetius, K. Jerosch, E. Damm, J. Foucher, and M. Klages. 2006. Methane discharge from a deep-sea submarine mud volcano into the upper water column by gas hydrate-coated methane bubbles. Earth and Planetary Science Letters **243**: 354-365.

Wynn, R. B., V. A. Huvenne, T. P. Le Bas, B. J. Murton, D. P. Connelly, B. J Bett, H. A. Ruhl, K. J. Morris, J. Peakall, D. R. Parsons, E. J. Smner, S. E. Darby, R. M. Dorrell, and J. E. Hunt. 2014. Marine Geology **352**: 451-468.