The future of chemical in situ sensors

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Abstract

Many of the sampling methods used in oceanographic sciences today date back decades, if not centuries. Although there has been a marked change in how sampling for chemical oceanography is carried out it still relies on taking samples of seawater from a research vessel in most cases. Assessing processes on small timescales as well as transient events requires higher temporal and spatial resolution of measurements; long time series stations require high duration deployments of instruments. Both requirements can only be adequately satisfied by in situ sensors; for the physical parameters off the shelf instruments are available, in the field of chemical oceanography only a few parameters, such as oxygen, are covered by off the shelf instruments, for most parameters adequate instrumentation only exists in the form of prototypes, if at all. Chemical in situ sensors are needed to gain new insights in how the oceans and the life in it works.

This paper will give an overview of several technologies used for developments of chemical in situ sensors over the last five years and what potential these technologies have for future sensors. The technologies covered are: optical absorption spectroscopy (e.g. for nitrate measurements from the low micromolar to high concentrations); Raman spectroscopy (demonstrated e.g. on polyaromatic aromatic hydrocarbons with detection limits (LOD) from ng l^{-1} to µg l^{-1}); microelectrodes (e.g. Cu(II), Pb(II) and Cd (II) with LOD in the pM range); optodes (e.g. for oceanic oxygen measurements with accuracy of 2 µM); in situ mass spectrometry (e.g. dissolved gases, volatile organic compounds (1–5 ppb LOD)) and microelectromechanical (MEMS) analysers (that could be used in situ to measure a variety of analytes with wet-chemical methods). The paper will also evaluate how it can be assured that measurements made with new in situ sensors are consistent with proven lab analysis.
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1. Introduction

Ocean processes span a vast range of scales, both temporal and spatial, from the subsecond and submillimeter scale of molecular processes to climate change spanning decades and ocean basins (see Fig. 1). To investigate this wide range of processes a large volume of data has to be gathered from this harsh environment. In chemical oceanography the measurement task is exacerbated by the low concentrations of many measurands, often in the presence of relatively high concentrations of compounds chemically similar to the measurand, necessitating good specificity, low level of detection, high precision and accuracy of measurements. These requirements were traditionally (and to a large extent are still) only met by taking water samples for analysis either on board of research vessels or in the home laboratory. It is widely recognised (e.g. Daly,

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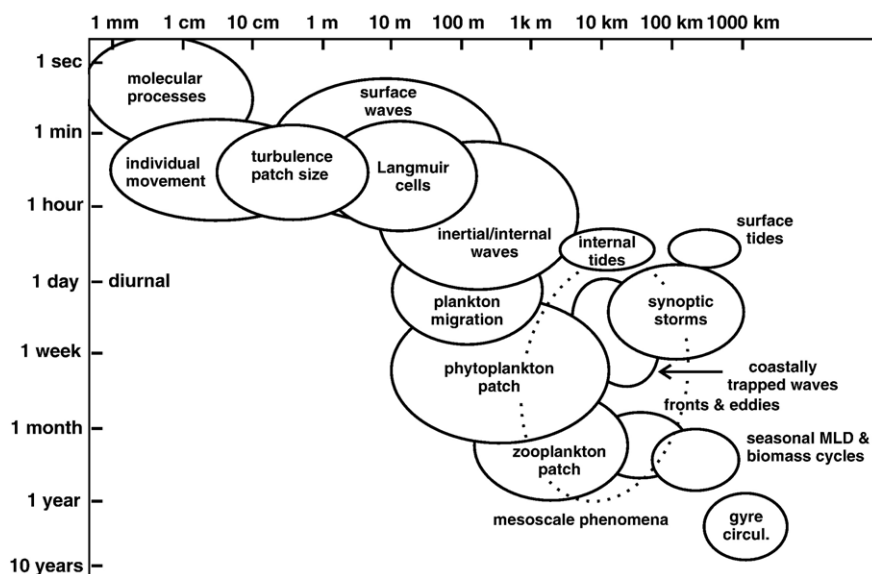 *URL:* http://www.io-warnemuende.de/homepages/prien/index.html.

Fig. 1. Temporal and spatial scales of ocean processes. Modified after Dickey (2001).

2000; Gallager and Whelan, 2004; Weisberg and Ruberg, 2004; Seyfried et al., 2000) that for a variety of scientific questions this method is inadequate in that it does not provide the necessary data for understanding the underlying processes. Many parameters of interest vary widely in time and space and cannot be characterised by infrequent fixed interval sampling. Episodic and transient events often are completely missed because no sampling is taking place at the time of their occurrence. An example is shown in Fig. 2: the dynamics in the nutrient concentrations that show in the hourly data is not captured by sampling weekly or even every three days. To increase spatial and temporal resolution of sampling in situ instruments are needed, operating on time scales at least comparable to the traditional physical parameters conductivity, temperature and pressure. The challenge is to develop devices that meet (or come close to) the same stringent precision and accuracy standards that are reached by laboratory analysis. In situ instrumentation, however, has to perform this task in the real world environment with variations in temperature, salinity, pH, concentrations of interfering compounds (often these concentrations are higher than the analyte concentration) and under high ambient pressures. Thus, in situ calibrations are necessary for performance evaluations of remote sensors.

Where chemical in situ instruments do not reach the required accuracy they still can be helpful, e.g. in support of smart sampling by triggering in situ samplers when a change in the target analyte (or its proxy) is sensed. In this way water samples from episodic or transient events can be captured during deployments that are too long to take water samples at high temporal resolution. After processing of the samples in the lab the sensor data can be recalibrated to obtain information of the variations of the measurand between samples.

Ocean observatory networks will also require extensive use of in situ instruments that can be deployed for long periods (of the order of one year), not least to keep the maintenance cost under control, as well as high measurement rates to cover transient events and for
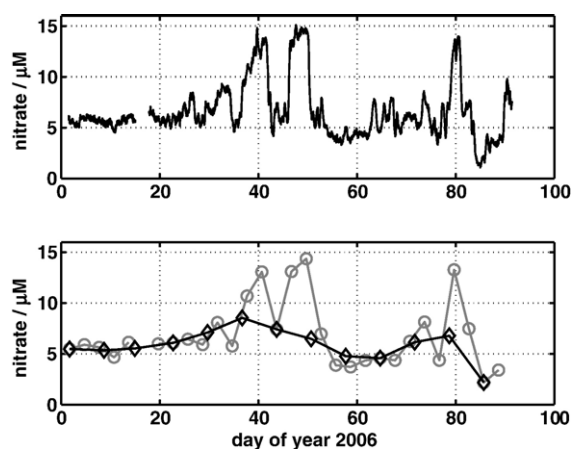

Fig. 2. Example for undersampling problem. Upper panel shows hourly nitrate data from MBARI mooring M1 as measured by the ISUS instrument for the first 91 days in 2006. Lower panel shows the same data sampled at 7 day intervals (black diamonds) and 3 day intervals (grey circles). Data downloaded from http://www2.mbari.org/coletti/m1_isus.cgi and used with permission.
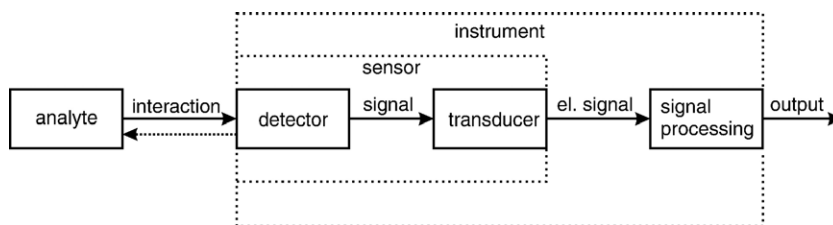
Fig. 3. Block diagram of a generalised chemical in situ instrument. The target analyte interacts with the detector (sometimes after a stimulus originating from the instrument). The detector produces a signal that is transformed into an electrical signal by the transducer. Detector and transducer together constitute the sensor. The electrical signal is fed to the signal processing (and conditioning) unit that creates the signal output of the instrument.

interactive experiments from mobile platforms. These sensors have to be reliable and easy to operate and maintain. For chemical and biological parameters there are big gaps in available sensors that can carry out such measurements (e.g. Daly et al., 2004). However, there are a variety of sensors in the development stage that will contribute to closing these gaps. In recent years various technologies have been employed for development of novel chemical sensors and instruments. The advances in understanding of chemical processes facilitated by high temporal resolution data are a powerful demonstration of the benefits of these new instruments (e.g. for nitrate Johnson et al., 2006).

This paper will give an overview of several of the technologies employed in chemical in situ sensors. It is not a complete overview of current chemical in situ sensors, for that the reader is referred to two comprehensive books (Buffle and Horvai, 2000; Varney, 2000) and the review article by Daly et al. (2004). With new ocean observatories going online in the near future large numbers of in situ sensors will be used. Making high temporal resolution measurements a high volume of data will be produced. Thus, data integration, quality assurance, reliability and ease of maintenance (e.g. exchange of sensors) become even more important for the viable operation of these observatories. It is therefore necessary to consider these issues already in the sensor

development process. Data integration and quality assurance issues are also covered in this paper.

A number of definitions of what constitutes a sensor exist; to clarify the terminology used in this paper Fig. 3 shows a block diagram of an instrument for measurement of an analyte. The instrument in some cases exserts a stimulus (e.g. light) into the medium; the analyte either interacts with this stimulus or directly with the detector. The detector signal induced by the interaction with the analyte can be optical, electrical or some change of property (e.g. colour of a fluid) that is converted into an electrical signal by the transducer. The block between the detector interface and the electrical signal output from the transducer constitutes the sensor. The signal processing unit converts the electrical signal from the transducer and carries out scaling and conversion into engineering units and the output data protocol. Sensor and signal processing together constitute the instrument.

2. Technologies for high resolution chemical measurements

In this section a selection of technologies is described that have the potential, or already have proven the ability, to measure chemical parameters in situ with high temporal and/or spatial resolution. The technologies

Table 1
Selected examples of specifications given for sensors or instruments using presented technologies

Technology	Analytes	Specification	Source
Optical absorption spectroscopy	NO_3^-, Br^-, HS^-	Precision ±0.15 μM NO_3^-	Johnson and Coletti (2002)
	CHC's	LOD 100 ppb	Mizaikoff (1999)
Raman spectroscopy	PAH's	LOD for 6 PAH's ng l^{-1} ... μg l^{-1}	Schmidt et al. (2004)
	SO_4^{2-}, CO_3^{2-}, NO_3^-	LOD 0.16 g l^{-1} SO_4^{2-}, 0.2 g l^{-1} CO_3^{2-}, 0.36 g l^{-1} NO_3^-	Battaglia et al. (2004)
Microelectrodes	Cu(II), Pb(II), Cd(II)	LOD 250 pM Cu(II), 30 pM Pb(II), 55 pM Cd(II)	Tercier-Waeber et al. (2005)
Optodes	Dissolved oxygen	Precision ±0.2 μM	Tengberg et al. (2006)
Mass spectrometry	Toluene	LOD<0.1 ppb	Short et al. (1999)

Note that some of these specifications are from laboratory experiments only. For details see the respective source.

discussed below provide examples that hopefully will serve to stimulate ideas for new in situ chemical sensors (Table 1).

2.1. Optical absorption spectroscopy

Optical absorption measurements are well established tools in the laboratory, most prominent in the form of absorption spectroscopy and its varieties. The absorption of light in a molecule is very selective as the energy of an absorbed photon has to match the difference in energy between the molecules relaxed and excited state. The spectra of target molecules, however, are modified within water through intermolecular interactions that modify the energy levels. Formation of lattice structures and association with other molecules further modifies the spectra in the water. In the case of seawater the absorption spectrum does change mainly in the ultraviolet region, where the salts exhibit electronic absorption peaks; in the visible part of the spectrum there are also some shifts of absorption peaks due to the change in refractive index of the seawater. This makes absorption spectroscopy in seawater more difficult as absorption peaks are broadened and peaks of different compounds in the seawater overlap. Johnson and Coletti (2002) introduced an in situ ultraviolet spectrophotometer (ISUS) for the measurement of nitrate, bromide and bisulfite that is capable of making measurements at a sample rate of 1 Hz. Similar instruments had been introduced before (Finch et al., 1998), but only with the availability of small, low-power spectrometers and UV light sources it is possible to apply robust techniques to separate overlapping spectra from various compounds in seawater in situ (Johnson and Coletti, 2002). An advantage of the ISUS and similar instruments is that the compounds exhibiting absorption in the UV portion of the spectrum can be measured at the same time and in the same water volume. For nitrate measurements Johnson et al. (2006) quote an accuracy of ± 2 μM and a precision of ± 0.15 μM for a 2.5 year deployment. The detection limit quoted is 1.8 μM for measurements made at 1 Hz; this can be lowered to 0.2 μM when integrating over a 30 s period. Detection limits of commercial wet-chemical analysers are in the region of 40 nM for nitrate (e.g. Systea, SubChem) but the deployment times are limited by reagent consumption and degradation to less than ten weeks. The deployment time of the ISUS is mainly limited by biofouling and continuous deployments of greater than 3 months without any apparent degradation of performance have been reported (Johnson and Coletti, 2002). With LEDs reaching down to wavelengths of 210 nm on the horizon (Taniyasu et al., 2006)

it can be expected that more compact and lower power UV absorption spectrometers of this type will be developed that also could be deployed on gliders for extended periods.

Another method to measure the absorption of target analytes is attenuated total reflection (ATR) spectroscopy. Total internal reflection occurs at the interface of two media M_1 and M_2 with refractive indices n_1 and n_2, $(n_1 < n_2)$, when light from the medium M_1 hits the interface under an angle greater than the critical angle θ_c (the angle of incident light to the normal of the interface under which the light along the interface between the two media would be refracted along the interface), that is resulting from Snell's law:

$$\theta_c = \arcsin\left(\frac{n_1}{n_2}\right) \qquad (1)$$

A part of the electrical field is penetrating into the medium with lower refractive index due to interaction of the incident and reflected light. The amplitude of this evanescent field is decreasing exponentially, and the penetration depth is of the order of the wavelength. The evanescent field can interact with the medium M_1 (e.g. seawater), and therefore information about this medium can be obtained. Sensitivity can be increased by using a length of waveguide or optical fibre as medium M_2 and thus summing the effects of multiple internal reflections. The performance of this type of sensor can be further increased by coating the surface of the medium M_2 with a chemically sensitive layer. Mizaikoff (1999) discusses such an in situ oceanographic sensor for the detection of chlorinated hydrocarbons. The laboratory experiments showed levels of detection of 100 ppb for tetrachloroethylene and 115 ppb for 1,2-dichlorobenzene in artificial seawater.

2.2. Raman spectroscopy

A third optical spectroscopic method is Raman spectroscopy. When a molecule does exhibit rotation or vibration (and its polarisability is changing with change of position) a part of light that is scattered by this molecule (about 1 in 10^7) encounters a frequency shift, the Raman shift, that is characteristic for the molecules rotational and/or vibrational state. This makes Raman spectroscopy an analysis method with high specificity, as it detects the fundamental vibrations of target analyte molecules. Raman spectroscopy is also suitable for use in water as the excitation wavelength can be in the visible part of the spectrum where absorption in water, and therefore interference by the water, is relatively low.

Raman spectra can be taken fairly rapidly (on the order of seconds) which makes the method suitable for profiling measurements. In recent years some prototypes of Raman in situ sensors have been built and tested; the focus of these developments was the design and construction of probe heads for in situ detection. Brewer et al. (2004) reported the development of a Raman spectrometer for deep ocean science and demonstrated the prototype in situ on gaseous, liquid and solid samples. Murphy et al. (2000) designed an in situ surface enhanced Raman scattering (SERS) instrument and tested it in the lab. SERS uses the effect that if a target molecule is adsorbed onto some metals (e.g. silver or gold) and the excitation light excites electrons in the conduction band of the metal, the Raman signal is enhanced greatly, usually by 6 to 8 orders of magnitude. An improved system was presented by the same group (Schmidt et al., 2004) for the detection of polyaromatic hydrocarbons (PAH) and subsequently tested in situ as part of the EU project SOFIE. Since these are two prototype systems it is expected that the levels of detection (Schmidt et al. (2004) reported values ranging from $\mu g \, l^{-1}$ to a few $ng \, l^{-1}$ for six PAH species) will be improved while the currently fairly bulky total size of the systems will be further reduced. Both prototypes use standard laboratory spectrographs adapted for operation in the sea as the main focus of the developments was on the probe heads.

A further Raman system was presented by Battaglia et al. (2004) for the measurement of sulfate, carbonate and nitrate in hydrothermal vent fluids. A compact portable Raman spectrometer system was tested in the laboratory on artificial vent fluid solutions. The reported detection limits were $0.33 \, g \, l^{-1}$ for SO_4^{2-} and $0.34 \, g \, l^{-1}$ for NO_3^-. Although this was not an in situ system it demonstrates that even with compact Raman spectrometers usable in situ sensors could be designed.

2.3. Microelectrodes

Electrode based sensors have been used in oceanography for a very long time, most prominently in the form of the Clark cell (Clark et al., 1953) for oxygen measurements. Recently the Clark cell sensor has been optimised (Carlson, 2002) for in situ applications; an excellent example of how modern design and production methods can improve sensors based on long-known principles.

While the Clark cell sensor does employ a membrane, microelectrodes can be used without a membrane and a supporting electrolyte, resulting in a very fast response time (in the order of milliseconds). This fast response is, for example, used in lab experiments investigating reaction kinetics. Even with membranes attached to the microelectrodes, to either enhance specificity or to enrich the analyte concentration, the response times can be on the order of seconds. A disadvantage of microelectrodes is that the reduction current is very small (in the order of pA) and therefore the precision of measurements carried out with a microelectrode often is limited by electronic noise. This limitation, however, can be counteracted by using arrays of microelectrodes; they still exhibit the advantage of hemispherical diffusion regions while at the same time the total electrode area, and therefore the signal, is increased. While microelectrodes are used routinely to measure a number of chemical species in sediment pore water (e.g. Gundersen and Jørgensen, 1990; Luther et al., 1998, 1999, 2001) microelectrodes without membranes are scarcely used for watercolumn measurements, although they have shown some potential for fast oxygen measurements (e.g. Atkinson, 1988; Atkinson et al., 1995; Prien et al., 2005; Sosna et al., in press).

A voltammetric in situ profiling system has been introduced by Tercier et al. (1998), using an agarose membrane-covered mercury-plated Ir-based microelectrode. This instrument performs in situ measurements of the mobile fractions of Cu(II), Pb(II), Cd(II) and Zn(II) as well as Mn(II) and Fe(II) using either square wave anodic stripping voltammetry (where the metal ions are enriched in an amalgam in the reduction step and then reoxidised to generate the signal), or square wave cathodic sweep voltammetry (without the enrichment in the amalgam). Measurements over a tidal cycle in the Fal estuary (South West England) made with the Multi Physical-Chemical Profiler (MPCP) (Tercier-Waeber et al., 2005) showed variations in the ratios of particulate/colloidal species, dynamic species and free metal ion concentrations that would be difficult to assess by sampling and subsequent laboratory analysis.

It can be expected that more in situ sensors based on microelectrodes will be developed for oceanographic applications. The technology has the potential for enabling small, low power instruments that can assess a variety of chemical parameters rapidly, similar to the electronic tongue concept (e.g. Buehler et al., 2002). With further advances in analogue electronics the higher resolution and lower level of detection of the current measurement will allow detection of smaller variations in concentrations of the analyte(s). Arrays of microelectrodes can also be used to investigate variations on small spatial scales by monitoring the currents of individual electrodes, or subsets of electrodes, within the array.

2.4. Optodes

Optodes, also referred to as optrodes, use indicator chemistries (e.g. ruthenium complexes) immobilised in sol–gel matrices or embedded in a polymer layer. The presence of the analyte modifies a property of the indicator (e.g. fluorescence) and thus forms the sensor. The modification of the indicator property is a measure for either presence or concentration of the target analyte. Commercial oxygen sensors based on the optode principle are available and have proven to have excellent long term stability on profiling floats (Körtzinger et al., 2005). For example, the oxygen sensors from Aanderaa (www.aanderaa.no) use a platinum porphyrine complex as the indicator fluorophore. The fluorescence is excited by an LED light and measured by a photodiode with an optical filter to exclude excitation light. In the presence of oxygen the fluorescence is quenched (because the excited fluorophore molecules can transmit the excitation energy by collisions with oxygen molecules without emitting photons), and therefore the measured fluorescence intensity and lifetime are reduced. Tengberg et al. (2006) report a high accuracy (± 2 μM) and long-term stability over a period of 20 months. The response time for the Aanderaa optode is given by Tengberg et al. (2006) as 23 s with an additional layer of silicone to shield ambient light and 6 s without this layer.

A further application of this technology is the use as a planar optode in conjunction with a camera recording fluorescence intensities to yield two-dimensional oxygen distributions at the sediment–water interface. Glud et al. (1996) reported measurements in the laboratory with a planar optode of a 13×17 mm^2 area with a spatial resolution of 26 μm. Glud et al. (2001) reported results from in situ measurements in shallow waters covering an area of 32×24 mm^2 with a spatial resolution of 50×50 μm^2. Indicator chemistries for other measurands (e.g. pH, CO_2, ammonia) exist but so far have not been developed for in situ oceanographic applications.

2.5. Mass spectrometry

Another prominent laboratory method that has been used successfully in situ is mass spectrometry. Short et al. (1999) described a system consisting of a membrane introduction interface coupled with a linear quadrupole mass filter for in situ detection and quantification of dissolved gases and volatile organic compounds (VOCs), e.g. chloroform, benzene, toluene, dimethyl sulfide and trichloroethylene (TCE) with detection limits of 1 to 5 ppb. All of the light stable gases (e.g. methane, nitrogen, oxygen, argon, carbon dioxide and hydrogen sulfide) can

be detected with a membrane inlet mass spectrometer (MIMS). The quantification is complicated by a residual (non-constant) gas background in the vacuum system of the mass analyser and by contributions from several different gases at specific mass to charge ratios (m/z) of the spectrum. Careful analysis of the spectra and consideration of the contributing components, however, does allow the quantification in most cases. One of the advantages of mass spectrometers is that a number of analytes can be measured in parallel and from the same water volume.

The power of in situ mass spectrometry as a tool for high resolution chemical mapping was demonstrated by Wenner et al. (2004), who used a 200 amu underwater mass spectrometer on a remotely guided surface vehicle to map distributions of dissolved gases and volatile organics in saltwater and freshwater environments. The sample rate ranged between 0.7 s and 3.6 s, the overall position error of the system was estimated at ± 3 m. Recently the mass spectrometry group of the Center for Ocean Technology (COT) of the University of South Florida has demonstrated profiling measurements of concentrations of dissolved oxygen and nitrogen in the Gulf of Mexico (Tim Short, pers. comm. unref.). Continuous, real-time measurements of dissolved gases (pCO_2, O_2, dimethylsulfide) with a shipborne MIMS have been shown by Tortell (2005). These results demonstrate the potential uses of in situ mass spectrometers once more mature instruments will become available.

Although the COT's in situ instrument is not small (1.14 m long with a diameter of 19 cm) and has a power consumption of 100 W it is well suited to be deployed on (bigger) autonomous underwater vehicles (AUV's) (Griffiths, 2002) or profilers (Langebrake et al., 2003) down to a depth of 500 m (limiting the depth capability is the high pressure membrane introduction probe). A recently reported miniature ion trap mass spectrometer (Chaudhary et al., 2006) developed by the same group might lead to a smaller in situ instrument that could be deployed on a variety of platforms. The resolution (1.8 m/z) is certainly much lower than for dedicated laboratory mass spectrometers but it can be used to measure quantitatively a variety of compounds in parallel.

Blain et al. (2004) report another approach to miniaturisation of ion trap mass spectrometers. They simulated and fabricated arrays of 10^6 one-micrometer cylindrical ion traps, including integrated ion detectors, on a 0.25 cm^2 silicon substrate. To reach a spectral charge density equivalent to that of a 1-cm quadrupole ion trap, Blain et al. (2004) estimated that 10^7 1-μm cylindrical ion traps would be needed that could be

fabricated on a 2.5 cm^2 substrate. While this would be a modest reduction in size, such an array of 1-µm ion traps would enable the integration of radio frequency (rf) drive and signal detection electronics monolithically in the silicon substrate. The overall size of the mass spectrometer could be further reduced, because miniature mass analysers also would reduce vacuum system demands and therefore allow a further reduction of power demands at the same time, making the hand-held sized mass spectrometer a viable future instrument. The driving voltages required would be in the region of 10's of volts, much lower than for standard sized mass analysers. The rf drive frequency would have to be higher, in the region of a few GHz. These frequencies, however, can be handled by modern electronics as proven in the telecom industry.

2.6. Microelectromechanical systems (MEMS) analysers

For many chemical parameters of interest for oceanographers the methods described above might not achieve the necessary accuracy and detection limits in the near future. For these parameters the established wet-chemical methods will remain the method of choice at least for a while. Thus, reagent and power consumption need to be minimised in order to effectively use wet-chemical methods in situ. Reduction of reagent consumption also allows higher measurement rates compared to macro analysers (although the measurement will in many cases lag behind the intake of sample) and longer deployment times. The application of (macro) wet-chemical analysers for profiling measurements (e.g. Hanson and Donaghay, 1998) and on board of AUV's (e.g. Prien et al., 2006) have already demonstrated the value of high sampling rate analysers even for limited deployment times. The combination of high sampling rates and long deployments would allow to cover processes on the longer timescales (e.g. as part of moorings where the analysers could be replaced at the same interval as the physical sensors are maintained) without missing transient events.

A technology with the potential to satisfy the demands of low consumption in situ analysers is microelectromechanical systems (MEMS) or, more specifically, micro fluidics. MEMS consist of mechanical systems fabricated by modified silicon fabrication techniques used in the electronics industry like etching, electro discharge machining and other technologies able to produce small mechanical features. While early MEMS were based on silicon as the base material other materials like polymers (e.g. McDonald et al., 2000) or printed circuit boards (PCB-MEMS) (Merkel et al., 1999) are also used for

microfluidic devices. These microfluidic devices already have had great impact on the bio-medical field under the labels of lab-on-a-chip and micro-total-analysis-systems (µTAS). One of the advantages of these analysers is the low production cost when produced in great numbers. This allows the use of MEMS analysers as disposable items, avoiding the need to clean after use and thus minimising the risk of contamination. Another advantage of microfluidic analysers is that it is comparatively easy to add an in situ calibration; by adding two valves and reservoirs, e.g. with blank and standard solution, analysers can perform control runs to check for detector drift at predetermined intervals.

There are a multitude of wet-chemical analysis methods for a vast range of analytes (such as nitrate, nitrite, phosphate, ammonia, silicate, iron, manganese) (see e.g. Grasshoff et al., 1999) that have been employed by in-situ wet-chemical analysers and/or could be adapted for use in MEMS analysers. Most of the methods, however, are optimised with the lab environment in mind where shelf life of reagents is not a major concern. For in-situ analysers these methods have to be re-investigated to optimise them for long deployment times. It can be anticipated that this will make the MEMS analysers more complicated, as the reagent has to be prepared in situ from several components. However, for all building blocks of a wet-chemical analyser (pumps, valves, flow sensors, mixers, heaters etc.) various designs have been published in the MEMS literature and many have been used in bio-medical applications. Not all of them will be suitable for in situ oceanographic sensors and some challenges have to be overcome such as the packaging for operation at depth. Biofouling is a big issue for all in situ sensors, for MEMS analysers with small fluidic channels that are blocked easily even by small particles the risk of malfunction due to biofouling seems to be exacerbated. With suitable filters this risk can be minimised and by deploying several analysers in parallel (taking advantage of the potentially low production cost of single analysers) a failing analyser can be switched off and replaced by the next one.

3. Data integration

The common use of in situ chemical sensors is expected to lead to a marked increase in the volume of data for chemical parameters. Accordingly, new methods must be developed to process these data. Physical oceanography has long been dealing with higher data rates (e.g. from CTDs and ADCPs) and robust methods for data handling and storage are well established for

profiling measurements as well as moored instruments. The operation of ocean observatories with their great number of sensors, however, does require new concepts for the data processing to allow scientists access to the gathered data in real or near real time.

To make the data acquisition during operation as seamless as possible standard interfaces and protocols have to be established (such as e.g. IEEE 1541) and metadata (sensor self identification, specification of sensor performance, calibration data etc.) stored within the deployed instruments. This is true not only for ocean observatories but will also benefit the use of sensors on other platforms, be it ships, AUVs, floats or gliders that currently requires a considerable amount of work to adapt each and every sensor on each platform. If the data from individual experiments (e.g. cruises, AUV or remotely operated vehicles (ROV) deployments) are to become part of a virtual ocean observatory system these standard interfaces have to be used on the whole range of platforms. Only when the management of metadata is automated and included as part of the database management, will the addition or exchange of sensors be a straightforward process. The engineering effort otherwise spent on interfacing sensors can be directed towards the creation of novel and improved platforms and sensors. It also will aid the quality assurance of the gathered data when sensor and calibration information can be processed automatically.

4. Quality assurance

Specificity, accuracy, precision, resolution and level of detection are the main specifications for any chemical sensor. New sensors have to undergo thorough performance analysis, first in the lab under various environmental conditions and later in field deployments, ideally in comparison to currently accepted, tried and tested standard methods. It is desirable (and in the long term indispensable) to trace sensor calibration back to a common standard; if no standard is available for the target analyte it should be established. The performance analysis, however, only validates the sensor performance under a special set of environmental parameters. Care also has to be taken in the evaluation of sensor performance in respect to the requirements of a planned deployment. Since the environmental conditions in the oceans vary widely, the potential cross sensitivities caused by other constituents than the target analyte in the seawater have to be considered. This is aggravated by the fact that concentration ranges of these constituents might not be known for the deployment site.

For extended deployments and/or in a dynamic environment in situ sensors need an in situ calibration and an integrated performance monitor, able to detect sensor drift, e.g. due to biofouling. There are several qualities of in situ calibrations. The best calibration can be achieved by substitution of the water sample with a (traceable) standard (or a series of standards) of known concentration of the analyte from time to time. This method allows detection of the true overall instrument drift, including effects of biofouling, assuming that the standard is not degrading over the deployment period. With degrading standard(s) substitution of the sample still allows to check instrument response qualitatively. Even with this 'gold standard' in situ calibration changes in the chemical composition of the sampled seawater and especially changes in the concentrations of constituents leading to cross sensitivities of the sensor cannot be detected.

A second possibility for in situ calibration is to replace the real world sensing by a simulated sensor stimulus at the earliest possible stage (e.g. for an electrode measurement replacing the reduction current by a calibrated electric current reference; for an absorption measurement replacing the absorption cell by a standard absorber). This allows to check for changes in the detector and transducer properties and subsequent electronics. Changes at the sensor interface with the seawater (e.g. fouling of the electrode or the optical interface and changes in the chemical composition of the sampled water) cannot be detected by this method.

A similar method is the substitution of the electrical transducer signal by a standard signal (e.g. current reference, voltage reference). This would allow the detection of changes in the signal conditioning and processing electronics, but does not assess changes of the detector and transducer properties.

Operating a number of sensors in parallel increases reliability of measurements and allows the detection of sensor failure. This is a viable way to avoid gaps in time series data sets caused by limitations in operation reliability of individual sensors, but there is a tradeoff between the increased reliability and the spatial distribution of sensors within budgetary constraints. Multiple sensors can also be employed to extend endurance of measurements by using individual sensors sequentially over the deployment duration and exposing the individual sensors to the medium only during operation. To determine effects due to cross sensitivities multiple sensors working on different detection principles (and therefore exhibiting different specificities) can be used. With multivariate analysis of the sensor data

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

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 lab environment
TRL 5	Component and/or basic sub-system technology valid in relevant environment
TRL 6	System/sub-system technology model or prototype demo in relevant environment
TRL 7	System technology prototype demo in an operational environment
TRL 8	System technology qualified through test and demonstration
TRL 9	System technology qualified through successful mission operations

this approach therefore can increase the specificity of the combined measurements.

5. Discussion

In situ sensor development is highly interdisciplinary as it involves the oceanographic science that the sensors are applied to, physics and chemistry for development of the detector and transducer, electronics for the signal processing and control, mechanical engineering for packaging the instrument and information technology for processing the data stream from the instrument. Only when all of these parts work together can a sensor be successfully developed. It is crucial that scientists intending to use the sensors are part of the development process during all stages to assure that the science goals of the development are met. Experience shows that the development of new in situ sensors is a long drawn process requiring multiple cycles of design, field testing, troubleshooting and redesign (NRC, 2003). This long process is not well suited to the current funding timescales of in most cases three to a maximum of five years. While this timescale is in some cases sufficient to design and build a new sensor the full characterisation and signal processing often cannot be carried out within a funding period. As a consequence many sensors exist as prototypes only that need expert operators; obtaining research grants to develop prototype instruments into industrial prototypes (that could be manufactured effectively without a complete redesign by industry) is virtually impossible as it is seen as an engineering task rather than research.

Daly et al. (2004) state that some prototype sensors that have been deployed for extended periods have better documentation of performance than those commercially available. This is a strong hint that the long development process poses a problem for companies as well.

In situ chemical sensors operated in ocean observatories together with physical and biological sensors will change our knowledge of the distribution of chemical analytes in the sea and help advance understanding of the mechanisms controlling these distributions. The comparison of these measurements with the sample-and-analysis approach is akin to the comparison of movies with still photography. In situ sensors are a step forward towards obtaining a series of synoptic pictures of the ocean (or at least parts of it). As the number of ocean observatories will increase the way in which oceanographers work will change and the individual researcher will more often get the necessary data to prove or disprove a hypothesis out of the databases of ocean observatories rather than by going out on a ship.

As technology in electronics, optics, chemistry, materials science, computer science and telecommunications progresses new sensor and instrument concepts will be devised and will expand the arsenal of tools at the hands of chemical oceanographers. Quality assurance and reliability of new instruments will play an important role for the acceptance of these tools in the scientific community.

6. Comments and recommendations

For many analytes of interest for chemical oceanography no standards exist that could be used as a reference for sensor calibration. Using community wide accepted standards would also ease the intercomparison of different sensors for the same analyte. For the area of coastal research tools and technologies the Alliance for Coastal Technologies (ACT, http://www.act-us.info/) carries out workshops, evaluations and comparisons of sensors and technologies. ACT is a NOAA-funded partnership of research institutions, resource managers, and private sector companies dedicated to fostering the development and adoption of effective and reliable sensors and platforms for coastal research. For the open ocean no comparable organisation exists that could serve as a central source for information exchange and coordinate the establishment of standard procedures and materials for oceanographic research.

The use of technology management tools that are used in space exploration and defence procurement is virtually non-existent in the assessment of oceanographic sensors. One example is the Technology Readiness Level (TRL)

approach for the assessment of the readiness of a technology to be deployed for a specific mission (see Table 2). It reflects the stages of sensor development from the first principles (TRL 1) to the successful in situ deployment (TRL 9). This approach is helpful to determine the current state of a sensor development (or an available sensor) and to assess what work is needed to raise the level to TRL 8 or TRL 9, necessary for a successful deployment of a sensor. The TRL table can also serve to identify the gap in research funding for a complete sensor development. While the steps up to TRL 4 and 5 (sub-system technology valid in lab or relevant environment) are perceived as research in the engineering disciplines (including here chemistry and/or physics) and the step from TRL 8 to TRL 9 (from demonstration to successful deployment) can be part of a scientific project that requires the finished instrument, the steps from TRL 5 to TRL 8 (sub-system validity to prototype demonstration in situ) are often perceived as engineering tasks with little scientific merit on their own, but at the same time as bearing too high risks to be funded as part of infrastructure development. For in situ instrumentation to fulfill the potential of high impact on oceanographic science the scientific community has to find mechanisms to fill this funding gap.

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