Electrochemical sensors for *in-situ* measurement of ions in seawater

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ABSTRACT

In the current water monitoring panorama, certain benefits are expected to arise when the *modus operandum* of analysis shifts from sampling-based to purely *in-situ* approaches. Since the appearance of the first submersible conductivity-temperature-depth (CTD) probe in the 80 s, clear efforts to move towards decentralized strategies have been reported in the literature, with some having even been brought to the stage of fruitful commercialization. Among the portfolio of available analytical techniques, only a handful of approaches offer clear potential for implementation in submersible devices, in terms of adequate analytical features, autonomy, feasibility of miniaturization, and ease of portability. Electrochemical sensors have demonstrated excellent characteristics for this purpose, particularly in the detection of ions. The present review analyses electrochemical sensors that have shown an aptitude for *in-situ* measurements of ions, including trace metals, nutrients, and carbon species in seawater. The previous 5 years have been selected as the main period for review, although in some instances comment is made upon earlier contributions to the field or commercialized devices, where these are deemed to exemplify crucial technological advancements. There is a notable lack of electrochemical sensors being deployed in *in-situ* applications, and this scarcity is even more stark when seawater is considered: only a very few cases have been demonstrated under such challenging conditions. With the aim of providing inspiration towards genuine advances in the field of *in-situ* seawater analysis, this work also highlights some laboratory scale research as well as studies concerning other environmental waters than seawater.

1. Introduction

Diagnostic analytical tools are crucial for the realization of serious clinical and environmental problems, as early tracking is essential when seeking to avoid severe consequences [1,2]. At this point in time especially, there can be no further doubt that the ability to detect a new virus early and in a widespread manner would provide a massive benefit in attempts to minimize its worldwide impact. The COVID-19 pandemic situation has served to dramatically increase human awareness about the importance of early clinical diagnosis and healthcare actions. This same philosophy applies to environmental scrutiny and, in particular, to water-care programs [1]. Thus, the development of affordable water diagnostic tools providing high spatial and temporal resolution is predicted to allow for investigation of the entire water landscape. This is then in turn expected to contribute greatly to preventing further losses, both ecologically and economically.

The concept of 'Environmental Intelligence' remains the Holy Grail regarding exhaustive control of water status by means of trustworthy predictions [3]. Achieving that imagined scenario will require the construction of a systemic understanding of interconnected environmental water resources, through massive-scale measurements. With this in mind, current water research programs rely upon water sampling methods accompanied by laboratory-centralized analyses [4,5]. However, this approach requires instrumentation which is bulky and quite expensive in terms of both overheads and maintenance, which limits the number of devices that can be placed in the area under study (*i.e.* low spatial resolution) [5]. Other drawbacks include the risk of water alteration during sampling, storage, transportation, and manipulation, the need for hazardous chemicals and pre-treatments with associated environmental footprints, as well as a certain delay in the provision of the analytical data [5].

The innovation of low-cost sensing solutions for *in-situ*, real-time multi-target analyses in water, most especially in seawater, is well recognised as the principal challenge in this field. In addition, the technology enabling this end-goal should consider the requisite high standards of independence and sustainability needed for remote operation. Importantly, the first example of this class of *in-situ* probe was conceived in the '80s by Neil Brown at the Division of Marine Research

in the Commonwealth Scientific and Industrial Research Organisation (CSIRO), which they named the conductivity-temperature-depth (CTD) probe or Sonde [6]. The CTD probe functioned by way of the innovative incorporation of a cluster of sensors, accompanied by electronics for control and data transmission, within a submersible, non-corrosive housing in such a manner as to facilitate reliable measurement at ocean depths of up to hundreds of metres. Moreover, mounting on a conventional titanium cage [7–9] allows for continuous depth profiling as well as the possibility of adding sensing modules and accessories, such as a carousel comprising several Niskin bottles for water sampling [8,10, 11]. Fig. 1a displays a picture of a commercially available CTD and a sampling bottle mounted in a titanium cage immediately prior to deployment in seawater [9].

Currently available CTD devices predominantly employ an electrochemical readout for ion detection, as this arrangement presents many inherent characteristics which facilitate compatibility with decentralized real-time measurements in seawater [1,8,10,11]. These include a propensity for miniaturization, autonomy, low power consumption, facile data interpretation, and efficiency in terms of both effort and economy [5,12]. With that said, *in-situ* measurements of any ion analyte in seawater is possible in theory provided that the analytical attributes of the electrochemical sensor (limit of detection, selectivity, response time, reversibility, stability, minimum calibration requirement) are sufficient [5]. The detection of ions falling into the categories of trace metals, nutrients, and carbon species in seawater presents a particular challenge, as these species are known to provide unique environmental information [1,13–15]. A great impediment is placed on the accuracy and selectivity of measurements concerning these analytes by the fact that they are often found in very low concentrations (micromolar or even nanomolar) in media containing high concentrations of other ions, such as sodium or chloride. The situation is complicated further when considering long term measurement by highly independent sensors, which requires a considerable degree of resistance to biofouling, in such a complicated environment as the ocean.

Apart from traditional titanium cages, CTD and related sensors can be engineered into a great plethora of submersible devices, as illustrated in Fig. 1b: (i) moored observatory platforms (*e.g.* profiling floats and buoys) for surface water analysis, (ii) submersed cabled-observatories, (iii) autonomous underwater vehicles (AUVs) that are pre-

programmed for underwater survey missions, (iv) remotely operated vehicles (ROVs, unoccupied underwater robots) connected to a ship for both control and data transfer by means of cables, (v) the 'Towfish' sonar system, and (vi) human-occupied underwater vehicles [9,16–19]. All in all, considerably advanced technology exists today for the purpose of submersing solutions in the oceanic environment; what is lacking is the sensor technology capable of providing reliable *in-situ* and real-time measurements in seawater. The answer to this challenge must be found in the provision of new probes that cover the detection of a wider spectrum of chemicals relevant to water quality assessment, which are not yet commercially available.

This review analyses the current status of *in-situ* ion measurement (trace metals, nutrients and carbon species) in seawater by means of electrochemical sensors. A special focus has been placed on publications of the last 5 years, although some relevant advances from before this time are also commented upon. Furthermore, some developments in the field of electrochemical sensors targeting other environmental waters, and at the laboratory scale, have been additionally inspected, with a view to providing inspiration for further advances in the field of *in-situ* water monitoring. If any relevant manuscript has been obviated, this was not done with the intention to undervalue those works, and the sole aim was to provide a generalized "big picture" of the current panorama of electrochemical sensors applied to *in-situ* seawater analysis of ions. An inspection of the literature swiftly reveals stripping voltammetry as the predominant technique that has been utilized for trace metal analysis, primarily for the detection of potential pollutants, whereas potentiometry using ion-selective electrodes is more restricted to the measurement of non-redox active ions. Despite some notable accomplishments at the laboratory scale, as yet only a few cases have shown suitability for *in-situ* deployment in seawater scenarios and fewer again of these are realistically on the way to commercialization, with many presenting certain limitations in the final field application. Indeed, the reported *in-situ* investigations (*i.e.* chemical concentration profiles in water) more properly represent a kind of halfway position between centralized laboratory approaches and entirely decentralized measurements [1]. In the majority of the cases, the *in-situ* probe can be handled by an expert (*e.g.* the person or team in charge of its development and laboratory validation), but it is not truly ready for autonomous end-user utilization.

Extravagant claims can be made concerning the value that can be

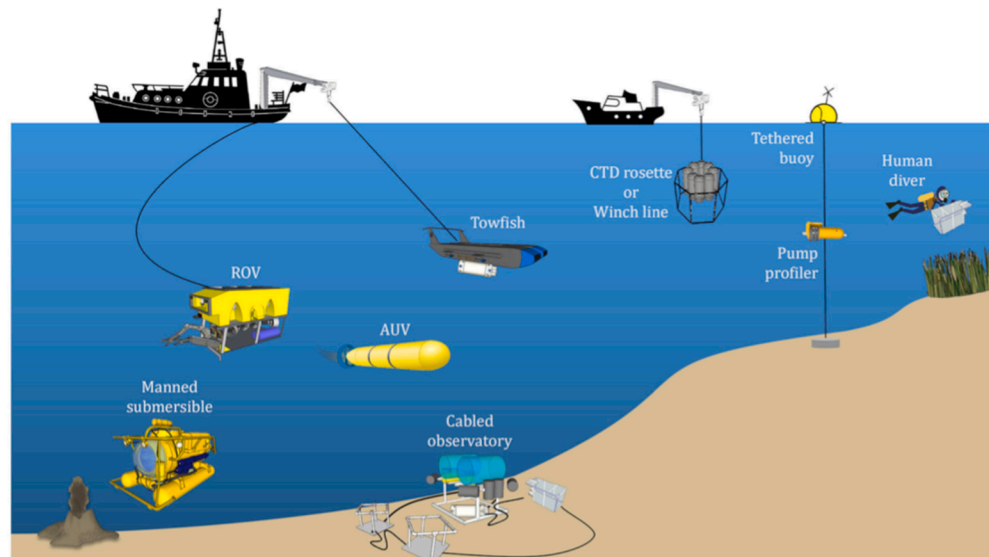## a) CTD   b) SUBMERSIBLE DEVICES

Fig. 1. (a) Image of the CTD and Go-Flo model bottle mounted in a titanium cage just before deployment in seawater. Reprinted from [9], Copyright 2020, with permission from Elsevier. **(b)** Schematic of the various platforms on which submersible sensors can be deployed. Image is reprinted from [16] with attribution 4.0 International (CC BY 4.0).

assigned to any (validated) field data collected by *in-situ* electrochemical sensors, as a unique environmental data source. Real-time information from sensors that can be deployed for depth profiling and/or long-term periods have the potential to revolutionize the current understanding of ocean processes, considering both natural and anthropogenically-influenced seawater systems [14,15,20]. To reach this projected ideal, as discussed in this review, investigations should be actioned in the direction of: (i) covering a wide range of chemicals identified as relevant in environmental studies; (ii) evaluating the performance of the sensors on the basis of realistic analytical needs; (iii) simplifying maintenance as well as any calibration related to signal deterioration (*i.e.* reversibility, drift, biofouling, effect of changes in environmental conditions, *etc.*); (iv) building in a fluidic design to the *in-situ* probe, (advisable in cases where pre-treatments and/or regeneration steps prove unavoidable); (v) establishing detailed protocols for the *in-situ* deployment of the sensors that facilitate the training of potential end-users; and (vi) validating the collected field data in a conscientious manner as to confirm sensor accuracy. Rigorous analytical assessment, first at the laboratory scale and then in the field, will bring electrochemical sensor technology much closer to expectations concerning *in-situ* ion monitoring in seawater.

2. Framing the current panorama of *in-situ* analysis of ions in seawater by means of electrochemical sensors

For the time being, remote sensing and regular deployments of sensors in oceans and coastal zones have provided a wealth of physical information, as well as O_2 and pH profiles [15,21–23]. However, our understanding of the biogeochemical processes occurring in such a complex water system remains incomplete as long as other chemicals are excluded, including ions such as trace metals, nutrients, and species relevant to the carbon cycle [5,21,22,24]. Although electrochemical technology for the detection of ions in different water matrices has made significant advances in recent years, as yet no sensor cluster for this purpose is available.

Especially considering the last five years and the particular context of seawater monitoring, there is a dearth of reviews in the literature regarding electrochemical sensors for *in-situ* detection of ions. These have traditionally been included in larger-scope reviews that provide a general vision concerning sensors for aquatic environments [5,12,22,23, 25–28], laboratory approaches with high potential towards *in-situ* applications [1,13–15,29–33], papers focused on specific analytes [34–44], and standardization of measurement protocols [21,45]. As a result, the true overview of electrochemical sensors applied to *in-situ* seawater monitoring becomes somewhat diluted within those extensive reviews.

Table 1 presents a series of devices based on electrochemical principles showing application (or potential) for *in-situ* seawater analysis that have been published recently. It can be seen that the *in-situ* analysis of some trace metals, nutrients and carbon species has been successfully covered within this time period. However, the list of approaches is not very extensive, and it is more common to find electrochemical sensors targeting other types of water than seawater, and mainly at the laboratory scale. In principle, a comprehensive analysis of the available literature may provide the reasons for this general lack of *in-situ* seawater analysis. Also, a thorough discussion of electrode designs and the analytical assessment can be expected to provide insights on water technology that could be expanded in the near future to *in-situ* seawater analysis. Concerning the electrochemical readouts, stripping voltammetry has been principally employed for trace metal analysis, whereas potentiometry with ion-selective electrodes (ISEs) has seen more use in measurement of non-redox active ions. Furthermore, amperometric biosensors making use of an enzymatic reaction are gaining momentum for the detection of nitrogen-based nutrients.

In this context, this review is structured according to the different ion analytes that have been targeted in *in-situ* seawater analysis using electrochemical sensors: metals present at trace levels (heavy metals and micronutrients) [46–50], nutrients (nitrogen and phosphorus species) [51–59] and species related to the carbon cycle [60,61]. Heavy metals and micronutrients are included within the same section because, as a general trend these two analytes are targeted simultaneously by the reported electrodes, due to their similar electrochemical reactivity and low expected presence in seawater. Voltammetric and potentiometric techniques are the main focus of the review within each analyte category, with any other approach of interest being considered separately. As mentioned above, literature related to other water matrices or laboratory scale cases are commented upon when deemed relevant to further *in-situ* and/or seawater application. A brief description of the general fundaments and expected responses of voltametric, amperometric, and potentiometric methods will now be given, as a support for readers less familiar with this field.

3. Primary working principles for the electrochemical detection of ions in seawater

3.1. Voltammetry and chrono techniques

In voltammetry, qualitative and quantitative information about a redox active analyte is obtained by measuring the current as the

Table 1

Electrochemical sensors demonstrating true application or high potential for *in-situ* seawater analysis, with special focus in the last five years.

Analyte(s)	Approx. levels in seawater	Sensor definition, LOD	*In-situ* solution	Year(s)	Ref(s)
Trace metals (Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+})	(Sub)Nanomolar	SWSV with a Hg-based electrode, 10^{-11} M	VIP (Voltammetric *In-Situ* Profiler)	1990−2020	[46,47, 48,49]
Trace metals (Zn^{2+})	Nanomolar	SWSV with a liquid crystal polymer bismuth film electrode, 1 nM	Sensors attached to an autonomous kayak	2017	[50]
Nutrients (NO_{3-} and NO_2–)	(Sub)Micromolar	Potentiometric ISEs based on ISMs after inline acidification + desalination, 1 μM	Submersible probe allowing for the microfluidic potentiometric detection	2015−2018	[51,52, 53]
Nutrients (NO_x^- and NO_2−)	(Sub)Micromolar	Amperometric biosensor with different bacteria chambers, 1 μM	Automatic profiler for controlling the depth of deployment	1997−2020	[54,55, 56,57]
Nutrients (TAN = $NH_3 + NH_4^+$)	Micromolar–Milimolar	GC/POT potentiometric electrode with a nonactine-based ISM, 1 μM	Not specified	2017	[58]
Nutrients (total phosphate)	(Sub)Micromolar	SWV with an Au electrode based on the Mo-P reaction, 1 μM	Through a microfluidic electrochemical cell	2016	[59]
C species (CO_3^{2-}, pH and Ca^{2+})	Milimolar (pH from 6 to 9)	GC/CNTs/ISM potentiometric electrodes with different ionophores, μM and pH = 9	Submersible probe allowing for the microfluidic potentiometric detection	2017	[60]
C species (Alkalinity)	pH<4	All-solid-state electrodes for electrochemically controlled acid-base titrations in thin-layer samples, pH<4	Microfluidic cell compatible with submersible probes	2019	[61]

SWSV = Square wave stripping voltammetry; ISEs = Ion-selective electrodes; ISMs = Ion-selective membranes; TAN = total ammonia nitrogen; GC = Glassy carbon; POT = poly(3-octylthiophee); CNTs = carbon nanotubes.

potential in a three-electrode cell is varied [62]. The three electrodes in the electrochemical cell for this purpose are referred to as the working, reference, and counter (or auxiliary) electrode. More specifically, the working electrode is designed in such a way as to (specifically) facilitate the transfer of charge to and from the analyte by way of reduction or oxidation. The role of the reference electrode is to control the potential at the working electrode, ensuring no current flows in the half-cell formed between these two electrodes. Finally, the counter electrode acts as a source or sink of current as needed, in order to balance the current observed at the working electrode [63].

Any voltammetric technique is classified according to the way that the potential is varied before each measurement of the current. In cyclic voltammetry (CV), the potential is linearly varied at a fixed rate (the "scan rate") and then the cycle is completed by returning to the original potential in the opposite direction (Fig. 2a). Conversely, in differential pulse (DPV) and square wave voltammetry (SWV) among others, the potential is varied in the form of pulses; see Fig. 2b and c [64]. In all of these cases, the current readout will present one or more peaks corresponding to each of the redox processes occurring at the working electrode. The peak current of such a current trace (current *versus* applied potential, the "voltammogram") ought to increase with increasing concentration of the analyte in solution, as illustrated in Fig. 2d [64]. For some specific analytes and mechanisms, it is instead the peak potential which is shifted according to the analyte concentration; however these cases lie outside of the scope of this fundamental section [65].

Another option, known as chronoamperometry, involves registering the current at a fixed potential. Instead of a voltammetric peak, the recorded current traditionally increases or decreases with the analyte concentration until reaching a steady-state value, as presented in Fig. 2e [66]. This is the most common form of readout for biosensors [67]. Of course, the possibility exists to combine one or more of these potential-application techniques, as in (anodic, cathodic or adsorptive)

stripping voltammetry, which is a widely used technique in the case of trace metal analysis [68]. One example is provided in Fig. 2f. An initial constant (cleaning) potential may be applied to the working electrode in order to regenerate its electroactive surface or original state. A subsequent constant potential is applied in order to preconcentrate the analyte at the electrode surface. According to the nature and/or effect of this potential, the technique is named either anodic-, cathodic-, or adsorptive- stripping voltammetry. Finally, a linear sweep potential is applied in order to oxidize or reduce the pre-concentrated analyte and hence obtaining the voltammetric signal for analysis purposes.

3.2. Potentiometry with ion-selective electrodes

Among potentiometric sensors, ISEs based on plasticized polymeric membranes (termed ISMs) are the most widely used at this current time. Furthermore, the all-solid-state configuration is preferred over the traditional inner-filling-solution setup, as it offers some unique advantages for decentralized measurements [1,2]. The core components of the ISM consist of a polymeric matrix, plasticizer, an ion exchanger, and a selective receptor known as ionophore [69]. In the all-solid-state concept, the ISM is conventionally deposited on top of a premodified electrode containing an ion-to-electron transducer [70]. Conversely, in the inner-filling solution configuration, the ISM is sandwiched between the sample solution and an internal reference solution placed in the core of the electrode [69]. Fig. 3a illustrates both of these configurations of potentiometric ISEs for an easy comparison.

In potentiometric ISEs, the analytical information is obtained based on the translation of an ion-exchange event at the ISM-sample interface into a voltage signal [71]. The electrochemical cell is based on a two-electrode system comprising the working electrode, that is the ISE, and the reference electrode. These two electrodes are designed in such a way that the potential at each interface is constant, except for that at the
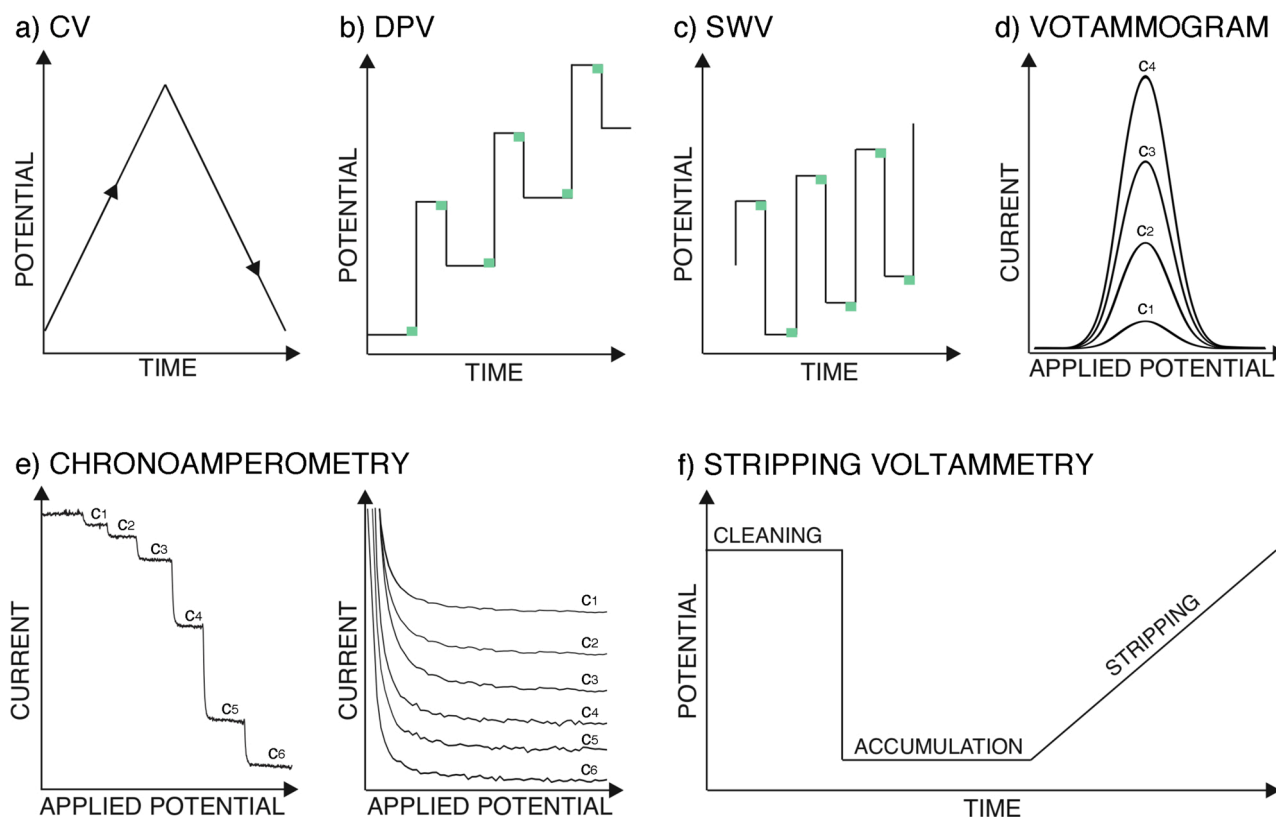

Fig. 2. Schemes for the applied potential in **(a)** cyclic voltammetry (CV), **(b)** differential pulse voltammetry (DPV) and **(c)** square-wave voltammetry (SWV). **(d)** Voltammetric peak increasing with the analyte concentration. **(e)** Time traces for the current in chronoamperometry upon subsequent (left) and isolated (right) concentration additions of the analyte. **(f)** Example of the variation of the applied potential in stripping voltammetry.
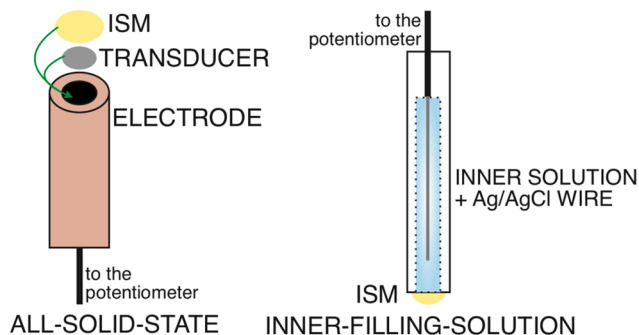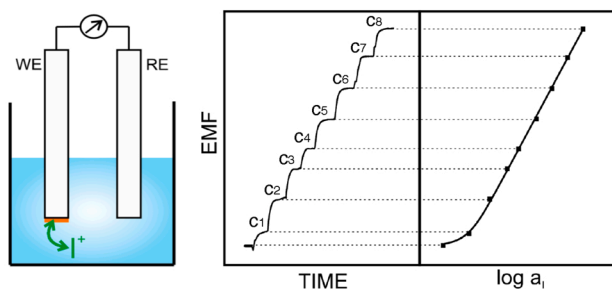
Fig. 3. (a) Schemes of the primary elements forming the all-solid-state and inner-filling-solution configurations of potentiometric ISEs. **(b) Left:** Illustration of two-electrode electrochemical cell for potentiometric measurements. The working electrode (WE) comprises an ion-selective membrane (sketched in orange). The electromotive force (EMF) is measured against the reference electrode (RE). I^+ is selected as a general cation analyte. **Right:** Typical trace of a dynamic potential response of an ISE for increasing concentrations of the cation analyte together with the corresponding calibration graph (logarithmic activity *versus* potential). Reprinted from [2] through open access Creative Common CC BY license in MDPI.

interface between the ISM and the sample. In this way, the voltage recognizes any perturbation of a sufficient magnitude that occurs in the ion activities, providing a local equilibrium. Essentially, a change in the activity of the primary ion in the bulk sample solution generates a corresponding variation in the potential the ISM-sample interface (the "membrane potential") [72]. The difference between the membrane potential and that provided by the reference electrode is given as the potentiometric readout: electromotive force (EMF) of the produced electrochemical cell.

As extensively demonstrated in the literature, the ion activity dependence of the potentiometric signal is accurately described by the Nernst equation, and the plot of the EMF *versus* logarithmic ion activity provides the calibration graph of the potentiometric ISE [71,72]. This calibration is in turn utilized to derive unknown ion concentrations in (aqueous) samples. Fig. 3**b** illustrates the working principle of potentiometric all-solid-state ISEs together with the expected response for a cation. In the case of an anion, the calibration graph is known to display negative slope [73]. Notably, potentiometric measurements occur at zero current conditions. However, voltametric ISEs in which the membrane is interrogated at a linear sweep potential, and the obtained current values depend on the exchange process at the ISM-sample interface, have been also reported [5,65,74]. In such cases, the electrodes formally belong to the voltammetric class, despite more properly being ISEs.

4. Detection of trace metals (including micronutrients)

Micronutrients are generally defined as essential elements required

by organisms in varying 'but small' quantities to orchestrate a range of physiological functions [75]. This definition applies also to the context of seawater and, therefore, information on the distribution (and speciation) of micronutrients is of critical importance for the establishment of correlations between their bioavailability and implication in biogeochemical cycles [76]. However, analytical detection of micronutrients in seawater is challenging due to its very low concentration.

Traditionally, micronutrients are classified as 'trace metals' together with other elements that fulfil the requirements 'do not contribute to salinity' and 'occur at levels of less than 1 mg kg^{-1}' [77]. More specifically:

(i) The list of micronutrients considered as trace metals in seawater includes cobalt, copper, iron, manganese, nickel, zinc, and to a lesser extent cadmium.

(ii) Mercury is also classed as a trace metal and has been identified by the World Health Organization (WHO) as the most toxic heavy metal in the environment, being one of the top 10 chemicals of public health concern.

(iii) There are some trace metals, such as lead, arsenic, and silver, whose presence in seawater can be related to certain anthropogenic activities and which are thus considered to be tracers of human-generated pollution [78–80].

Since the late 1970s there has been profound debate on the validity of trace metal analysis by means of sampling based approaches, and artefacts induced by sampling and sample handling have been demonstrated to give rise to erroneous biogeochemical interpretations. This concept is particularly important in the detection of low concentration targets, which suffer from the greatest errors in sampling-based strategies [32,46,81–83]. Thus, the very first submersible probe for seawater analysis beyond the CTD technology emerged to alleviate the need for reliable *in-situ* measurements of the less concentrated compounds in seawater, *i.e.* trace metals. In 1990, De Vitre and co-workers demonstrated for the first time *in-situ* voltammetric detection of trace metals in seawater [46]. It is not surprising that voltammetry based on the mercury electrode was selected as the first option to be adapted for *in-situ* measurements of trace metals, both in fresh and seawater: this technique has been for many years the gold-standard for the simultaneous detection of trace metals at the laboratory scale. As further benefits, the measurements require no (or very little) sample pretreatment, the instrumentation is compact and inexpensive, and automation is relatively simple [46,82].

The voltammetric probe proposed by De Vitre et al. was composed of three units (Fig. 4a): a flow-through electrochemical cell, submersible housing and control box with a communication cord [46]. The Plexiglas electrochemical cell permits the use of either a sessile mercury drop electrode (SMDE) or a mercury film electrode (MFE) in complementary manner when deploying the probe in freshwater or seawater resources. The unprecedented *in-situ* determination of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} concentrations were performed in oxygen saturated seawater over a period of one month by means of the MFE interrogated with square-wave stripping voltammetry (SWSV). Significant changes in metal concentrations were observed during the day, seemingly correlated with certain physical and biological parameters (temperature, tide, turbidity, and chlorophyll, measured with a CTD probe in a specific marine area). Although the measurements were not validated, these preliminary observations highlighted the potential utility of the probe even for the detection of species at concentration levels of 10^{-11} M [46].

Interestingly, the authors continued advancing the development of the probe, and have produced a commercially available version (Idronaut, Italy), which has been called the Voltammetric In-Situ Profiler (VIP) [48]. The VIP performance were reported academically for the first time in 1998, demonstrating discrete measurements of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} over a 60 h period in different seawater stations at a depth of up to 500 m [47]. Engineering improvements in the
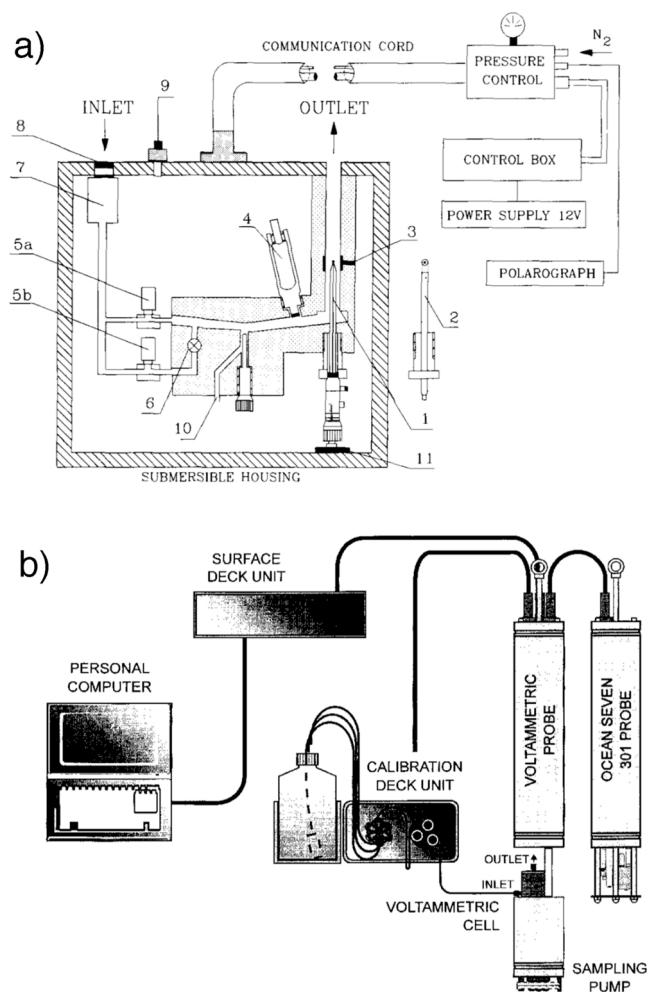
Fig. 4. (a) Schematic diagram of the *in-situ* voltametric probe. 1 = SMDE; 2 = MFE; 3=auxiliary electrode; 4=reference electrode; 5=electromagnetic valves; 7=pump; 8=filter; 9=safety valve; 10=waste; 11=stepping motor. Reprinted from [46], Copyright 2020, with permission from Elsevier. **(b)** Schematic diagram of the voltammetric *in-situ* profiling system (VIP System). Reprinted from [47], with permission from John Wiley & Sons, Inc.

submersible probe (Fig. 4b) as well as the voltammetric sensor were noticeable. For example, the incorporation of a deck unit allows for the renewal of the Hg layer in the electrode, the calibration of the probe, and the measurements of standard or collected samples. The sensor consisted of an agarose-membrane-covered, mercury-plated, iridium-based microelectrode, with alternatives available for greater biofouling resistance. Specifically, the gel acts as a dialysis membrane and thus permits the diffusion of small ions and molecules while retaining colloidal and particulate material. Furthermore, the commercially available version of VIP from Idronaut (VIPPlus) contains an even more advanced version of the sensor that is based on an on-chip microelectrode array with 5×20 interconnected iridium micro-discs, having a diameter of 5 μm and a center-to-center spacing distance of 150 μm produced by thin film technology and thereafter, electrochemically coated with Hg micro-layers and covered by the hydrophilic gel [49].

To all appearances, the VIP is the only commercially available submersible electrochemical probe for trace metal detection in seawater. Unfortunately, this probe does not detect all micronutrients, or pollution tracers beyond lead. A further inconvenience is the use of Hg in the electrode preparation, whose handling is indeed forbidden in many countries and whose use in monitoring environmental issues brings the drawback of a marked environmental footprint. A look in the literature immediately reveals great efforts at the laboratory scale to provide

electrochemical sensors for a wide variety of trace metals which can be prepared without the use of mercury. However, it is extremely difficult to find effective electroanalytical approaches that have demonstrated functionality for *in-situ* measurements in seawater.

4.1. Voltammetric methods for the detection of trace metals beyond mercury-based electrodes

Within a historical perspective, the hanging mercury drop electrode with stripping voltammetry readout has been the most widely used for trace metal detection since the mid-20th century [84]. As an alternative to the use of mercury, more recent approaches have explored the use of 'precious metals' (*e.g.* polycrystalline Au, Ag, and Pt) as well as carbon-based electrodes, which have been claimed to provide low background current, wide potential range, and considerable chemical inertness [31,85]. Even more recently, films of bismuth or other metal (loid)s (lead, tin, antimony) have been proposed as a "green" alternative, showing rather good analytical performances, although never quite reaching the excellent characteristics of the mercury electrode [30]. Such approaches have demonstrated the detection of trace metals (Cd^{2+}, Pb^{2+}, Tl^{2+}, Cu^{2+}, and Zn^{2+}, among others) at ppb levels (*ca.* nanomolar concentration), thus far demonstrated only at the laboratory scale. The electrodes require frequent polishing and surface renewal steps that in principle impede any *in-situ* application. Also, it seems that the provision of good analytical performance strongly depends on the capability of the experimentalist [86–88].

Regarding carbon-based electrodes, the spread of their use in the last decade seems to be connected to their ease of miniaturization using the screen-printing technique, together with affordability. Thus, a plethora of carbon materials have been reported for voltametric detection of trace metals: graphite, glassy carbon, carbon black, carbon nanotubes, graphene, graphene oxide, carbon nanofibers, and carbon nano-powders, to name but a few [30,89,90]. Generally speaking, these materials are accompanied by specific chemical and/or physical modification of the surface, *e.g.* adsorption, covalent grafting, electrochemical polymerization, electrochemical deposition, and nanoparticle combination [40,41, 91]. This most recent strategy in electrochemical trace metal sensor development encompasses the concepts of simultaneous single-electrode multi-element detection, and meta-statistical analysis of multi-electrode arrays.

For example, Chaiyo et al. reported a simple, low cost, and highly sensitive voltammetric sensor based on a composite that contained Nafion, an ionic liquid (IL), and graphene, modifying a screen-printed carbon electrode to simultaneously determine Zn^{2+}, Cd^{2+} and Pb^{2+} in drinking water at the nanomolar level [92]. Del Valle and co-workers described the immobilization of 4-carboxybenzo-18-crown-6 and 4-carboxybenzo-15-crown-5 on aryl diazonium salt monolayers anchored to the surface of graphite–epoxy composite electrodes for the simultaneous determination of Cd^{2+}, Pb^{2+} and Cu^{2+} by differential pulse anodic stripping voltammetry in synthetic water samples at ppb (*ca.* nanomolar) levels [93]. Then, Perez-Rafols et al. proposed an electronic tongue for the detection of Cd^{2+}, Pb^{2+}, Tl^+, and Bi^{3+} in synthetic water samples using analogous electrode modification [94]. Ion and molecular imprinted polymers [95–97] as well as metallic-shaped nanoparticles [98,99] have also been proposed for trace metal detection. Other highlighted efforts in the last five years include voltammetry analysis of Pb^{2+} in spiked water using a flower-like MoS_2/rGO composite with ultra-thin nanosheets [100], a Ni/NiO/MoO_3/chitosan 3D foam at the interfacial barrier of a p-n junction for the detection of Cu^{2+} at the micromolar levels [101], and Mn-mediated MoS_2 nanosheets as a new approach for Pb^{2+} sensing [102].

Although all of these approaches display genuine promise [30,41], there is a worrying lack of *in-situ* measurements. Moreover, analytical applications normally focus on spiked water samples and there are only some few papers related to the simultaneous analysis of trace metals in seawater in the last five years. Between those, in 2016, Zhang et al.

reported on a simple electrochemical method termed 'double stripping voltammetry' for the detection of Pb^{2+} and Cd^{2+} in seawater within a linear range of response of 0.2–3.2 μg/L and 0.1–3.2 μg/L respectively, and with a slightly below nanomolar limit of detection in each case [103]. The method consisted of three steps: (i) Pb^{2+} and Cd^{2+} present in the solution are concentrated at a working electrode based on an IL-graphite paste, which exhibits a dramatic capacity for accumulation of these two trace metals in the presence of Bi^{3+}; (ii) the electrode is transferred into an acetate buffer solution followed by a stripping procedure; and (iii) stripping voltammetry using a regular glassy carbon electrode is performed. Evidently, this is not applicable for *in-situ* measurements due to all the "by-hand" steps involved in the procedure. Nevertheless, the authors demonstrated on-site analysis of Pb^{2+} and Cd^{2+} in seawater samples after being filtered and acidified to pH 4.5, by means of a standard addition method to correct for any matrix effect. The analysis was validated with lab-based atomic absorption measurements showing an impressive correlation and extraordinary accuracy considering the high number of steps involved in the overall approach, which can be an important source of accumulative error [103].

Afkhami and co-workers recently reported the simultaneous detection of Cd^{2+}, Cu^{2+} and Hg^{2+} using SWSV by means of carbon paste electrode modified with N,N′-bis(3-(2-thenylidenimino)propyl)piperazine coated silica nanoparticles [104]. The electrode displayed detection limits of 0.3, 0.1 and 0.05 ng mL^{-1} for Cd^{2+}, Cu^{2+} and Hg^{2+} (picomolar concentration), eminently suitable for the analysis of various environmental water samples. In particular, the authors demonstrated validated lab-based analysis of non-spiked gulf water samples, providing a content of *ca.* 1, 10 and 4 ng mL^{-1} for Cd^{2+}, Cu^{2+} and Hg^{2+}.

Some interesting examples of voltammetric electrodes described for the detection of a single trace metal (beyond the traditional multi-ion analysis) will be expounded upon presently. An *in-situ* sensor based on a liquid crystal polymer bismuth film electrode has been reported in the literature that can be directly deployed for the determination of Zn^{2+} concentrations as low as 1 nM at a deposition time of 180 s by SWSV [50]. A flexible sensor array consisting of four paired sensors was attached to the hull of an autonomous kayak, which was remotely operated to calculate traces of Zn^{2+} in seawater. Regular surface measurements in three different locations were carried out and the results were validated by ICP-MS analysis of collected water samples. However, no concentration calculation was shown in the paper and, uncommonly, the validation was accomplished by converting the Zn^{2+} concentrations provided by ICP-MS (values not reported) into the current expected from the electrochemical method and comparing these results with empirically measured *in-situ* currents.

Regarding lab-based approaches for seawater sample analysis, Han et al. reported an interesting approach for Cu^{2+} speciation in seawater based on acupuncture needles functionalized with dendritic gold nanostructures and Nafion, reaching a limit of detection of 15 picomolar [105]. Dissolved active copper was directly analyzed in seawater samples, whereas for the dissolved acid extractable and total acid extractable fractions sample pretreatment was needed before using the electrode. Wei and co-workers demonstrated the detection of Cu^{2+} (5 nanomolar) in seawater by a glassy carbon disk electrode modified with core-shell microspheres of gold/manganese dioxide interrogated by anodic stripping voltammetry [106]. Hrastnik et al. have recently published a paper on Ni^{2+} detection in seawater with a new copper film electrode as a simple and environmentally-friendly sensor by means of adsorptive stripping voltammetry [107]. However, the sensor has to be used in conjunction with nioxime as nickel-binding ligand, and with pH adjustment to 9.2, which evidently hinders any further development of the concept for *in-situ* applications. Although a very deep interference study was presented, which envisions the success of the sensor in seawater samples, only one spiked seawater analysis was performed.

Ma et al. presented a novel poly(sodium 4-styrenesulfonate)/wrinkled reduced graphene oxide composite modified glassy carbon electrode for the detection of Zn^{2+} in seawater by differential pulse voltammetry [108]. Only seawater samples containing around 300 nmol L^{-1} (sub-micromolar levels) of Zn^{2+} were analyzed, despite the sensor presenting a limit of detection of *ca.* 2 nanomolar. Lahrich and co-workers showed sub-micromolar detection of Cd^{2+} in seawater samples from different locations by means of a carbon paste electrode modified with potassium lacunar apatite $KCaPb_3(PO_4)_3$, after the sample was acidified to a pH value of 1.37 [109].

In 2018, the determination of Fe^{2+} in seawater was extensively reviewed, showing an interesting description of all available analytical techniques and focusing on real potential towards *in-situ* analysis of seawater [29]. The authors concluded that, currently, there is no clear solution for Fe^{2+} detection, and indeed for any other trace metal, that can exceed the VIP [29]. Nevertheless, in the last five years, several researchers have reported on endeavours towards iron determination. Of special interest are the papers published by Pan and coworkers on Fe^{2+} voltammetric detection based on graphene oxide electrodes combined with nanoparticles [110,111]. The authors successfully demonstrated nanomolar detection in seawater samples from different locations.

The *in-situ* provision of Hg^{2+} and Pb^{2+} levels in seawater together with arsenic speciation has become a 'hot topic' in recent years, likely because of an increasing worldwide concern with water pollution issues [112]. However, the voltammetric approaches published until now are far from *in-situ* applicability, mainly due to the required pre-treatments that become even more complex if speciation is desired. Scientific publications of the last five years regarding Hg^{2+}, Pb^{2+} and arsenic speciation, providing an appropriate limit of detection for true applicability in seawater, are lacking in the literature, even if only lab-based or shipboard measurements are considered. Lahrich and co-workers demonstrated the detection of Hg^{2+} with an electrode based on lacunar apatite $NaPb_{4-x}Cd_x(PO_4)_3$ (where $0 \leq x \leq 2$) [113]. However, the limit of detection achieved only allowed for Hg^{2+} analysis at concentrations higher than micromolar in seawater. Izquierdo's group has recently reported on the comparison of the modification of screen-printed carbon graphite electrodes with single-walled carbon nanotubes, electro-reduced graphene oxide and gold nanoparticles for Pb^{2+} detection at sub-nanomolar levels in seawater [114]. Despite the sensors reaching a limit of detection of *ca.* 3×10^{-10} M (slightly lower than nanomolar), analytical applicability was demonstrated only in spiked samples. Finally, for arsenic detection/speciation, some recent reviews confirm the current lack of effective voltammetric tools in seawater [39,115].

4.2. Ion-selective electrodes for the detection of trace metals

Very recently, Banks and co-workers have discussed current advances related to electrochemical methods, electrode materials, and modifications that have potential as the foundations of a new generation of portable electrochemical sensors for trace-level *in situ* heavy metal sensors [30]. Although the review focuses on drinking water applications, it offers a clear inspection of the panorama of electrochemical detection of trace metals. In particular, the use of potentiometric ISEs based on ion-selective membranes (ISMs) that are formulated for very low limits of detection is highlighted against traditional stripping voltammetry for trace metal detection. In this context, and going back in time to 2006, it is important to mention the elegant approach reported by Pretsch et al. that proved suitable for the detection of subnanomolar concentrations of Ca^{2+}, Pb^{2+} and Ag^+ with separate electrodes comprising ISMs with a different receptor for each cation [116]. However, the principle relied on the use of inner-filling solution electrodes in a nanopipette tip inserted in a silicone tube that can analyze 3 μL of sample, which is not suitable for *in-situ* measurements. Most notably, it was demonstrated that the control of ion fluxes is crucial to reach such a low limit of detection with potentiometric sensors. Taking inspiration from that seminal paper, several groups have reported various approaches for this purpose, although only one that could be deployed for

in-situ measurements, involving the application of current polarization. This latter concept is in fact applicable to all-solid-state ISEs. Overall, the reported protocols have demonstrated limits of detection which differ from those at zero current measurements by no more than one order of magnitude [117].

In another approach, Cui et al. recently reported an array of micro-ISEs working in potentiometric mode with membranes containing receptors for Pb^{2+}, Cd^{2+}, Hg^{2+} and AsO_2^- [118]. The micro-ISE array demonstrated the determination of ppb levels (*ca.* nanomolar) in drinking water thanks to a reduction of the thickness of the ISM to the micrometer range, compared to the millimeter size traditionally used in ISEs. The next step that the reader may expect is the extension of the concept to seawater analysis, and implementation for *in-situ* measurements. The group of Qin presented the detection of anionic mercury species ($HgCl_3^-$) using *tert*-butylcalix [4]arene-tetrakis(*N,N*-dimethylthioacetamide) as anion-selective ionophore in the ISM [119]. An asymmetric membrane in a rotating ISE configuration was used for the detection of mercury at nanomolar levels in samples containing 0.05 M NaCl background electrolyte, *i.e.* seawater diluted by a factor of ten.

Anyone working in the field of ISEs based on ISMs that contain ionophores as the selective element for the potentiometric signal is aware of the difficulty in seawater analysis arising from strong interference of the 'saline content' (Na^+ and Cl^-, in the detection of cations and anions respectively). Limitations are especially tangible in cases where the ion analyte is present in the sample at trace levels and the NaCl concentration is between 6 and 9 times higher: even using very selective ionophores for the trace metal, reliable potentiometric measurements could be called into question [120,121].

In an attempt to improve the selectivity of ISMs, Xu et al. recently reported on all-solid-state silver-selective ultrathin membranes for the subnanomolar detection of Ag^+ ions [122,123]. The ISM is interrogated under an accumulation/stripping protocol, rather than potentiometry, in order to control ion fluxes at the sample-membrane interface as a strategy to reduce Na^+ interference in seawater. Detection of Ag^+ concentration in the range of $0.1-10$ nM in different water samples was presented. Granado-Castro and co-workers showed an analogous approach based on a liquid membrane containing 2-hydroxybenzaldeydebenzoylhydrazone in toluene for the separation and preconcentration of Fe^{3+} [124]. The process was very selective for Fe^{3+} with respect to Fe^{2+} in the submicromolar level, even in seawater matrix. Thus, the authors were able to obtain the distribution of total dissolved iron, non-labile iron, labile Fe^{2+} and labile Fe^{3+} fractions in real seawater samples subjected to different pre-treatments. The results were in good agreement with those obtained by regular adsorptive cathodic stripping voltammetry. The potential for this system to be translated into a pure electrochemical method is evident.

Overall, the development of ISEs for trace metal detection in seawater has not expanded much in the last five years, despite their undeniable potential to be easily implemented into submersible probes [1,5,27]. To address the strong influence of the seawater matrix, it is necessary to adopt inline strategies that allow the selectivity of ISEs to be improved (see below the case of nutrient detection). The lack of any such strategy in the literature renders it difficult to see membrane-based ISEs for trace metals operating in *in-situ* measurements, until the detection principle is fundamentally proposed and demonstrated for real seawater samples at the laboratory scale.

5. Detection of nutrients related to nitrogen and phosphorous cycles

Nutrients in seawater are defined as dissolved chemical constituents important for the growth of organisms that inhabit the medium [125]. The most critical of these nutrients are nitrogen and phosphorus compounds, which play a major role in stimulating primary production by plankton in the oceans [37]. Importantly, the disturbance of its natural equilibrium by the addition of excessive concentrations of certain species, mainly caused by human activity, is known to be detrimental to the aquatic ecosystem. Uncompensated levels of nitrogen and phosphorous generally reach seas and oceans through anthropogenic discharges along recessed coastal water bodies. Then, it is possible that the sea or ocean is not able to dilute these inputs as a natural sink, leading to a serious impact on living organisms (*e.g.* losses in biodiversity, ecosystem degradation, harmful algae blooms), deterioration of water quality, and ultimately affecting human health [125,126].

The monitoring of species relevant to the nitrogen and phosphorus cycles in water has been extensively accomplished by environmentalists, but again, using sampling-based approaches with all the associated drawbacks [26,127]. An alternative to these analyses is the remote control of the 'color of the ocean' by satellite images that reveal the global grow of phytoplankton and/or chlorophyll-a [128]. Nevertheless, the challenge is to prevent water equilibrium alteration by the early detection of alarming situations before the damage is done to the water landscape [12,129,130]; it is this that constitutes the ultimate goal of submersible probes based on electrochemical sensors [1,5].

5.1. Nitrogen species: nitrate, nitrite and ammonium (NO_3^-, NO_2^- and NH_4^+)

Among nitrogen species, various inorganic compounds may be found depending on water properties. In aerobic waters, nitrogen is mainly present as N_2 and NO_3^-, and it may also occur as N_2O, NH_3, NH_4^+, NO_2^- and, more rarely, as HNO_2 and HNO_3 [131]. In particular, NH_4^+, NO_3^- and NO_2^- ions play the most important role in biochemical processes, and thus several articles have been published over the years concerning their electrochemical detection in seawater and other waters.

5.1.1. Amperometric/voltammetric electrodes for NO_3^- and NO_2^-

Voltammetric/amperometric sensing of nitrate (NO_3^-) is possible owing to its electrocatalytic reduction, which has been studied for decades [132]. Generally, the reduction reaction is accomplished on metallic electrodes and leads to the generation of many intermediate products, including nitrite, hydrazine, hydroxylamine, ammonia, and oxygen species [132]. Notably, it seems that the mechanism of nitrate reduction is still an open discussion today [35]. It has been demonstrated that the analytical performance of electrochemical sensors based on NO_3^- reduction strongly depends on the composition and structure of the electrode materials, as well as sample matrix composition and pH. The majority of electrodes show limits of detection in the order of micromolar levels, indeed very similar to that observed in potentiometric determination of NO_3^- (see below). However, seawater analysis has not been really explored in the last five years [35].

The group of Garcon has recently reported on the electroreduction of NO_3^- in synthetic samples with high salinity by a gold electrode modified with silver nanoparticles [133]. The authors demonstrated limits of detection covering the expected levels of NO_3^- in open sea, *i.e.* 0.39–50 micromolar. Later on, Lebon et al. demonstrated electroreduction of NO_3^- in artificial seawater at the sub-nanomolar level by similar electrodes prepared with a new *in-situ* metal organic deposition method [134]. SWV was successfully used without any pre-concentration or pH adjustment in the sample. Seemingly, the characteristics of the nanoparticles largely influence the analytical features of the sensor, a factor which could be advantageous in developing an effective strategy for *in-situ* NO_3^- determination in seawater.

Voltammetric/amperometric detection of nitrite (NO_2^-) is also possible, and indeed has been extensively demonstrated in the last five years in the analysis of a variety of samples, although again not in seawater. Thus, different electrode materials can be found in the literature as the basis of NO_2^- detection: boron-doped diamond electrode (limit of detection of 20 µM) [135], Ag/Cu/MWNT nanoclusters (1 µM) [136], gold nanoparticles/poly(methylene blue)-modified pencil graphite electrode (5 µM) [137], glassy carbon electrode modified with gold-copper nanochain networks (10 µM) [138], rose-like

AuNPs/MoS$_2$/graphene composite (5 μM) [139], palladium-nanoparticle-functionalized multi-walled carbon nanotubes (0.05 μM) [140], Prussian blue (9 μM) [141], CeO$_2$−SnO$_2$ nanocomposite loaded on Pd (0.1 μM) [142], nickel (II) phthalocyanine modified graphite (0.1 μM) [143], carbon electrode modified with hemin/titanium dioxide nanotubes nanocomposite (0.6 μM) [144], graphene nanoribbons (0.2 μM) [145], NiO nanoparticles and multi-walled carbon nanotubes (0.3 μM) [146], interdigital electrodes modified with nanogold film and chrome-black T (10 μM) [147] and different carbon nanomaterials [34], among others.

Overall, limits of detection slightly lower than micromolar can be attained with the above-listed approaches, with few examples demonstrating seawater application based on spiked samples that attempt to mimic nitrite polluted cases. For example, Zhang et al. reported on a glassy carbon electrode modified with Ag/Cu nanoclusters and multi-walled carbon nanotubes [136]. Nitrite ion sensing with a limit of detection of 1 μM by means of cyclic voltammetry was shown. The analytical applicability of the sensor was presented in seawater samples spiked with 0.1 mM of NO$_2^-$. Jin and co-workers presented a micro-fabricated silicon-based electrochemical sensor with a limit of detection of *ca.* 30 μM [148]. The electrode was utilized to detect NO$_2^-$ concentration in spiked seawater samples in the concentration range of 0.5−7 mM, which is quite high in comparison to the expected levels in seawater.

Amperometric biosensors have been described for the determination of both NO$_3^-$ and NO$_2^-$ [25]. Essentially, both anions can undergo redox transformations induced by living cells (including enzymes) as the basis of the biosensor working mechanism. While some excellent efforts have been put forward in this field, the biosensors generally present really short lifetimes. It is important to highlight the nitrate/nitrite microbiosensors presented by Revsbech et al. in 1997 and 2004 [54,55], even though that papers were published before the period under scrutiny in this review. The biosensor for NO$_3^-$ contained immobilized denitrifying bacteria and a reservoir with a liquid growth medium, as depicted in Fig. 5**a** [54]. The bacteria are able to reduce NO$_3^-$ to N$_2$O that is subsequently quantified by a built-in electrochemical transducer for N$_2$O. However, it was found that the sensitivity to NO$_2^-$ was identical to that for NO$_3^-$, and therefore in a real sample the biosensor would respond to both NO$_3^-$ and NO$_2^-$. The limit of detection for NO$_3^-$ was *ca.* 1 μM and the biosensor was used in synthetic seawater and for concentration profiling in sediments that were incubated with seawater samples spiked with nitrate. The NO$_2^-$ biosensor is based on bacterial reduction to N$_2$O by *Stenotrophomonas nitritireducens*, which is an organism with a

denitrifying pathway deficient in both NO$_3^-$ and N$_2$O reductases [55]. The limit of detection for NO$_2^-$ was *ca.* 1 μM and the biosensor was tested in synthetic water with different levels of salinity and was used to measure NO$_2^-$ profiles in marine sediments. Despite the potential of this type of biosensor towards accurate nitrate/nitrite measurements being evident, the authors realistically stated in their publications that the construction of the electrodes is complicated, and specified that the bacterial cultures used in the biosensors should always be kept fresh.

The commercial version of the nitrate/nitrite biosensors proposed by Revsbech and co-workers was used to be served at Unisense [25] as a NO$_x^-$ biosensor that can measure NO$_x^-$ and NO$_2^-$ concentrations as low as 0.5 μM, claimed to be suitable for measurement in soil slurries, drinking water, wastewater, and water from lakes, streams and seas [57]. Essentially, the biosensor is compatible with two versions of the biochamber depending on the bacteria: one for nitrate/nitrite (NO$_x^-$) and the other for nitrite (NO$_2^-$) measurements. In the case of a psychrotrophic bacteria, the biosensor can be used in low–temperature seawater for the analysis of nitrate + nitrite (NO$_x$–) [56]. The sensor demonstrated to resolve concentrations below 1 μM at low temperature (< 2.5 °C) and high salinity (35‰). Furthermore, *in-situ* utilization in the deep sea was presented by measuring NO$_x$– profiles in sediments down to 1500 m depth, where the temperature was 2.5 °C. For example, at 70 m depth the measurements showed very heterogeneous NO$_x$– profiles with pronounced maxima due to nitrification in the oxic surface layer, as observed in Fig. 5**b** [56].

In the context of amperometric biosensors, an inspection of the literature reveals a great number of papers related to NO$_2^-$ detection and a clear absence of NO$_3^-$ biosensors in the last five years. This is likely due to the scarcity of bacteria or enzymes with satisfactory specificity for NO$_3^-$ rather than for total NO$_x^-$. In the case of NO$_2^-$, Gahlaut et al. recently published a very complete review about enzyme-based biosensors for its detection mainly in drinking water and foods [149]. The paper commented on the preparation of biosensors with non-specific proteins as well as nitrite reductases (either through nitric oxide or ammonia forming), highlighting the use of nanomaterials to enhance the analytical performance. In particular, the authors anticipated that nanomaterials such as nanorods, nanowires, nanoparticles, nanohybrids, carbon nanotubes, and nanocomposites will soon emerge as powerful elements of bioelectronic devices, especially for NO$_2^-$ detection. As an example of this trend, Liu and co-workers reported on Co$_3$O$_4$ nanosheets immobilizing horseradish peroxidase together with reduced graphene oxide to modify a glassy carbon electrode for a mediator-free nitrite biosensor [150]. The electrode showed a limit of detection of 0.2 μM but,
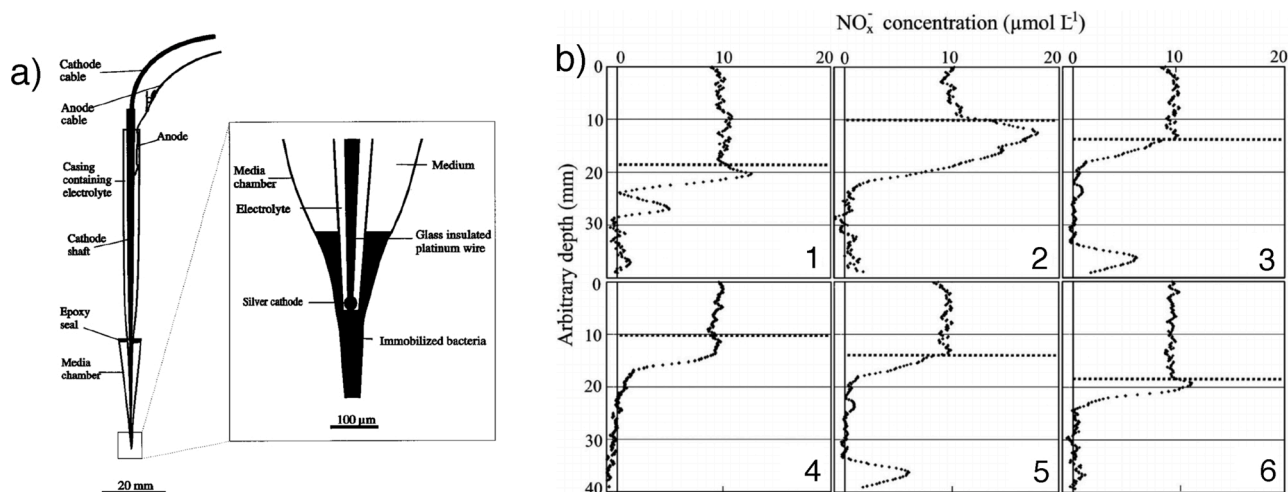

Fig. 5. **(a)** NO$_3^-$ biosensor based on bacterial reduction of NO$_3^-$ to N$_2$O with subsequent detection of the N$_2$O. Reprinted from [54] with permission form the ACS. **(b)** *in situ* NO$_x$– profiles measured at 70 m depth and 12 °C. The estimated sediment surfaces are indicated with broken lines. Reprinted from [56], with permission from John Wiley & Sons, Inc.

unfortunately, the applicability was demonstrated only in spiked water samples containing 100 μM of NO_2^-.

5.1.2. Potentiometric ion-selective electrodes for NO_3^- and NO_2^-

Potentiometric nitrate and nitrite-selective electrodes based on ISMs have been thoroughly described in the literature, both in the inner-filling solution configuration and all-solid-state format, and nitrate-selective electrodes are commercially available from many companies [151–157]. Some methods comprising nitrate and nitrite-selective electrodes are indeed included in the Environmental Protection Agency (EPA) protocols for water analysis [158,159]. Despite being extensively applied in agricultural samples, wastewaters, and fresh-water, among others [151,160–164], nitrate and nitrite-selective electrodes have not often been applied directly to non-spiked seawater samples. The greatest challenge in the potentiometric detection of nitrate and nitrite with membrane ISEs is the strong interference caused by chloride ions, which are present in high concentrations in saline water compared to NO_3^- and NO_2^- (0.6 M chloride *versus* (sub)micromolar

concentration) [52].

Five years ago, it was demonstrated that online desalination of seawater allowed for chloride reduction to millimolar level prior to potentiometric readout with an all-solid-state nitrate-selective electrode in flow mode [52]. The response of the sensor was presented over a linear range of response from 5×10^{-5} to 1×10^{-3} M compared to the almost zero response towards NO_3^- in (untreated) highly saline matrix. The desalination occurs in a fluidic cell that is inline coupled with the potentiometric flow cell. Essentially, the application of a constant potential is responsible for the electroplating of chloride in the form of AgCl in the working electrode of the desalination cell. Then, the linear range of response of the ISE can be widened to include micromolar levels if the seawater sample is acidified [53]. The same outcomes were demonstrated for NO_2^-, which was found to be detectable in acidified-desalinated seawater at the micromolar levels, as can be seen in Fig. 6a and b [51,53].

The inline acidification-desalination-potentiometric detection of NO_3^- and NO_2^- was implemented in a microfluidic circuit (Fig. 6c and d)
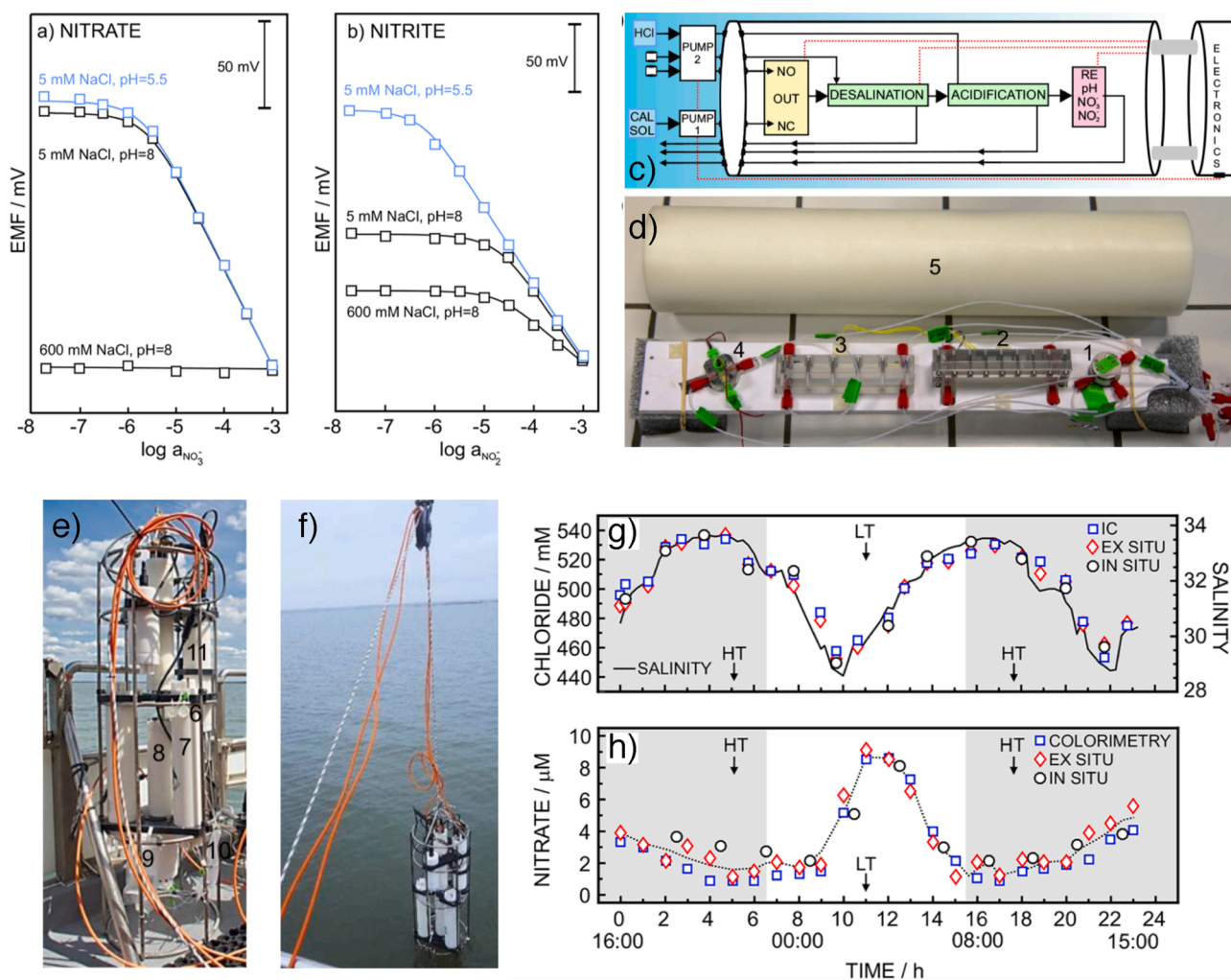

Fig. 6. Calibration graphs obtained for **(a)** nitrate and **(b)** nitrite using a flow potentiometric cell based on miniaturized all- solid-state electrodes. **(c)** Scheme of the fluidics developed for *in situ* measurements (NO = normally open, NC = normally closed, CAL SOL = calibration solution, RE = reference electrode). **(d)** Image of the submersible probe based on the valve (1), the desalination module (2), the acidification module (3), and the potentiometric flow cell (4). The system is placed inside a water- and pressure-proof cylindrical housing (5) made of acetylic copolymer (Deldrin). **(e)** Probe incorporated into a titanium cage together with a submersible peristaltic pump and a CTD multiparemeter probe (6=filter for seawater; 7=pump; 8=unit containing the electrochemical sensors; 9=bag containing the calibration solution; 10=bag containing the HCl solution; 11 = CTD). **(f)** Submersible device deployed in the Arcachon Bay from a boat using a small onboard crane. **(g)**Salinity and chloride profiles. **(h)** Nitrate profile during the deployment of 23 h (starting from May 15, 2017 at 16:00 to May 16, 2017 at 15:00) in the Arcachon Bay (44°40.822′N 1°06.007′W). The deployment depth was 2.3 ± 0.3 m. Light hours are shaded in gray. HT = high tide; LT = low tide. Reprinted from [51] (https://pubs.acs.org/doi/abs/10.1021/acs.analchem.7b05299), with permission from the American Chemical Society (ACS). Further permission related to the material should be directed to the ACS.

inside a programmable and autonomous submersible probe developed in collaboration with the company Idronaut (Italy), see Fig. 6e and f [51]. Specialized (and miniaturized) peristaltic pumps are programmed to pump seawater through the submersed sensors. The entire device follows a similar design to the VIP in terms of materials, fabrication and operation. The submersible probe for NO_3^- and NO_2^- detection was deployed in the Bordeaux Bay to monitor changes in these two nutrients under the low and high tide regimes [51]. Nitrite levels were too low to be detected by the sensors, whereas *in-situ* nitrate measurements showed a tidal influence on the nitrate concentration: maximum nitrate levels (*ca.* 9 μM) coincided with low tides, and low salinity, aligned to a higher influence of freshwater inputs in the bay, as can be observed in Fig. 6g and h [51]. All results were validated with the appropriate gold standard techniques.

5.1.3. Potentiometric ion-selective electrodes for NH_4^+

Very recently, a review has discussed the various reason why ammonium detection with ISEs based on ionophore-containing membranes is so challenging [165]. Even though an abundance of ammonium ionophores have been proposed in the literature, these always suffer the effect of interference from K^+ (and to a lesser extent Na^+) rendering complicated their application in real samples such as seawater. Examples can be found of ammonium-selective electrodes, mainly based on nonactin as ammonium ionophore, which can function in freshwater samples, even for *in-situ* measurements in lakes (depth profiling) [166,167], whereas very few papers of recent times show NH_4^+ detection in seawater. Of these, only one includes *in-situ* demonstrations.

Ding et al. presented a solid-contact potentiometric sensor for *in-situ* detection of total ammonia nitrogen (TAN, free ammonia plus the ammonium ion) in seawater [58]. The electrode consisted of a glassy carbon electrode modified with poly(3-octylthiophene) as the ion-to-electron transducer with a nonactin-based membrane on top. Then, a polyvinyl alcohol hydrogel film (pH 7.0) and a gas-permeable Ag/AgCl electrode are deposited on this selective membrane, as illustrated in Fig. 7a-c. The total amount of NH_3 gas dissolved in the seawater sample passes through the gas-permeable layer and is consequently converted into NH_4^+ at the local pH of 7.0. The NH_4^+ thus formed is then detected by the nonactin-based membrane operating in potentiometric regime [58]. The electrode was demonstrated to respond to TAN in seawater from a concentration of 1 μM and was tested in non-spiked seawater samples. A good correlation between the TAN calculated by a continuous flow analyzer and from the data provided by the new sensor was observed. This contribution is undoubtedly an elegant approach that could be easily implemented into a submersible probe for *in-situ* water analysis. Nevertheless, it would be beneficial for the authors to expand the investigations to include analysis of synthetic NH_4^+/NH_3 mixtures, in order to demonstrate indisputably that the sensor quantifies TAN and not simply NH_3.

The lab-on-a-chip microfluidic device proposed by Gallardo-Gonzalez et al. for real-time *in-situ* detection of NH_4^+ is a relevant example, although not applied to seawater analysis [168]. The results presented were concerned exclusively with sewage analysis; however, it seems probable that the system can be adapted for compatibility with *in-situ* seawater measurements [168]. The device is based on a microfluidic structure made of poly-(dimethylsiloxane) that contains all-solid-state gold microelectrodes modified with the conducting polymer polypyrrole[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$] and an ISM containing nonactin as ammonium ionophore. The electrode presented a limit of detection in the range of 10^{-5} M. The device was immersed in a real municipal sewage pipe, and the observed potentiometric profiles were compared in terms of response time with a conductivity sensor. Unfortunately, the authors did not provide calculations of the NH_4^+ concentration in the sewage, and no gold standard technique validation was presented [168].

At the time of writing, the lowest limit of detection for NH_4^+ in environmental water (*ca.* 10^{-7} M) has been reported by using a
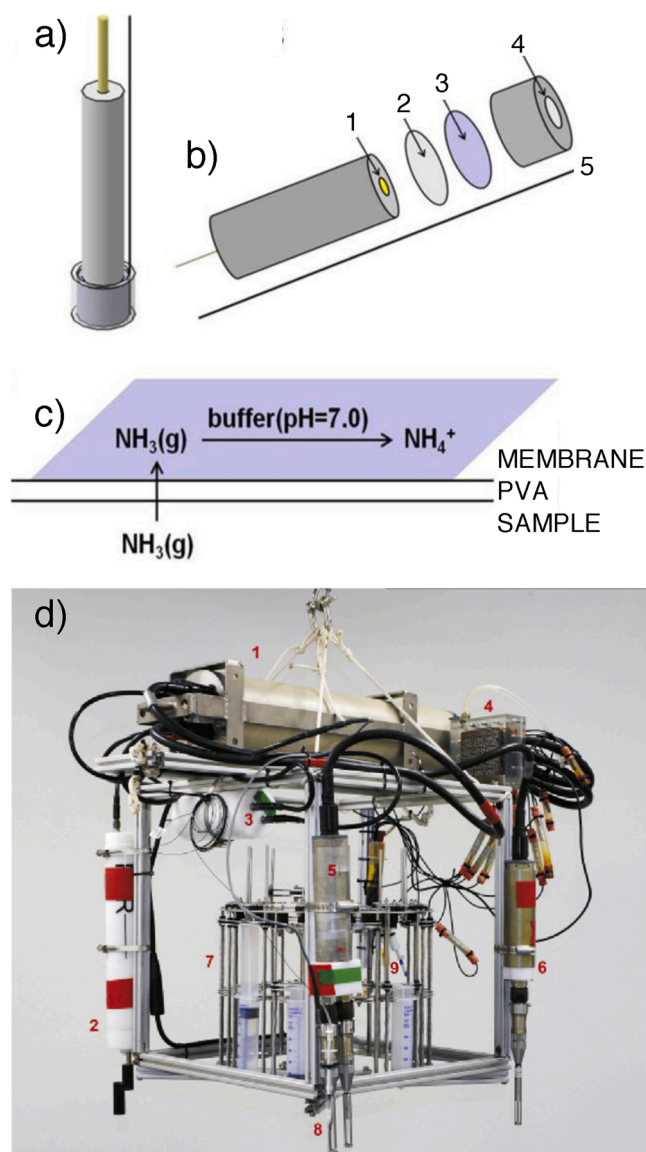
Fig. 7. (a) Schematic diagram of the solid-contact potentiometric sensor for TAN. **(b)** Components of the sensing system. **(c)** Processes occurring at the sample-membrane interface and in the thin film of poly(vinylalcohol) (PVA) hydrogel. Labels of 1, 2, 3, 4 and 5 refer to the hydrophobic conductive polymer poly (3-octylthiophene) coated on the glassy carbon electrode, ammonium-selective polymeric membrane, buffered PVA hydrogel film of pH 7.0, outer hydrophobic gas-permeable membrane and Ag/AgCl electrode, respectively. Reprinted from [58], open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/). **(d)** Portrayal of setup of the PIA: 1=pressure housing (containing computer, electronics and batteries); 2 = CTD probe; 3=optode module; 4=impedance converter for potentiometric channels (for example pH, redox, S^{2-}); 5=O_2 preamplifier; 6=S^{2-} preamplifier and amperometric S^{2-} microsensor; 7=syringe sampler; 8=O_2 sensor (micro-optode embedded within a syringe); and 9=ammonium-selective electrode and reference electrode with galvanically separated amplifiers. Reprinted from [5], Copyright 2020, with permission from Elsevier.

potentiometric sensor reported by Alfaya's group in 2007 [169]. Although the sensor presents selectivity coefficients for K^+ and Na^+ in a similar range as ISEs based on nonactin (logarithmic selectivity coefficient of $logK_{NH4, J}^{pot} \sim -1.2$, for J = K^+ and Na^+) [165], it would be worthwhile to test the sensor in seawater in view of its very low limit of detection. The electrode consisted of a carbon paste with the SiO_2/ZrO_2/phosphate-NH_4^+ composite, which behaves in a similar

manner to the ISM in regular ISEs, by exchanging cations (in this case NH_4^+) with the sample solution. The ammonium content of 13 natural water samples was determined to be in the range of $1-14$ mM, without any visible matrix interference. The results were validated using the Barthelot method, showing an excellent correlation [169].

Finally, for the potentiometric detection of NH_4^+, the profiling ion analyzer (PIA) that Athavale et al. demonstrated to obtain *in-situ* ammonium depth-profiles in lakes is deserving of comment [166,167]. The PIA is a truly smart device, combining many different sensors for a complete characterization of the water column and including sample collection that is programmed for different depths (see Fig. 7d) [5]. Any all-solid-state ISE can be simply incorporated to obtain different concentration profiles. The ISEs are in direct contact with the water, as opposed to using a fluidic inlet, and hence it is not possible to implement any in-line pretreatment to improve the limit of detection of the sensors, which would provide a tremendous advantage in seawater measurements. Undoubtedly, the PIA could serve as an inspiration for further NH_4^+ measurements in seawater.

5.2. Phosphates: HPO_4^{2-}, PO_4^{3-} and H_2PO_4-

5.2.1. Amperometric / voltammetric electrodes for phosphate detection

Some of the most successful voltametric phosphate electrodes reported to date are based on the same chemical principle as the colorimetric gold standard technique for phosphate: the molybdenum blue reaction [170–174]. For example, the approach reported by Murphy and Riley described the use of ascorbic acid to reduce the phosphomolybdate complex which is generated in the reaction of phosphate with the molybdenum blue in the presence of potassium antimony tartrate as catalyst in acidic medium [175,176]. The Mo-P complex can be reduced electrochemically with ascorbic acid, or other reductants.

The group pf Garcon reported in 2016 the electrochemical generation of molybdate by the oxidation of a molybdenum electrode accompanied by the electrochemical release of hydrogen ions (for the required sample acidification) through a cation-exchange membrane [59]. Then, the electrochemical detection at the gold electrode of the complex resulting from the reaction between PO_4^{3-} and the molybdate, $\left[PMo_{12}^{(VI)}O_{40}\right]^{3-}$, provides the total phosphate concentration in the sample. The phosphate speciation at the autogenerated acidic pH is entirely in the form of PO_4^{3-}. Impressively, a specially designed electrochemical cell fulfils the bifunctional purposes of delivering the required reagents *in-situ* to the sample solution and the final electrochemical detection, as shown in Fig. 8. This artful concept is the result of some years of extensive work by the group of Garcon the field of *in-situ* detection of phosphate in seawater [177]. One alternative to this method is the use of microfluidic devices for the delivery of the needed reagents, which was demonstrated by Chen et al. in 2018, with the advantage of being compatible with colorimetric and electrochemical detection of the Mo-P complex [178]. However, while the authors proposed that the device is suitable for *in-situ* measurements, issues related to pressure are expected to arise during such deployments.

Sun et al. recently reported on the direct electrochemical determination of phosphate based on the oxidation of coordinated OH during the phase transition of calcium phosphates [179]. The reagents needed for the creation of these calcium phosphates were generated *in-situ* by means of immobilization on Nafion-modified glassy carbon electrode. The sensor presented a linear response for phosphate in the range of $0.1-10$ μM, in the presence of 1 mM Ca^{2+}. Application in real samples was not shown, although the analytical features are highly promising.

A novel type of electrochemical sensor for the detection of phosphate in water samples has been published by Ding et al. [180], which combines the interfacial barrier of a p–n junction with the adsorption of phosphate. The electrochemical response was generated by inducing a change in the barrier height, which was caused by the specific adsorption of phosphate. The limit of detection was not quite sufficient for
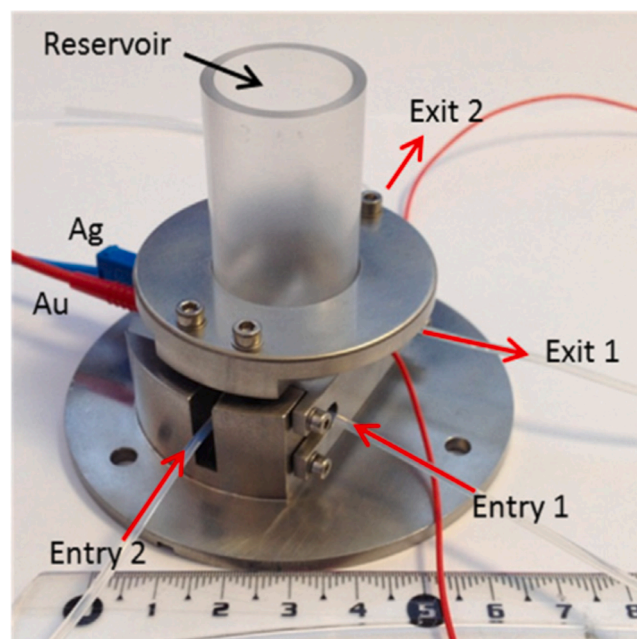

Fig. 8. Image of the laboratory prototype for *in-situ* detection of PO_4^{3-} in seawater without any liquid reagent addition but creating the phosphate complexation as well as its detection in the same compartment by electrochemical control. Reprinted from [59], Copyright 2020, with permission from Elsevier.

seawater measurements, but the sensor meets the requirements of the World Health Organization for drinking water (1 mg L^{-1} of phosphate). This approach, although still immature, shows promise for application in seawater samples while providing simplicity to the electrode fabrication and readout. In contrast, other recent strategies based on biomaterials appear rather complicated when attempting the translation into an *in-situ* context [181,182].

5.2.2. Potentiometric ion-selective electrodes for the detection of phosphates

The most recent advances described in the literature for potentiometric detection of phosphate species (mainly HPO_4^{2-}, which is the predominant species at environmental pH) [183] are based on strategies beyond the use of traditional phosphate-ionophore-containing ISMs [12, 44,184]. This is a consequence of the difficulty, even when using the most selective examples of such receptors, in achieving a limit of detection lower than micromolar concentration [185–189]. Evidently, some interesting new potentiometric approaches have been reported, but these remain far from clear suitability for deployment in *in-situ* seawater analysis.

Topcu et al. introduced a HPO_4^{2-} potentiometric electrode based on a chitosan-smectite nanocomposite that was prepared by intercalation of protonated chitosan molecules into the interlayer space of smectite by a cation exchange mechanism [190]. The nanocomposite was then incorporated into a plasticized polymeric matrix and finally conditioned in Cr(III) solution. Seemingly, the response towards HPO_4^{2-} is reliant on the presence of both the nanocomposite, which acts as both ion-exchanger and ionophore, and the Cr(III) ion in the membrane lattice; however, this effect was unfortunately not fully explained by the authors. While a limit of detection lower than the micromolar level and a rather good selectivity towards chloride (logarithmic selectivity coefficient of $logK_{phosphate, J}^{pot} \sim -3$, with J = chloride anion, which could be suitable for seawater measurements) were achieved, no demonstration in real samples was provided in the paper.

Alizadeh and co-workers reported imprinted polymer nanoparticles based on methacrylic acid and vinyl-pyridine, prepared with phosphoric acid as template [191]. This was used as the recognition element for

HPO_4^{2-} in a carbon paste potentiometric sensor, again reaching a limit of detection slightly lower than micromolar and with a slightly lowered response towards chloride ion (logarithmic selectivity coefficient of $logK_{phosphate, J}^{pot} \sim -3.6$, with J = chloride anion). The electrode was demonstrated in potentiometric titrations of HPO_4^{2-} with La^{3+} solution. The reported analytical performances indicate that imprinted polymers may be further exploited for phosphate detection in seawater.

Bralic et al. presented a potentiometric ISE with an ISM prepared with silver salts (AgS and $AgPO_4$) and carbon nanotubes, achieving a limit of detection of 5×10^{-6} M for HPO_4^{2-} [192]. However, the paper omits a study of the selectivity, and the ISE was not applied to any real sample. Li et al. developed a HPO_4^{2-} ISE based on the reaction between Mo and the corresponding phosphate anion under alkaline conditions using a molybdenum rod as electrode [193]. However, although the ISE presented almost no response to the chloride ion, no demonstration in real seawater samples was provided. In a similar direction, Zeitoun and Biswas recently published a $Co_{63}Mo_4$ alloy for use in potentiometric phosphate-selective ISEs [183]. While the approach has not yet been fully developed, the authors claim that it provides new opportunities for improving electrochemical phosphate sensors. Stoikov and co-workers presented a new solid-contact potentiometric sensor developed for HPO_4^{2-} recognition on the basis of ILs containing tetrasubstituted derivatives of thiacalix [4]arene in the *cone* and *1,3-alternate* conformations with trimethyl- and triethyl-ammonium fragments as the lower rim substituents [194]. According to the results, this configuration enhances the analytical performances for HPO_4^{2-} sensing.

6. Detection of species related to the carbon cycle: dissolved inorganic carbon (CO_2, HCO_3^- and CO_3^{2-}) and alkalinity

Total dissolved inorganic carbon (DIC) is formally described as the sum of all chemical species formed in seawater directly through the addition of CO_2 from the air [195]. Thus, DIC should represent the sum of CO_2, HCO_3^- and CO_3^{2-} according to the fundamental definition of the equilibrium chemistry of CO_2 in aqueous medium, with the major DIC species being strongly dependent upon the pH of the medium [196]. In principle, determining the concentration of any one carbonate species together with pH under known salinity and temperature conditions allows for the calculation of the concentrations of the other compounds, and thereby the derivation of DIC [197–202]. For example, with pH values measured in seawater using deployable glass electrodes, HCO_3^- and CO_3^{2-} are commonly calculated from total inorganic carbon or total alkalinity, and CO_2 is detected using submersible probes that measure CO_2 in the gas phase, such as the Severinghaus approach [203,204]. Moore et al. demonstrated in 2015 accurate field measurements of DIC based on the direct detection of dissolved CO_2 using a commercial carbonation meter [205]. In addition, the quantification of dissolved Ca^{2+} can be related to the carbon cycle: Ca^{2+} is involved in carbonate precipitation and dissolution processes and it has been claimed that monitoring this species is essential to contribute to a more complete description of the marine system [60,206,207].

There are some commercially available devices that measure DIC and (p)CO_2 in seawater at the laboratory scale based on optical principles [208–211]. Traditionally, alkalinity obtained by way of acid-base titrations (endpoint pH 4.0) has been used as a proxy measure for the sum of CO_3^{2-} and HCO_3- (these are the principal alkalinity contributors in water, with minor contributions from inorganic nutrients such as HPO_4^{2-} and $SiO(OH)_3^-$) [212–215]. Overall, electrochemical techniques are not abundant in the available catalogue, but researchers in the field are moving the wheel in the direction of *in-situ* solutions based on electrochemical sensors; particularly in terms of avoiding the alterations associated with sampling, as all carbon species exist in fine equilibrium with the air.

6.1. Potentiometric ion-selective electrodes for the detection of carbon species

In-situ detection of CO_3^{2-}, pH and Ca^{2+} in seawater has been addressed by means of potentiometric ISEs coupled into a flow cell that is in turn implemented in a submersible probe, which is analogous to that described for NO3- and NO2-, see Fig. 9a-c [60]. Indeed, the device works on the basis of a shared core containing the electronics and peristaltic pumps, with the modules for NO_3^-/NO_2^-/pH or CO_3^{2-}/pH/Ca^{2+} being then exchangeable. The functioning of the submersible prototype was assessed in an outdoor mesocosm and *via* long-term monitoring in Genoa Harbor (Fig. 9d). The electrodes worked properly for 3 weeks, and the system demonstrated the capacity for autonomous operation with routines for repetitive measurements, data storage, and management. It was found that CO_3^{2-} and Ca^{2+} levels were slightly lower during the daylight hours, and the carbonate-to-calcium ratio was in agreement with the speciation [60]. All results were validated by means of gold standard techniques, showing rather good correlations.

Special attention should be given to the validation of CO_3^{2-} measurements, which was accomplished through a potentiometric Severinghaus CO_2 sensor operating in the laboratory. The authors found that the values observed for onsite detection using the CO_2 sensor were always higher than those measured *in-situ* (differences of 15−22 %, respectively), likely due to equilibration of the sample with atmospheric CO_2. On the other hand, the use of the CO_2 probe implies a series of calculations to obtain the carbonate concentration, which are also susceptible to errors. Overall, the results showed great potential, and illustrated well the possibility of using the CO_3^{2-}/pH system for the indirect provision of (p)CO_2 measurements in seawater.

In the same area, Athavale et al. reported analogous CO_3^{2-} and pH potentiometric electrodes adapted to the PIA for depth profiling of CO_2 in a lake [201]. Interestingly, the CO_3^{2-}/pH system showed improvements when compared to the Severinghaus CO_2 probe in terms of response time and insensitivity to dissolved sulfide, with this latter advantageously allowing for measurements in anoxic zones of eutrophic systems. In principle, it seems straightforward to adopt the same approach in freshwater or seawater because of the exceptional selectivity of potentiometric (ionophore-based) CO_3^{2-} and pH sensors in both media with regards to other ions [216–218]. Indeed, plentiful examples of successful CO_3^{2-} and pH sensors applied to environmental samples are to be found in the literature [219–225].

Combinations of potentiometric measurements can be exploited in order to calculate CO_3^{2-}/HCO3- while measuring pH/CO_2 with potentiometric probes. This concept has been demonstrated substantially in freshwater systems over the years, as a result of great efforts in measuring dissolved CO_2 [226,227]. While direct detection of CO_3^{2-} is fully plausible with ISEs, owing to very selective ionophores, HCO3- is been shown considerably less attention in the literature [227]. One of the most recent approaches, published by the Lewenstam group, consists of polystyrene cross-linked with divinylbenzene and functionalized by a quaternary ammonium cation site as the membrane [228]. The polystyrene matrix membrane improves selectivity with respect to interfering lipophilic ions in comparison to previously described PVC-based ISMs, essentially due to the coupling of ion-exchange and pore-diffusion processes in the membrane providing kinetic discrimination of interfering ions. The electrode was successfully used for determination of HCO3- in mineral drinking water.

CO_2 can be monitored *via* amperometric sensors, although no clear advances regarding seawater analysis have been reported over the last five years. To comment upon one example, Revsbech and co-workers reported on a microsensor based on a layer of acidic O_2 trap solution containing Cr^{2+} placed in front of a Clark-type electrochemical sensor [229]. This latter contains a silver cathode in an IL and a silver guard cathode behind the sensing cathode to prevent interference from reducible contaminants in the ionic liquid [229]. The constructed sensor
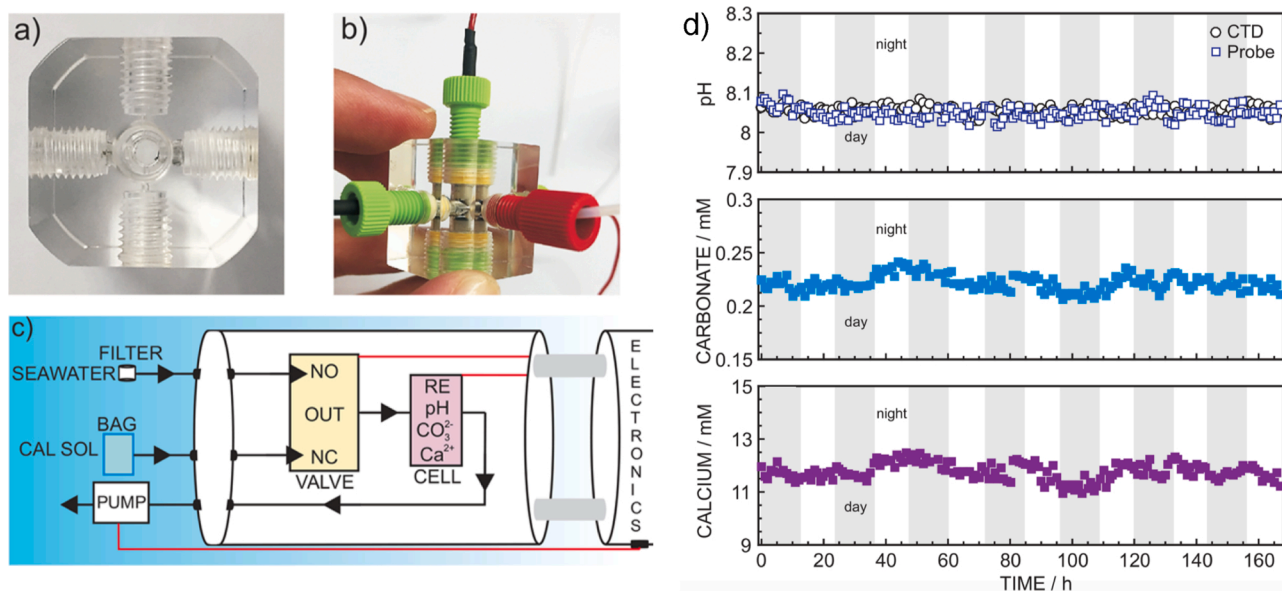
Fig. 9. Images of **(a)** potentiometric flow cell and **(b)** the assembled flow cell incorporating the electrodes for pH, CO_3^{2-} and Ca^{2+} together with the reference electrode, inlet, and outlet. **(c)** Developed fluidics for the *in situ* potentiometric measurements. The pump draws either filtered seawater or the calibration solution according to the valve position (NO, normally open; NC, normally closed), whose outlet (OUT) is connected to the potentiometric flow cell. **(d)** *In situ* profiles obtained for pH (CTD and potentiometric electrode), CO_3^{2-}, and Ca^{2+} during a 167-h deployment (from April 3, 2017, at 07:00 to April 10, 2017, at 12:00) in the CNR Station in Genoa Harbor (Italy). The deployment depth was 4.2 m. Light hours are shaded in gray. Reprinted from [60] (https://pubs.acs.org/doi/10.1021/acs. estlett.7b00388), with permission from the ACS. Further permission related to the material should be directed to the ACS.

exhibited linear response over relatively large intervals of CO_2 partial pressure, but for CO_2 partial pressures of < 20 Pa the response was only about 60 % of that observed at 20–1000 Pa, therefore presenting limited application in real contexts. The CO_2 sensor has been used for analysis of CO_2 metabolism in plants and macroalgae.

6.2. Determination of total alkalinity

Aiming for *in-situ* alkalinity detection, Afshar et al. reported on local acid-base titrations of freshwater samples by means of two opposing potentiometric pH electrodes: one to release protons into the sample to be titrated and the other to read the pH changes in the sample as a consequence of the proton release [230]. The sample is confined between these two electrodes and the proton release is generated by a hydrogen-selective membrane polarized at a constant potential: different time pulses are responsible for increasing release of 'proton packs' to the sample, which is then calculated using the charge (current) profile at the electrode. The second pH electrode monitors the pH in the sample, which tracks the released charge of proton required to reach pH 4.0; thus, alkalinity can be calculated as bicarbonate concentration according to the Faraday law [230]. This device was used onsite to obtain discrete profiles of total alkalinity in stratified lakes [231]. However, the concept was not demonstrated for seawater samples, nor for *in-situ* applications, with the additional impediment of the two ISEs containing inner-filling solutions, which are known to suffer from issues related to pressure.

Crespo and co-workers recently reported on a lab-on-a-chip microfluidic device based on two pH all-solid-state electrodes comprising polyaniline (PANI) as the material for both proton release and pH sensing [61]. Sample replacement is considerably simpler and faster in comparison to previous approaches, providing thereby a relatively high sample throughput. The titration occurs in a matter of minutes due to the thin layer confinement of the sample. This configuration allows for facile implementation into submersible probes, though the applicability in seawater still remains to be demonstrated.

7. Conclusions

Electrochemical sensors for *in-situ* measurements of trace metals, nutrients, and carbon species in seawater have been reviewed, with special focus on the last five years. In the case of trace metals, the VIP (Voltammetric In-Situ Profiler) for the detection of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} using a Hg-based electrode, [47] and a kayak fitted with Zn^{2+} voltammetric sensors based on a liquid crystal polymer bismuth film [50] are the only two cases reported in the literature that have demonstrated *in-situ* operation in seawater. Different alternatives, ranging from the search for alternatives to mercury in electrode materials, to ion-selective electrodes (ISEs) interrogated with cyclic voltammetry, have been explored in the last 5 years for single- and multi-analyte detection. As a result, a plethora of electrochemical approaches for the detection of trace metals can be found in the literature, although demonstrated applications in non-spiked seawater samples remain somewhat limited. Regarding nitrogen nutrients, there are two *in-situ* solutions that have been successfully applied to obtain NO_3^- and NO_2^- profiles in seawater. Potentiometric detection of NO_3^- and NO_2^- is possible at the micromolar concentration with separate electrodes combined in a flow cell after seawater acidification and desalination [51]. The in-line system has been deployed in a bay thanks to its implementation into an autonomous submersible probe. Amperometric biosensing of NO_x^- and NO_2^- is accessible by means of different bacteria chambers in an electrode configuration that can be deployed in any water system making use of profiler or submersible device allowing direct contact of the sensors with the water column, as well as sediments and surface measurements [56]. Total ammonia nitrogen in seawater can be addressed with a potentiometric sensor modified with a gas permeable membrane, coupled with the conversion of dissolved NH_3 to NH_4^+ [58]; this sensor has a great potential for *in-situ* seawater measurements. In the case of phosphate, all-solid-state (reagent solution free) generation of Mo-P complex (in acidic medium) with electrochemical activity in regular electrodes seems to be the most promising approach for total phosphate detection in seawater thus far, although no demonstration of *in-situ* analysis capabilities has been provided as yet [59]. Concerning the carbonate system, there are a range of options

involving the direct measurements of some species followed by the indirect calculations of the others considering the chemical equilibria involved. The most recent efforts consist of the combination of potentiometric ISEs for pH/CO_3^{2-} implemented into submersible probes [60], pH/CO_2 (CO_2 available with the ubiquitous Severinghaus sensor, as well as amperometric detection), and thin-layer titrations for alkalinity detection [61]. Having inspected the field of electrochemical sensors for *in-situ* ion measurements in seawater, a lack of demonstrated *in-situ* applications has been discovered. New advances remain at the laboratory scale, with *in-situ* deployment compatibility promised but very rarely actually achieved. It seems that the few sensors truly implemented into submersible devices are still at a halfway point towards commercialization and therefore, meaningful data is uniquely obtained through the developers' measurements. Electrochemical sensors have the potential to spark a revolution in seawater analysis programs, but making a reality of this scenario will require well-directed steps and dedicated research.

CRediT authorship contribution statement

Maria Cuartero: Conceptualization, Data curation, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Software, Visualization, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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