

Sensors and technologies for in situ dissolved methane measurements and their evaluation using Technology Readiness Levels

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Dissolved methane measurements rely on the time-consuming collection of discrete water samples followed by gas-chromatography analysis. To date, this approach has proved useful for broad interpretation of environmental processes. However, it limits comprehension of environmental processes that are highly variable in space and or time. This has led to increased interest in in situ dissolved methane sensors to augment data from point sampling.

So far, three sensing strategies have been explored using:

- 1) gas-phase measurements after gas extraction through semi-permeable silicon membranes;
- 2) measurements using biosensors; and,
- 3) optical measurements (e.g., surface-plasmon resonance and surface-enhanced Raman spectroscopy).

Optical measurements may represent the future for in situ dissolved methane sensing.

We review and evaluate different in situ methane sensors and technologies using Technology Readiness Levels.

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Keywords: Aquatic environment; Dissolved methane; Gas measurement; Gas-permeable membrane; In situ sensor; Optical measurement; Sensor; Surface-enhanced Raman spectroscopy; Surface-plasmon resonance; Technology Readiness Level

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1. Introduction

Since atmospheric methane is thought to contribute up to 20% of the greenhouse-gas effect [1], accurate determination of dissolved methane (CH_4) concentrations is vital for the study of methane dynamics in a variety of natural aqueous environments.

CH_4 emissions from aquatic ecosystems (e.g., lakes, rivers, deep oceanic waters and surface seawaters) cannot currently be measured continuously over long time periods and large spatial scales. This limits considerably the estimation of aquatic ecosystem contributions to the global budget of CH_4 . As Reeburgh [2] stated: "measurements of dissolved methane lagged [historically] those in the atmosphere because of the need to separate the dissolved methane from the aqueous phase".

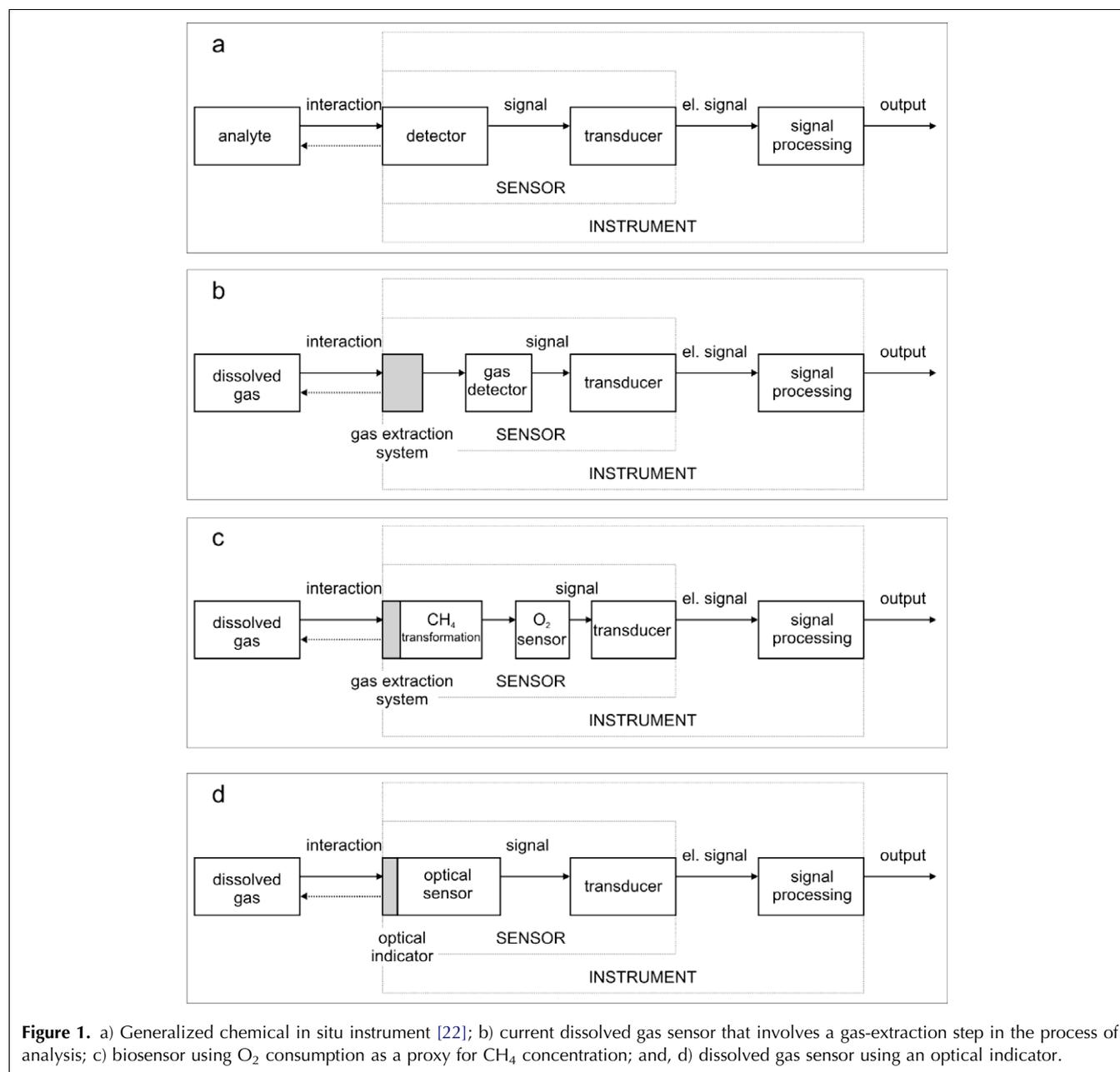
Dissolved CH_4 measurements, as is the case with most dissolved gases, are usually

performed by collecting discrete water samples into glass bottles followed by a gas-extraction step (i.e. headspace or purge-and-trap) and gas chromatographic (GC) analysis. Both headspace and purge-and-trap extraction techniques are efficient, but it may take up to a few hours to extract all the gas from the dissolved phase [3–5].

Since the mid-1980s, in situ chemical sensing (Fig. 1a) has been proposed for the integrated study of biogeochemical processes and cycles in aquatic environments as a complement to conventional analytical approaches [6]. A methane sensor, in this case, would be a valuable tool to locate and to monitor point sources in highly dynamic environments (e.g., hydrothermal vents along mid-ocean ridges and cold seeps along continental margins, [7–9]) and to assess their role in the global methane cycle. This technology would also be a useful tool for monitoring

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the release of methane from large methane-rich basins (e.g., estuaries and lakes) over long periods of time [10,11].

A sensor must be applicable to the environment in which it is used: a sensor developed for methane-rich systems [e.g., estuarine environment (typically 100 nM–1 μ M)] will not need to be adapted to low-concentration measurements, whereas, in deep oceanic environments, the requirement may be that a sensor should detect dissolved CH_4 with a limit of detection (LOD) of <5 nM, show a fast response (seconds) and have a resolution better than 1 nM [2].

To date, a limited number of techniques have been developed for dissolved gases following three general approaches:

- 1) extraction of the dissolved methane into the gas phase prior to transduction;
- 2) biosensing using methane-oxidizing bacteria; and,
- 3) partitioning of the gas into an indicator layer (Fig. 1).

The first approach (Fig. 1b) is to develop an in situ gas-extraction system with subsequent detection and transduction of methane gas. This can be achieved using flame-ionization detection (FID) [12], photoacoustic detectors [13], metal-oxide semiconductors [14], infrared (IR) spectroscopy (e.g., Contros GmbH, [15]), or mass spectrometry (MS) [16]. The most commonly used gas-extraction system is a silicone membrane characterized by hydrophobic properties and high permeability

Table 1. In-situ dissolved methane-sensing technologies (current and under investigation). TRL, Technology Readiness Levels. Note that the column “Measurements/environments” takes into account both the phase in which the gas is measured and the type of environment for which the sensor is designed. Usually, “water column” environments are considered low-methane systems (typically <10 nM) and “sediments, pore water” as high-methane systems (typically 10 μM–1 mM). However, in “water column” environments, the concentrations can be highly variable depending on the vicinity of the methane sources

Sensor	Measurement/environments	Technology	Membrane/Sensitive layer	Concentration range	Limit of detection	T 90	T°C	Depth range	Power supply	Manufacturer/Research Institute/Reference	TRL
METS–CAPSUM	Gas phase/water column	SnO ₂ semi-conductors	Silicon rubber (5–100 μm)	10 nM–150 mM	10 nM	1–30 min	2–40°C	0–3500 m	35–100 mA at 12 V	Capsun GmbH/Franatech GmbH [26]	TRL 7
HydroC/CH ₄	Gas phase/water column	Direct IR absorption spectroscopy (3.4 μm)	Modified silicon rubber (2–100 μm)	30 nM–500 μM	<10 ppm (<6 nM)	17–30 s	0–50°C	0–6000 m	250 mA at 12 V	Contros GmbH http://www.contros.eu	TRL 7
Deep-sea methane sensor	Gas phase/water column	Laser absorption spectroscopy (3.3 μm)	Silicon-membrane tubes	40–320 ppm (25–200 nM)	40 ppm (25 nM)			0–2000 m		Hokkaido University (Japan) [15]	TRL 6/7
Deep-sea gas analyzer*	Gas phase/water column	NIR-off-axis integrated-cavity output spectroscopy	Silicon rubber			less than 1 min	0–45°C	0–2000 m	Internal battery	Iginc (USA) [33]	TRL 6/7*
Equilibrator	Gas phase/surface water	Photoacoustic spectroscopy	Glass marbles in tube	up to 400 μM	20 μM	12 min at 7 m depth**					TRL 6
In situ mass spectrometer	Gas phase/water column	In situ mass spectrometer	Semi-permeable membrane inlet	no data	Sub-ppm (<1 nM)			0–30 m (200 m possible)	20 W	WHOI (USA) [36]	TRL 8
In situ mass spectrometer	Gas phase/water column	In situ mass spectrometer	PDMS membrane inlet	no data	1–5 ppb (<1 nM)			0–30 m (200 m possible)	20 W	University of South Florida (USA) [35]	TRL 8
Biosensor	Dissolved phase/sediments, pore water	Amperometry	Silicon membrane	up to 350 μM	5 μM			surface		University of Aarhus (Denmark) [19]	TRL 5/6
Biosensor	Dissolved phase/sediments, pore water	Dissolved oxygen sensor	“bacterial beads”	0.4–2 mM	100 μM	100 s		surface		[44]	TRL 5/6
FEWS	Dissolved phase/water column	Evanescent wave spectroscopy	Optical fiber/sensitive layer					Possibly up to 6000 m		[50]	TRL 2/3
SERS	Dissolved phase/water column	Surface-enhanced Raman scattering	Silver-colloid SERS substrate		nM–μM			Possibly up to 6000 m		Technical University Berlin (Germany) [60]	TRL 4/5
SPR	Dissolved phase/water column	Surface-plasmon resonance	PDMS/crytophane-A	0–400 nM	0.2 nM	2–5 min	45°C	Surface	1 mW	[64] (Appendix 2)	TRL 4/5

* Note that for the dissolved gas analyzer, it is difficult to state the TRL as there are no real environmental trials. The suggested TRL is based on comparison with similar systems employing gas-permeable membranes.

** No indication is given whether or not the response time is the T 90.

to methane [17]. However, these membranes influence the performance of the whole sensor in terms of response time or LODs [18].

In the second approach (Fig. 1c), methane concentrations are measured indirectly by measuring oxygen (O_2) concentration, which is modulated by respiration of bacteria in a gel matrix in a biosensor [19]. To avoid the negative effects of gas-permeable membranes, current research is focusing on a third approach (Fig. 1d) using optical technologies and optical indicators to perform direct measurements. We describe these different approaches in more detail in the following sections.

The different analytical methods for detection and measurement of methane gas have been reviewed previously [20] as well as the technologies available for in situ chemical sensing [21]. The purpose, here, is to give an overview of, and to describe recent trends in, the sensors and the technologies available – or potentially available – for in situ dissolved CH_4 sensing in different types of environments. We will evaluate the systems and the technologies described in the following sections through the approach of Technology Readiness Levels (TRLs, Tables 1 and 2), used in space exploration and defense procurement [22], based on the performance of the instrument with regard to requirements of a particular application, reliability of data, and adaptation of the system to field conditions. The TRLs used are based on the available data (Table 2).

2. Measurements in the gas phase

2.1. Gas-permeable membranes

The techniques developed for air monitoring [20] cannot be applied directly for dissolved gases. As a result, they require a gas-extraction step, which is realized by semi-permeable materials that can cause artifacts in the measurement, as discussed below.

According to Pandey et al. [17], three types of permeable membranes exist – porous, non-porous and asymmetric. The last type is a combination of a thin, dense, non-porous membrane with a thick, porous

material that acts as a physical support for the thin layer. Hence, the gas-permeable membranes employed in the construction of the dissolved methane sensors described below can be considered asymmetric, as they are generally made of a solid substrate with open porosity and a continuous polymeric layer [17].

The mechanisms of gas transport through the different types of membranes were described in Pandey et al. [17]. Diffusion is a spontaneous process that is strongly influenced by polarity and chemical and physical characteristics of the polymeric layer and the permeate. As noted in Pandey et al. [17]: “virtually every environmental factor affects membrane structure and, hence, the permeability of the membranes”.

Temperature and pressure are probably the most important environmental variables, as they directly influence the physical state of the membranes. Material thicknesses and surface area can have a strong influence on the diffusivity of the membrane and the response of the sensor. It is obvious that the diffusion through a thick, dense layer will be slower than that through a short, thin membrane. In the context of sensors that consume methane as a function of their operation, a decrease in membrane diffusivity will result in a greater concentration differential across the membrane at equilibrium, thus reducing sensor sensitivity. Flow variations also cause variations in the measurement, as convective transport of the analyte alters the concentration of the analyte at the surface of the membrane [23]. In non-consumptive sensors, decreased diffusivity has no effect on the calibration on long time scales, but does reduce the temporal responsiveness of the sensor.

The common materials used for membranes are silicon rubbers [e.g., polydimethylsiloxane (PDMS), which exhibits both high permeability and low selectivity due to significant free volume [17] (i.e. the volume fraction that is not occupied by the molecules of the polymer)]. As with other silicone rubbers, temperature variations modify the free volume of the PDMS membrane (i.e. at low temperature, permeability can be reduced due to a decrease of the free volume) and influence the mobility and the solubility of the gas molecules in the silicone

Table 2. Technology Readiness Levels framework, modified from a UK Defence Procurement Agency version (http://www.ams.mod.uk/ams/content/docs/trl_guide/trlguide.pdf) [22]

Level	Description
TRL 1	Basic principles of technology observed and reported
TRL 2	Technology concept and/or application formulated
TRL 3	Analytical and laboratory studies to validate analytical predictions
TRL 4	Component and/or basic sub-system technology valid in laboratory environment
TRL 5	Component and/or basic sub-system technology valid in relevant environment
TRL 6	System/sub-system technology model or prototype demonstrated in relevant environment
TRL 7	System technology prototype demonstrated in an operational environment
TRL 8	System technology qualified through test and demonstration
TRL 9	System technology qualified through successful mission operations

membrane [24]; variations of pressure differential across the membrane result in variations in permeability of the membrane [24]. More details on permeability coefficients in silicone membranes are available [25].

To date, full characterization of membrane permeability and hydrodynamic flow effects has not been completed under variable conditions (i.e. switching between high flow and stagnant conditions). Bell et al. [18] have characterized a membrane-inlet system (with MS detection) in seawater from 0–2000 m depth but only at constant temperature and hydrodynamic conditions, so there is considerable uncertainty in measurements made with sensors using gas-extraction membranes as variations in membrane permeability are not fully quantified.

2.2. Commercial devices

The METS methane sensor [14] (Fig. 2a) was introduced in 1999, as the first sensor for methane monitoring and detection underwater, using a gas-permeable membrane with tin-oxide (SnO_2) semiconductor detection (Fig. 2b). It is quoted as being able to detect concentrations of methane in the range 50 nM–10 μM in its standard version, and up to 2 mM for some versions; at water depths down to –3500 m and temperatures of 2–40°C [26].

The METS sensor has been widely used for the detection of methane-rich plume signals in the water column overlying cold-seep environments or for long-term monitoring [27]. The system can detect changes of +10 nM, but because of the long diffusive path, the response is characterized by a significant hysteresis effect [27], which dramatically limits its deployment during CTD (conductivity, temperature, depth) hydrocasts, where a fast response is needed. The t_{90} (the time required for 90% change in the sensor signal), claimed by the manufacturer, varies from 1 min to 30 min,

depending on the configuration of the sensor (i.e. depending on the thickness of the membrane). Fukasawa et al. [28] shortened the t_{90} by reducing the volume of the detector chamber to about 22% of the standard sensor.

The major drawback in the METS sensor is the use of a SnO_2 semiconductor, which can respond to any kind of gas that can be oxidized [20]. In other words, all gases passing through the silicon membrane can be detected and interfere with the measurement. As a result, the selectivity of the semiconductor must be controlled by setting a temperature of 400°C, which is the temperature of methane oxidation by a SnO_2 semiconductor [29]. A good correction for the effects of varying temperature in the environment is then necessary to improve the resolution of the METS data, as noticed during deployments in the Lau Basin (Connelly, personal communication).

Though it has not been reported, it is likely that there is also flow sensitivity, as the sensing principle consumes analyte and a membrane inlet system is used. The combined effects of these performance characteristics will probably limit the widespread acceptance of this device for at least some scientific applications. Though this device is reliable, performance difficulties suggest a TRL level of 7 for deep-sea applications where flow insensitivity, low level detection, and rapid response (<2 min) are required.

HydroC (Contros GmbH) is comparable to the METS sensor except that the detection principle is based on direct IR absorption spectroscopy in the 3.4- μm region. This detection method does not consume methane, so simplifying calibration and reducing measurement errors in flowing fluid. The system can measure concentrations of methane in the range 30 nM–500 μM with a resolution of 3–30 nM. The t_{90} of the detector is quoted to

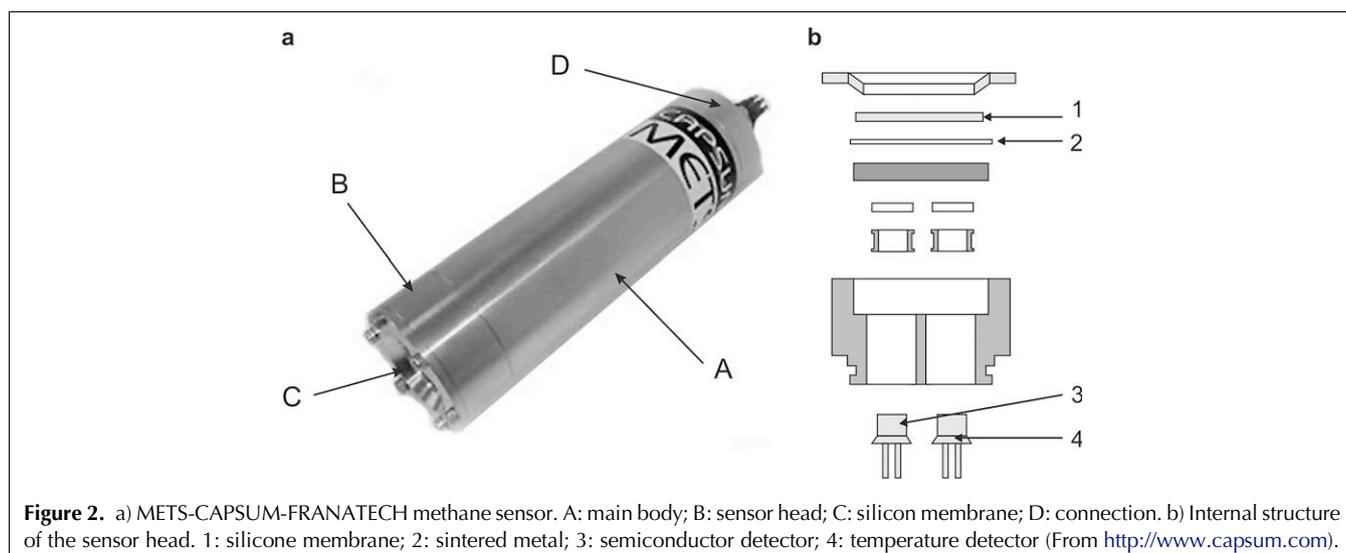


Figure 2. a) METS-CAPSUM-FRANATECH methane sensor. A: main body; B: sensor head; C: silicon membrane; D: connection. b) Internal structure of the sensor head. 1: silicone membrane; 2: sintered metal; 3: semiconductor detector; 4: temperature detector (From <http://www.capsum.com>).

be ~ 30 s. However, no data are available for characteristics that affect the performance of the sensor (e.g., the diffusivity of the membrane, which may be slower in the deep ocean where thicker membranes have to be used).

To date, there are no previously published papers involving data collected by a HydroC/CH₄ or feedback from users. That limits our ability to assess the reliability of the in situ measurements. The HydroC/CH₄ was deployed in 2007 during RV Sonne cruise 190 (27/02/07–22/03/07) and was able to measure methane plumes (10–50 nM) over the New Zealand continental margin (Contros GmbH, personal communication). Later, the system was deployed during the ROV Jason Dive 275 (Expedition to the Deep Slope 2007), but the sensor developed electrical (ground) faults that did not allow collection of reliable data (NOAA, personal communication). Despite the reliability of the device and the sensitivity/specificity of the detector, its performance may be reduced by the limitations of the membranes described earlier, which suggests a TRL of 7 for biogeochemical sampling applications where high temporal sampling is required.

Also using IR spectroscopy in 3.3- μm region, Tsunogai et al. [15] developed an in-situ methane analyzer, which uses gas-permeable membrane tubes. The system is calibrated up to 320 ppm (200 nM) in the gas phase with an LOD of 40 ppm (25 nM). No details on the sensor set-up or information on aquatic in situ deployments are available for this system, but the set-up suggests similar performance to the previous sensor, which raises the system to a TRL of 6–7.

Finally, the Deep-Sea Gas Analyzer from Los Gatos Research Inc (<http://www.lgrinc.com>) employs a gas-permeable membrane and a detection method based on fast, sensitive off-axis integrated-cavity output spectroscopy. However the use of semi-permeable membrane may limit the response time of this method, which is intrinsically sensitive [30]. The lack of real environmental trials prevents us from making a statement on the TRL of this instrument.

2.3. Equilibrators associated with gas sensing

Equilibrators have been used with a number of different detection strategies. Equilibrators comprise tubes filled with gas-partitioning material, which increases the gas-liquid exchange area, with water flowing in the opposite direction to gas pumped in an air circuit [31].

Most equilibrators were developed for air-sea exchange studies with an open air circuit, which makes those systems unsuitable for underwater studies. However, Frankignoulle et al. [32] developed an equilibrators with a closed air circuit to be completely immersed in water. The air is permanently pumped to allow circulation of the gas through the system and equilibration with the dissolved phase. Due to the differences in pressure and the pressure dependence of the gas-extraction

process, closed air circuits are limited to water depths of a few meters [31].

Equilibrators connected to an IR analyzer were developed, initially, for the in situ study of carbon dioxide (CO₂) fluxes from oceanic systems to the atmosphere [32]. The technique was subsequently modified by Abril et al. [33] for the measurement of methane concentrations in seawater, using photoacoustic spectroscopy detection. This technology is based on the modulation of a pulsating light that is absorbed by a gas sample present in a gas cell containing microphones.

Calibration of the field system ranges up to 10,000 μatm for methane (up to 400 μM). However, at low concentrations (<0.5 μM), the equilibrators are affected by a hysteresis effect from high concentrations to low concentrations [33], which represents a significant limitation for sensors to be used in highly variable environments. In addition equilibrators are difficult to construct, to operate and to calibrate in situ. Currently, the performance of such systems implies a TRL of 6, which must be modulated, as response time depends on the immersion depth. Abril et al. [33] noted a maximum response time of 12 min at a depth of 7 m.

2.4. In situ mass spectrometers

Since the development of small MS instruments, portable ones are available [34], and this has driven researchers to adapt MS to aqueous environments, using semi-permeable inlets to separate the sample from the aqueous phase [35]. This inlet must be designed to allow adequate introduction of gases into the vacuum chamber while maintaining an internal pressure of 10^{-8} – 10^{-9} bar [16]. Hence, membrane geometry and material are selected as a compromise between performance (response time and selectivity) and resistance to the pressure differential between the environment and the internal cavity. In situ MS instruments can measure dissolved methane at the nM level [36,37] with typical analysis cycle times of 5–15 min [7,25,27].

Combined with measurements of other chemical parameters, in situ MS instruments are powerful for mapping and characterizing the sources of hydrocarbons on the seafloor, as shown in Camilli and Duryea [38]. However, the payload, the power consumption and the cost of such systems limit their deployment to specific, stand-alone operations. The development of a deep-water MS is challenging due to a lack of an effective membrane-introduction interface that would work remotely for extended periods at high pressure, although membrane-introduction systems have been tested up to 400 bar [39].

We suggest a TRL of 8, as the technique has been qualified through tests and demonstrations but raising the TRL to 9 will imply a reduction in overall cost in order to operate the instrument routinely.

3. Biosensors

Turner et al. [40] gave the following definition of biosensors: "biosensors are analytical devices incorporating a biological material, biologically derived material or biomimetic, intimately associated with or integrated within a physicochemical transducer or transducing microsystem, which may be optical, electrochemical, thermometric, piezoelectric or magnetic". Initially driven by medical applications [41], biosensors have become of interest in environmental applications for chemical sensing [42]. In recent years, attention has been given to the association of organic molecules to optical and electrochemical measurement devices (i.e. the association of highly specific detection methods to highly sensitive detectors [41]).

In the case of dissolved methane measurements, the first reported works are from Daamgard et al. [19] using oxygen as a proxy for CH_4 . They developed a biosensor based on immobilized methane-oxidizing bacteria to measure the methane emissions from rice paddies. The variations in oxygen concentrations, due to the microbial oxidization process, were measured by an internal oxygen amperometric microsensor [19]. The range of utilization for this sensor was 50–100 μM of methane, with a sensitivity of 5 μM [43]. The performance described by the authors would suggest a TRL of 5–6.

Wen et al. [44] developed a similar biosensor for the measurement of dissolved CH_4 using a mixed culture of methane-oxidizing bacteria *Pseudomonas aeruginosa* and *Klebsiella sp.* together with a dissolved O_2 sensor. The response of the sensor was linear in the range 0.4–2 mM with an LOD of 100 μM and a 100-s response time.

The sensitivity and the response time of these biosensors can be varied by increasing or decreasing the number of bacteria (i.e. increasing the amount of bacteria will increase the sensitivity of the sensor). However, environmental factors (e.g., pH and temperature) can have a strong influence on the response of the sensor, as they control the physiological state of the bacteria. Hence, such biosensors are limited to a very restricted range of environments. They offer cost effectiveness, simple sensing design, rapid response and ease of operation. However, relatively high LODs, and sensitivity to other environmental factors limit the widespread use of such biosensors, so their TRL is limited to 6.

4. Optical measurements

4.1. Infrared fiber-optic evanescent wave spectroscopy

Due to a strong, broad water-absorption band in the IR (3750, 3650 and 1590 cm^{-1}), IR absorption spectroscopy cannot be directly performed in aquatic systems as the possible penetration depth cannot exceed a few μm [45]. Some researchers have overcome this problem with

infrared fiber-optic evanescent wave (IR-FEW) spectroscopy, which uses attenuated total reflection (ATR) transducers (frequently in the form of optical fibers) (Fig. 3). When a light beam is passed through the ATR element, it reflects off the internal surface in contact with the analyte and forms an evanescent wave that extends a few μm into the sample.

A breakthrough in this technique is to use polymer-coated sensitive areas, designed to act as an extractor phase enriching the hydrophobic analytes close to the sensor surface (thus increasing interaction between the gas and the evanescent wave) and as protection against water [46]. The polymer (e.g., PDMS or silicone) is generally thick enough (a few μm) so the background absorptions caused by water and other constituents are excluded.

This technique has been investigated for the detection of methane in both gas and dissolved phases [47], and in both mid-IR (MIR) and near-IR (NIR) ranges [48].

Mizaikoff et al. [46] developed a MIR-FEWS sensor for chlorinated hydrocarbons and different pollutants underwater and showed the feasibility of the method in terms of response time, specificity, and sensitivity ($\ll 0.5$ nM). No significant influence of salinity, turbidity or cross-sensitivity was noted. However, detecting dissolved CH_4 would require further development, particularly in the polymer used for sensing, possibly using specific polymers [46] able to discriminate methane and optimize the response of the sensor [49]. In addition, the cost and the mass of these sensors are relatively high, due to specific components required to work in the MIR [46]. We therefore suggest a TRL of 2–3 for a methane sensor using this technique.

In the NIR, Buerck et al. [50] developed a FEWS sensor for monitoring hydrocarbon concentrations in water at the μM level using common silica fibers from the telecommunications industry. The adaptation of this technique to measurement of dissolved methane, based on the same set-up, showed insufficient sensitivity, although calculations for dissolved methane detection

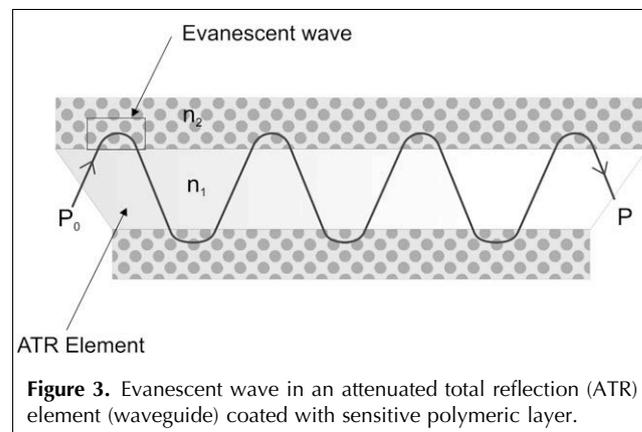


Figure 3. Evanescent wave in an attenuated total reflection (ATR) element (waveguide) coated with sensitive polymeric layer.

suggested an LOD at the μM level (Boulart et al., unpublished). The lack of sensitivity was most likely attributable to low methane partitioning into the optical-fiber coating. Hence, in its current design, the technique did not pass the TRL of 3. However, despite the initial results, the FEWS technique merits further investigation, using enhanced affinity polymers or molecular imprinted polymers (MIPs). As an example, Benounis et al. [51] developed an NIR optical-fiber sensor for detection of gases, including methane, in oil transformers by coating the sensing part of the fiber with a specific polymer that includes cryptophane-A able to trap methane reversibly. They have been able to detect methane concentrations at the 2% (v/v) level [49], which makes this technique suitable for further developments and reach the TRL 4.

Polymers used in these devices show the same limitations as the gas-extraction membranes used in consumptive sensors (i.e. long response time and hysteresis effects). However, the effect of changes in membrane diffusivity on non-consumptive sensors is reduced due to the principle of equilibrium binding (i.e. in the steady state, the membrane concentration is always at equilibrium with the dissolved phase concentration [17]). In this case, changes in membrane diffusivity caused by flow conditions at the membrane surface, temperature and pressure differential between the dissolved phase and the partitioned gas, do not produce sensor inaccuracy. Accuracy is more strongly influenced by any variation in the partition ratio (concentration in the solid-phase indicator or concentration in the dissolved phase). Variation in membrane diffusivity will cause variation in the temporal response of the sensor. However, in devices where the membrane is in direct contact with a solid substrate, there is no differential pressure across the membrane. This allows the membrane to be thinned considerably, enabling improved temporal response.

4.2. Raman spectroscopy and surface-enhanced Raman spectroscopy

For several decades, Raman spectroscopy [52] has been used for identification and analysis of gases, solids and liquids [53].

In situ Raman spectroscopy has been successfully used to analyze seawater directly in deep marine environments (e.g., hydrothermal vents and cold seeps) for identification and analysis of gas mixtures [54], although there are some difficulties due to the highly variable optical properties of the emission plumes. This variability can prevent focusing of the laser in the fluid because of turbulence effects caused by mixing the chemically complex plumes with the cold water [54].

Whilst the ability to analyze seawater directly is attractive, the main disadvantage of Raman spectroscopy is its low sensitivity due to the weak Raman scatterer and the extremely small cross section of the Raman process (10^{-31} – 10^{-29} cm^2 per molecule).

Raman spectroscopy also suffers from fluorescence interferences, which are abundant in natural waters (e.g., chlorophyll and related pigments) and can completely mask the Raman spectrum [53].

In seawater, dissolved methane, despite being Raman active, is present at only very low concentrations (nM), thus limiting Raman scattering [53]. The surface-enhanced Raman scattering (SERS) effect, discovered in 1974 [55], using specifically roughened metal surfaces, allows significant improvement of the Raman effect [56]. The SERS effect is based on resonance of surface plasmons, which enhance the Raman signal by producing an electromagnetic field around the analyte [57], and on the chemical interaction between the adsorbed molecule and the metal surface [57]. The 10^{14} – 10^{15} enhancement factor of the Raman effect provided by a SERS substrate therefore allows detection of single molecular species at very low levels of concentration [57]. Fluorescence interferences are also greatly reduced due to adsorption of the analyte on the metal surface [58].

The development of a continuously operating in situ SERS system for the marine environment is complex due to the difficulties with reproducing and stabilizing SERS substrates [59] and the sensitivity of the SERS surfaces to photodegradation, which can occur with high-intensity laser sources [56]. The adsorption of molecules on SERS substrates is highly unpredictable and depends on the concentration of the analyte; at low concentrations (nM), SERS enhancement may be significantly reduced because a critical concentration is required to start aggregation of molecules on the substrate [57]. Sackmann and Materny [57] showed that slight variations in the preparation of SERS substrates may result in changes of the adsorption geometry and, hence, large variations in enhancement factor.

Recent work has improved the long-term stability of SERS surfaces in seawater, and therefore the sensitivity of such sensors for different species. Schmidt et al. [60] showed that sol-gel-derived SERS substrates with colloidal silver are suitable for detecting low-molecular-weight aromatic hydrocarbons in seawater down to the μM level. Several instruments have been, or are currently being, developed, for in situ applications in aqueous environments. Provided that the SERS substrate has been especially designed for methane, these systems can be adapted to detection of dissolved methane [61].

Despite the encouraging performance of the current systems, we suggest here TRLs of 4–5 for Raman spectroscopy (which has poor LODs) and SERS (which suffers from instability).

4.3. Surface-plasmon resonance

A number of research teams are involved in the development of extremely compact sensors for gas detection using specific optical indicators [62]. Urashi and Arekawa [62] showed the potential to detect methane in

the gas phase using layers sensitive to low-molecular-weight hydrocarbons by means of surface plasmon resonance (SPR).

SPR sensors have been reviewed elsewhere [63]. In this configuration and in presence of the analyte, the sensitive material – or optical indicator – has a variable refractive index, which depends on the concentration of the gas.

In the case of dissolved methane, we have previously shown promising results in terms of LODs (0.2 nM) and range (1–300 nM) employing a specific indicator for methane [64], also used by Benounis et al. [49] in the NIR-FEWS configuration (Fig. 3). This indicator, based on the association of PDMS and cryptophane-A, has a variable refractive index depending on the concentration of dissolved methane in aqueous environments. However, this technique is at very early stage of development (TRL of 4). Further developments are now focusing on the implementation of this technology for a number of aquatic environments.

5. The future

There are three strategies for in situ, real-time, dissolved methane measurements, using a gas-extraction step, biosensing or solid-state optical measurements. All three have advantages and drawbacks and there is no clear leading technology. In all cases, the major barrier to routine deployment is performance, particularly low LODs and stability.

The main limitation of sensors operating in the gas phase is the use of gas-extraction membranes, which are sensitive to environmental conditions, influence and response time and which show strong hysteresis effects. These problems are exacerbated if the sensor consumes methane, as changes in membrane diffusivity cause changes in calibration of the sensor.

Only one technique – in situ MS – has been successfully used in the environment, although this involves significant cost, power and size. Future directions include reduction of sensor size, minimization of internal sensor volumes and analyte consumption, and development of less variable inlet systems.

Whilst their simplicity and size are attractive, biosensors have yet to show sufficient performance and stability under variable environmental conditions, so their use in such applications is limited. Future developments are focusing on reducing this sensitivity to matrix effects.

It is interesting to note that SPR, traditionally used in biomedical applications, has been transferred to environmental application and has shown great promise as a tool for ecosystem studies. Recent advances in optical technologies, associated with the development of new, sensitive, and specific optical indicators represent a further step in the development of in situ dissolved methane sensing, and more generally dissolved gas sensing. The

main characteristics of these non-destructive, non-consumptive techniques is direct detection of methane, in the aqueous phase, without any gas-extraction step, and a sensitive interface whose optical properties are modified in the presence of the analyte.

Surface-enhanced Raman spectroscopy is one technique currently under investigation that offers promising applications but still suffers from technical limitations that could be overcome by FEWS and SPR, provided the sensing set-up has been well designed. An important area for future development is the improvement of indicator layers. Improved partition ratio, partition-ratio stability, and thinner, more robust layers would all improve sensor performance.

Future avenues in methane sensor development may involve the transfer of techniques and technologies from other fields external to environmental science, which could result in better sensitivity, better selectivity and better response times.

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