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Novel frontiers in voltammetric trace metal analysis: Towards real time, on-site, in situ measurements

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abstract

Metal speciation analysis has wide applicability and reveals how and when metals are available to engage in chemical processes. Real systems can be physically hard to reach, chemically dynamic, and sample collection and pretreatment fundamentally alter speciation. Therefore, there is great interest in in situ trace metal speciation sensors that can be integrated into on-site, portable analysis devices. Electrochemistry is an attractive method since the sensing component can be fashioned into a submersible probe. In this review, we define a set of criteria that an electrochemical approach must conform to for in situ metal analysis and review methods that closely follow these criteria. As an emerging technique, fast-scan cyclic voltammetry is introduced. Next, design and material of analysis probes is detailed, followed by a discussion of portable instrumentation. Finally, studies that show promise towards a portable, in situ metal analysis device are showcased and ongoing analytical challenges are outlined.

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1. Introduction

Trace metals play critical roles in environmental processes as well as in manufacturing and other industrial practices. To better understand and control these systems, it is desirable to analytically determine the concentration of 'free' metal, or speciation. Speciation, as defined by the International Union of Pure and Applied Chemistry (IUPAC), is 'the distribution of an element amongst defined chemical species in a system. Isolating analytical measurements to one specific chemical species, in this case, electrolabile or hexa-aqua complexed metals is best because of the likelihood of 'free' metals to engage chemical and biological processes [1]. Furthermore, speciation can be dynamic [2e7], thus the most useful measurement would be at high time resolution. For example, storm drainage or runoff can introduce metal ions into natural water systems quickly, where their presence is pervasive and damaging to ecological and human health. Additionally, discharge of industrial effluents that include metals (widely used as catalysts and components) often lead to rapid environmental contamination and pollution.

With reference to analysis, it is important here to define the difference between on-site and in situ measurements. On-site indicates that the data acquisition platform is portable, allowing analysis to be performed at the site of interest, whereas in situ signifies that the sensor is directly probing the ambient environment of its sample (i.e. sample is not collected). Thus, the most useful analytical speciation data would qualify as both on-site and in situ. However methods that can provide on-site, in situ speciation data are severely limited [8]. This is because of the difficulty of accessing hard to reach environmental systems, in addition to the complexity of real matrices. Additionally, natural organic matter (NOM), other natural ligands, and interfering metals can lead to fouling, clogged membranes and probes, and masked detection of the target analyte [9e11].

Spectroscopic techniques coupled with chromatography, have been used on-site in mobile laboratories, for trace metal analysis because of their excellent sensitivity and reproducibility [12,13]. In situ analysis here is challenging though because of bulky instrumentation and high energy needs. In addition, sample collection and pretreatment alter speciation [4,14,15].

Electrochemical techniques are portable, and show more promise for in situ analysis because electrodes can be immersed into samples of interest with minimal perturbation. In this work, we identify a set of critical criteria the sensing probe must conform to for in situ analysis, originally coined the 4 S's: sensitivity, selectivity, size, and speed, plus two additional ones we add here, stability and safe materials [16]. Methods that closely follow these criteria are reviewed, with a focus on voltammetric analysis because most

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voltammetry modes fulfill 5 or more of our criteria. Specifically, fast-scan cyclic voltammetry (FSCV) is highlighted as an emerging technique. The design and material of analysis probes is detailed with respect to probe size, disposable vs. reusable probes, surface functionalization, and material toxicity. Finally, portable electrochemical instrumentation and ongoing challenges associated with on site, in situ analysis are discussed. Overall, this review identifies a current technological gap for in situ, on site metal detection and provides an in-depth account of recent, promising developments in electrochemical methods towards this type of analysis.

2. Criteria for on-site, in situ analysis - the 6 S's

The electrochemical sensing component of an in situ trace metal sensor should ideally conform to 6 conditions; we coin these benchmarks the 6 S's: sensitivity, selectivity, size, stability, safe materials and speed. Many electrolabile metals of interest are present at trace concentrations (<1 parts per million) and are similarly sized and charged, for example Hg(II), Cu(II), Pb(II), and Cd(II) are all divalent cations, thereby high analytical sensitivity and selectivity are essential. The size of the sensing probe is critical when sampling delicate or elusive systems. Due to the inability to control the sensor's environment, limited opportunities to calibrate on-site, and tendency for fouling, a high degree of signal stability and reproducibility must be maintained. Historically, the majority of metal analysis employs Hg as the sensing component; the risks associated with Hg however have necessitated a new generation of Hg-free, safe electrode materials.

The most challenging criteria remains speed. Under unremarkable circumstances, an analysis temporal resolution of several minutes is acceptable for risk assessment and safety. However, aqueous metal chemistry can change dynamically in response to tides, storms and effluent discharge where minute to minute analysis is advantageous [15,17e19]. Furthermore, sub-minute analysis is needed to observe chemical changes associated with more delicate processes, such as microbial respiration, that would labilize or complex metals in specific systems quickly [20,21]. Speed is a challenging and complex facet of metal detection. For traditional metal electroanalysis, diffusion, equilibration, nucleation/growth and stripping are time consuming processes but are the price of ultra-high (parts per trillion) sensitivity. It has been greatly challenging to reach an analytical compromise that delivers on both speed and sensitivity, in addition to the other criteria. Furthermore, other considerations to address for in situ sensing include: minimal sample treatment, insensitivity to pressure changes, dissolved oxygen, unpredictable flow, and biofouling.

3. Voltammetric techniques

3.1. Stripping voltammetry

Stripping Voltammetry (SV) is the most widely used electroanalytical technique for trace metal analysis. It is generally performed using the steps shown in Fig. 1. Two waveform application modes of stripping voltammetry, square wave anodic stripping voltammetry (SWASV) and differential pulse anodic stripping voltammetry (DPASV), have been extensively employed for trace metal monitoring mainly due to heightened sensitivity, decreased analysis time, and the ability to make measurements in the presence of dissolved oxygen, given acidified or well buffered media [22,23].

3.1.1. SV sensitivity, selectivity and speed

SV is an extremely sensitive electroanalytical method because of the lengthy pre-concentration step, allowing the maximum concentration analyte to deposit onto the electrode surface prior to analysis. Additionally, SV facilitates multi-elemental analysis because different metals can be stripped off the electrode surface at different discrete energies, giving SV a fundamental advantage in selectivity.

The temporal resolution of SV is limited by the lengthy preconcentration step, optimized with respect to holding potential and deposition time for each target analyte, electrode material and matrix for analysis. As speed is often times compromised for sensitivity, a preconcentration time of 1e20 min is standard. For this reason, stripping voltammetry is extremely effective for measuring resting metal concentrations; however collecting real-time information in dynamically changing systems is still a difficult task. Limits of detection and temporal resolution for all of the studies discussed in this review are listed in Table 1.

3.2. Fast-scan cyclic voltammetry

Cyclic voltammetry is perhaps the most generally applied voltammetric method throughout various scientific disciplines, though is less prevalent for metal analysis because traditionally there is not sufficient sensitivity [22] and to the best of our knowledge, there have not been any studies in the last decade with the potential for in situ measurements. Instead, a unique mode of cyclic voltammetry called fast-scan cyclic voltammetry (FSCV) has emerged as a promising approach for environmental analysis to fulfill the 6 Ss.

3.2.1. FSCV sensitivity, selectivity and speed

FSCV utilizes scan rates typically from 100 to 2500 V s ^{1} and is most commonly used among neuroscientists to quantify small, cationic biomolecules at low concentrations and high time resolution with carbon fiber microelectrodes (CFMs) [24]. In recent years the sensitivity, rapidity and relative simplicity of this method have been exploited to make trace metal measurements. FSCV was first introduced in 2012 and 2013 as an electrochemical tool for real-time quantification of aqueous, laboratory Cu(II) and storm water Pb (II) samples [25,26].

Selectivity between biological analytes has thus far been achieved via optimization of detection waveforms based on the electron transfer kinetics of different species [27e29]. Unlike SV, FSCV peaks do not provide good selectivity for multielemental analysis because they are broad (due to fast scan rates). For this reason, surface functionalization of the electrode surface with an ion-specific ionophore has been used to boost selectivity of the probe in the presence of interfering metal ions (vida infra). Furthermore, with limits of detection (LOD) in the low ppb's for Cu(II) and low ppm's for Pb(II), improvements are in process for environmental monitoring for Pb(II) via modification with ionophores [30].

The temporal resolution of FSCV is the most striking feature of this technique, as typically, CVs are collected every 100 ms. Because metal analysis on metal electrodes can be slow (minutes to 10s of minutes to allow for nucleation/growth preconcentration), the phenomenon of the rapid response on CFMs was underpinned by a thermodynamically favorable adsorption equilibrium of metal (similar to small cationic biomolecules) to oxygen functionalities on the activated CFM. This adsorption is rapid enough such that 100 ms is sufficient for monolayer adsorption that enabled adequate preconcentration for parts per billion analysis [31].

FSCV is able to report metal speciation because the original waveforms were optimized to investigate authentic, non-acidified samples. This is a particularly important characteristic of this method since the majority of studies included in this review require significant sample pre-treatment and/or acidification. Furthermore, since authentic systems are usually chemically dynamic, the temporal resolution of this method paves the way for real-time analysis. This was evidenced in Fig. 2 by measuring rapid changes in

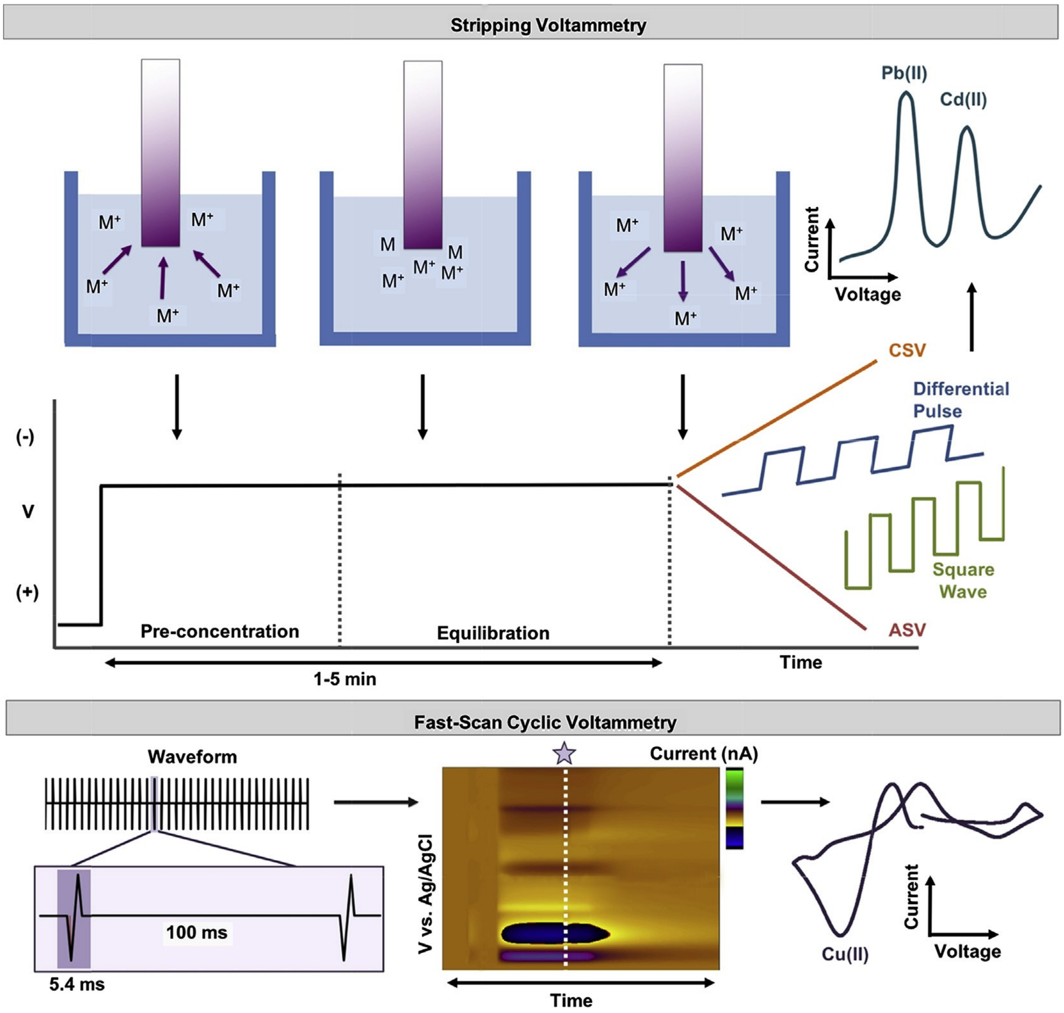

Fig. 1. Scheme of the main voltammetric techniques and modulations used for metal analysis. In SV, a discrete potential is applied to attract and deposit the analyte of interest onto the electrode surface for up to several minutes. Then the deposited metal is stripped off the surface by ramping the potential in the positive (anodic stripping voltammetry (ASV)) or negative (cathodic stripping voltammetry (CSV)) direction. In FSCV, a unique cyclic waveform, specific to the metal of interest, is applied every 100 ms. The output of both techniques results in a voltammogram with peaks at distinct potentials for each metal ion.

Cu(II) complexation (speciation) in real-time with respect to 5 ligands with differing formation constants of Ligand e Cu(II) binding [32]. In this experiment a near complete complexation reaction was captured in under a minute (panel B). To put this into context, the fastest of the other available methods provide readings every minute at best and could not capture these events.

3.2.2. FSCV analysis modes

The high rates of scanning between potentials creates a large, capacitive current, which must be subtracted out to analyze Faradaic processes during FSCV measurements. This has traditionally meant that FSCV could not provide ambient, or basal, measurements, a major hindrance for trace metal studies. To overcome this limitation, fast-scan controlled adsorption voltammetry (FSCAV) was developed to directly measure absolute analyte concentrations in vitro and in vivo [33,34]. FSCAV differs from FSCV in that a controlled adsorption period is integrated, in which maximum adsorption of the analyte is achieved. An ambient measurement can be collected every 30 s, an improvement on the temporal resolution of SV (1e5 min).

To demonstrate the applicability of fast voltammetry for fast speciation analysis, FSCAV was employed to identify electrolabile Cu(II) in complex matrices and a mathematical relationship (Fig. 3) was constructed to explain the correlation between FSCAV current, free Cu(II), and the formation constants of different Cu(II) binding ligands. By measuring electrolabile Cu(II), this model successfully predicted the formation constant of an unknown ligand in seconds [35].

4. Electrochemical probe design and material

4.1. Size

Electrode configuration and size influence both the sensitivity and the reproducibility of a given method and greatly play into feasibility for on-site studies. Microelectrodes are generally considered to have dimensions no greater than 25 mm and exhibit enhanced sensitivity for monitoring small molecules. Additionally, small, low-cost disposable sensors have since emerged as an attractive approach for preventing fouling in complex media and replacing the electrode for subsequent measurement. Screen printed electrodes and lab-on-a-chip technology possess innovative and portable sensing platforms that are promising for on-site environmental analysis.

Table 1
Electrochemical detection methods that show promise for on-site and in situ trace metal monitoring described in this review are compiled here by order of appearance.

Material	Configuration	Analyte	Deposition Time, s	Limit of Detection, μg/L	Methodology	Reference
Carbon Fiber	CFM	Cu(II)	0.1	15.8	FSCV	[25]
Ionophore Grafted Carbon Fiber	CFM	Cu(II)	0.1	0.32	FSCV	[30]
Bi-MEA	LOC	Pb(II)	120	0.6	SWASV	[41]
		Cd(II)	120	0.7		
DMG		Ni(II)	60	0.7	SWAdCSV	
Bi-MEA	LPE	Pb(II)	120	8.2	SWASV	[42]
		Cd(II)	120	28.2		
DMG		Ni(II)	60	6.9	SWAdCSV	
DMG, Bi-MEA	LOC	Co(II)	30	0.18	SWAdCSV	[43]
BiFE	LOC	Cd(II)	90	9.3	SWASV	[49]
Bi-BDDPE	μPAD	Pb(II)	300	1	SWASV	[58]
		Cd(II)	300	25		
C	Pyrolyzed Paper	Pb(II)	180	0.19	SWASV	[59]
		Cd(II)		0.16		
BiFE,CNT	μPAD	Pb(II)	240	1	SWASV	[61]
		Cd(II)		1		
Sb-SPAN-EG	SPCE	Pb(II)	180	0.2	DPASV	[62]
		Cd(II)		0.41		
Ag	LOC	Pb(II)	300	0.55	SWASV	[68]
Ag	Rotary Disk	Pb(II)	180	1.28	SWASV	[69]
BiFE	LPE	Pb(II)	120	0.5	SWASV	[70]
		Cd(II)		1		
BiFE	LOC	Pb(II)	60	8	SWASV	[72]
Graphite Foil	LOC	Pb(II)	180	1.8	SWASV	[73]
		Cd(II)	60	1.2		
AuNP	SPCE	As(III)	120	0.03	SIA-ASV	[92]
Au	VGME	As(III)	120	0.005	SWASV	[94]
Au	VGME	Mn(II)	300	0.07	SWASV	[97]
		Zn(II)		0.02		
AuNP	SPCE	Hg(II)	360	1	SWASV	[102]
DMG, BiFE	LOC	Ni(II)	90	0.1	SWAdCSV	[105]
DMG, Nafion	GCE	Ni(II)	120	1.5	SWAdCSV	[106]
DMG, Nafion, BiFE	CSPE	Ni(II)	240	5	SWAdCSV	[107]
		Co(II)	240	1		
BiFE,CNT	SPCE	Pb(II)	60	0.01	SIA-SWASV	[108]
		Cd(II)		0.01		
PANI-PDTDA	SPCE	Pb(II)	120	35	DPASV	[115]
		Cd(II)		33		
		Hg(II)		26		
		Ni(II)		56		
IIP, MWCNT	CPE	Ag(I)	180	0.013	DPASV	[117]
IIP	CPE	Pb(II)	80	0.003	DPASV	[118]
Mag-IIP-NPs	MCPE	Ag(I)	240	0.015	DPASV	[119]
IIP-PANI, MWCNT	GCE	Pb(II)	60	0.16	DPASV	[120]
SbNP,MWCNT, Nafion	SPCE	Pb(II)	120	0.65	SWASV	[173]
		Cd(II)		0.77		
BiFE	LOC	Cd(II)	90	9.3	SWASV	[187]
Au	SPGE	Pb(II)	240	1.2	SWASV	[188]
		Cu(II)		1.1		
		Hg(II)		1.1		
DMG, Nafion	SPCE	Ni(II)	120	30	DPASV	[190]
Au	SPGE	Pb(II)	90	4	SWASV	[191]
		Cu(II)		2		
		Hg(II)		4		
Ag	VGME	Cu(II)	300	0.003	SWASV	[193]

Acronyms:

BiFE	Bismuth Film Electrode	MEA	Microelectrode Array
BDDPE	Boron Doped Diamond Paste Electrode	MPCE	Magneto Carbon Paste Electrode
CFM	Carbon Fiber Microelectrode	MWCNT	Multiwalled Carbon Nanotubes
CNT	Carbon Nanotube	μPAD	Microfluidic Paper-Based Analytical Device
CPE	Carbon Paste Electrode	NP	Nanoparticles
CSPE	Carbon Stencil Printed Electrodes	PANI	Polyaniline
DMG	Dimethylglyoxime	PANI-PDTDA	Polyaniline-Poly(2,2′-Dithiodianiline)
EG	Expanded Graphite	SPAN	Sulfonated Polyaniline
IIP	Ion Imprinted polymer	SPE	Screen Printed Electrode
LOC	Lab-on-a-Chip	SPCE	Screen Printed Carbon Electrode
LPE	Lithographically Printed Electrode	SPGE	Screen Printed Gold Electrode
Mag-IIP-NPs	Magnetic Ion Imprinted Polymer Nanoparticles	VGME	Vibrating Gold Microelectrode

4.1.1. Microelectrodes

A cylindrical carbon fiber microelectrode (CFM) is typically used to perform fast voltammetry, ranging from 5 to 10 μm in diameter and 0–150 μm in length. The advantageous features of CFMs include improved mass transport of analyte to the electrode surface facilitated by hemispherical diffusion, low iR drop, low

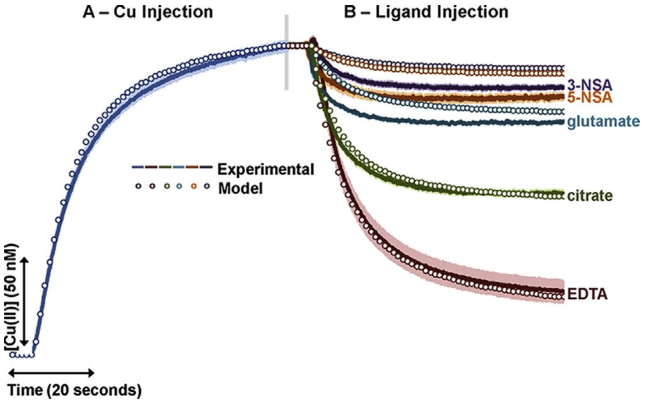

Fig. 2. (A) An injection of 1 μM Cu $(NO_3)^2$ was allowed to reach a steady state, followed by (B) an injection of 5 metal ligands with known formation constants. The complexation of Cu binding can be seen in real-time to each ligand and closely followed a model of this response. Reprinted with permissions from T. Siriwardhane, A. Sulkanen, P. Pathirathna, A. Tremonti, S.P.McElmurry, P. Hashemi, Anal Chem, 88 (2016) 7603e7608. Copyright © 2016 American Chemical Society.

charging current, and high signal to noise ratio. The hemispherical diffusion of microelectrodes increases the mass transport to the electrode surface and mimics convection, thus a non-zero steady state current is obtained quickly and stirring becomes negligible, a benefit for in situ sensing [36,37]. The low iR drop and high signal to noise ratio permits measurements in high resistance environments such as low-ionic strength media without need for addition of a supporting electrolyte (i.e. no sample pretreatment) [37e39]. Furthermore, using SV, microelectrode arrays (MEA) have become a particularly useful tool for multi-elemental analysis [40e44].

4.1.2. Screen printed electrodes

The introduction of screen-printed electrodes (SPEs) was a major breakthrough for the development of portable tools and devices for rapid trace metals measurements [45]. While screen printing technology is not novel in itself, researchers from different fields have innovated several methods of designing and fabricating low-cost SPE sensors. In general, SPEs are comprised of a 3-electrode system, screen printed on a chemically inert substrate [46,47]. The fabrication process typically involves a surface modification step, serving to change the composition of the working electrode and enhance electrochemical responses [47,48]. SPEs can take the form of a stick, disk, or wafer, and one platform can include up to 300 replaceable sensors [43,49]. One unique substrate, microfluidic paper-based analytical device (μPAD), has emerged as a simple, inexpensive option with potential for commercialization [50]. While most often coupled with colorimetry [51e57], more voltammetry-based μPADs have been developed (Fig. 4) and show great promise for on-site trace metal monitoring [58e63].

4.1.3. Lab on a chip

Lab-on-a-chip (LOC) is another attractive approach for on-site analysis because multiple steps, including sampling, separation, and detection, can be combined on a single analysis platform [64e66]. LOCs satisfy the recent trend in miniaturizing electrochemical systems [67] and incorporating microfluidics for environmental analysis, as seen in Fig. 5. The automated nature of microchips and the small quantity of reagent, sample, and time necessary for multiple measurements show promise for field portable environmental monitoring. A key advantage of LOC technology is versatility, as they can incorporate a suite of analysis modes and electrode materials to enhance sensitivity and allow for multicomponent analysis. Commercially available microchips are generally inexpensive, thus a number of both disposable and renewable working electrochemical sensing platforms have been used including planar Bi, Bi film and Ag rotary disk electrodes [49,68e72]. Such methods are effective for distinguishing between similar divalent ions, Cd(II) and Pb(II), in natural waters [49,73]. One notable study incorporated Bi-MEAs on a disposable LOC device for analyzing Pb(II), Cd(II), and Ni(II) concentrations in lake and tap water [41,42].

In recent articles reviewing LOCs use for aquatic ecotoxicology, the authors note that LOCs are relatively newer technologies, underutilized for environmental monitoring due to the many logistical challenges that limit their robustness for raw samples, including pressure resistance, air bubbles and clogging within the microfluidic channels, operational complexity, and unsuitability for large or complex samples [74,75]. Additionally, the need for sample preparation is eliminated for some natural water samples such as acid mine drainage that have low pH, however, for samples with higher pH that needs adjustment, speciation is altered [15], and ultimately compromises the integrity of the sample. Thus, there are ongoing efforts to create sensors that are more robust, easy to use, and do not require sample preparation to make LOCs applicable for on-site analysis.

4.2. Stability

There have long been efforts to minimize fouling and improve stability because natural systems are complex and rich in organic material that can poison electrode surfaces. Moreover, metals themselves are prone to build up on and foul the electrode. A highly reproducible electrode response can be garnered using dropping Hg electrodes, which reproducibly preconcentrates analytes of interest as an amalgam [76e78]. However, for toxicity reasons there has been significant impetus to develop alternate strategies. Here we highlight two recent approaches for designing electrodes that afford high reproducibility: one that is based on low-cost disposable sensors and the other that focuses on sensing materials with a renewable surface.

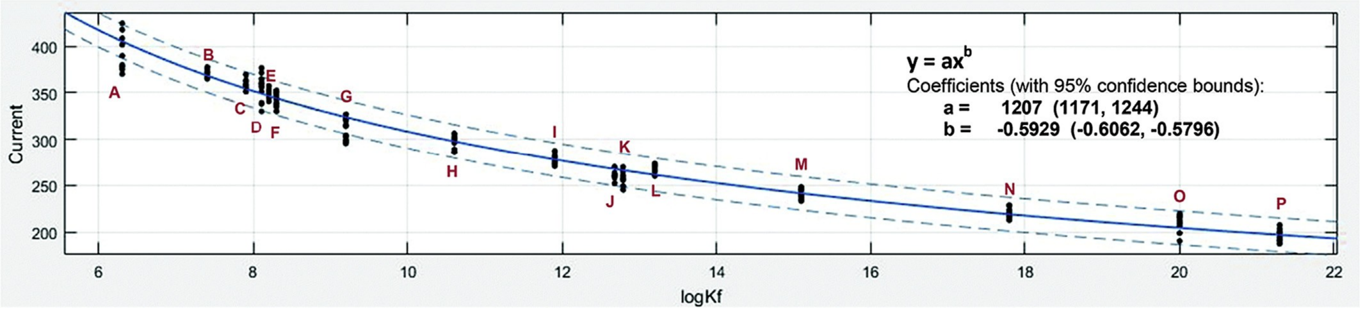

Fig. 3. The FSCAV response and formation constants for 16 different Cu(II) e ligand complexes was fit to an exponential curve. Reprinted with permissions from P. Pathirathna, T. Siriwardhane, S.L.Morgan, S.P.McElmurry, P. Hashemi, Analyst, 141 (2016) 6025e6030. Copyright © 2016 American Chemical Society.

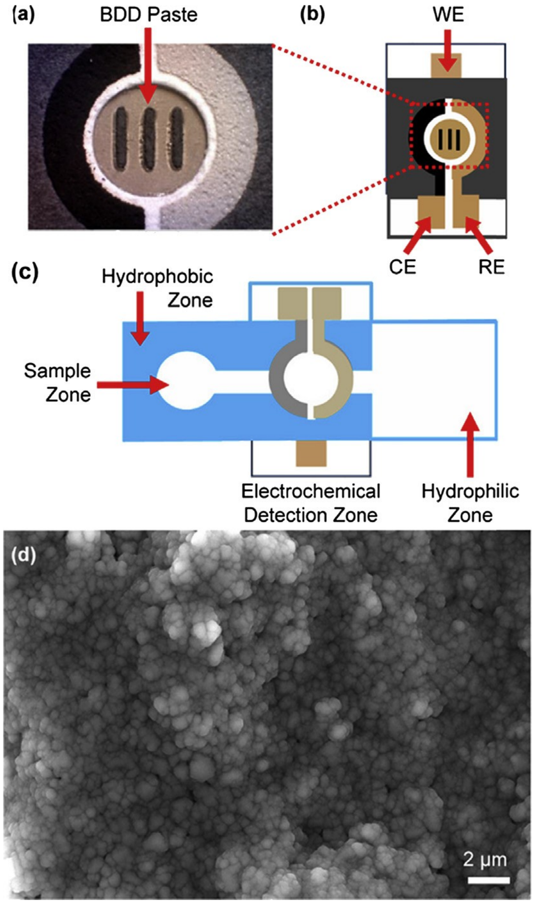

Fig. 4. Scheme of a Boron Doped Diamond Paste Electrode (BDDPE) on an electrochemical paper based analytical device. (a) photograph of the BDDPE (b) 3-electrode system is screen printed onto a paper substrate as the electrochemical sensing component (c) design of sampling microfluidic paper device (d) SEM image of Boron Doped Diamond Paste surface structure. Reprinted with permission from S. Nantaphol, R.B. Channon, T. Kondo, W. Siangproh, O. Chailapakul, C.S. Henry, Anal Chem, 89 (2017) 4100e4107. Copyright © 2017 American Chemical Society.

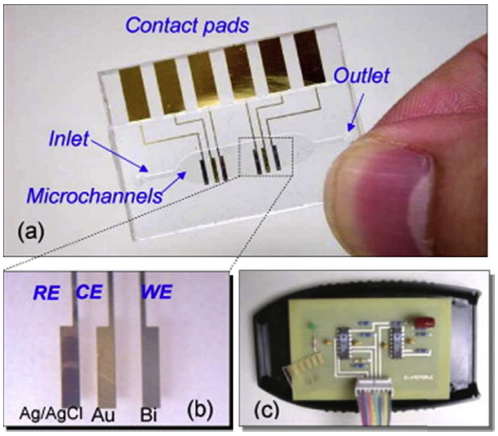

Fig. 5. Representative assembly of a three-electrode system, microfluidic channels, and customized detection circuits fabricated onto a microchip. Reprinted from Sensors and Actuators, B: Chemical, 134, Z.W. Zou, A. Jang, E. MacKnight, P.M. Wu, J. Do, P.L. Bishop, C.H. Ahn, Environmentally friendly disposable sensors with microfabricated on-chip planar bismuth electrode for in situ heavy metal ions measurement, 18e24, Copyright (2008) with permission from Elsevier.

Disposable sensors including SPEs and LOCs are popular for simple, portable sensing. Briefly, the sensing component is printed and a stable film of Hg, Bi, or Sb is deposited on top; this significantly curbs toxicity issues since the coating is contained. This approach facilitates reproducibility but not stability since the majority of amalgam and fused alloy-based sensors do not allow for repeated measurements on one device. While attractive for its simplicity and reproducibility, this strategy can be tedious, especially since often times submersed probes are difficult to frequently access and replace. Additionally, measurements cannot be automated to continuously monitor the site of interest, because it is necessary to replace the sensing component in the probe between each measurement.

For all electrode materials, biofouling from natural organic matter and microorganisms is a major limitation for continuous monitoring [79]. In an effort to extend the probes' stability over time, the design and characterization of electrode materials with a renewable surface and efficient cleaning procedure has been explored. Several groups have introduced ‘antifouling steps’ into the electrochemical waveform to prevent microbial adsorption [80,81]. Often, this involves the generation of biocide gases such as H_2 or Cl_2, however, it is difficult to use in tandem with surface functionalization methods that prevent such reactions from happening or are destroyed from the process. An alternate approach is the incorporation of non-toxic antifouling reagent into surface functionalization process, including zwitterionic or cation exchange polymers [82e86] and peptides for non-specific protein adsorption [87e89]. Though most studies are not applied for environmental metal monitoring, there is great interest in developing marine antifouling coatings [90] without compromising the method's sensitivity or speed.

Materials such as Ag, Au, and carbon have potential to be renewed; target analytes adsorb to the surface in a monolayer and a cleaning step can be incorporated into the voltammetric sweep to oxidize and renew the surface [31,68,91e93]. Using similar materials for the working, reference, and counter electrodes contributes to enhanced regeneration of Ag, attributed to the movement of Ag ions between electrodes, redepositing and continuously renewing the working electrode [68]. Van Der Berg et al. introduced a unique approach by vibrating a microwire electrode of Au or Ag to increase mass transport to the electrode, due to a decrease in the diffusion layer thickness. This method was robust and effective for improved sensitivity and reproducibility for determining speciation of As, Sb, Cu and others [94e97].

Measurements on CFMs using FSCV are generally stable and reproducible in complex biological matrices [98], due to a potential cleaning step included to renew the electrode surface between scans. By ramping the applied potential up to and over þ1.3 V, the oxygen moieties on CFMs are regenerated, thus re-primed for further adsorption [91]. Studies of surface functionalized CFMs also show voltammetric responses remain stable over 50 consecutive scans and for up to 16 weeks in open air during storage [30]. Additionally, unfunctionalized carbon fibers have been employed for studying monoamines in brain tissue for up to several months at a time [98]. Thus, the stability and reproducibility of the CFM, along with their use in both complex biological (brain tissue) and environmental (rain water) matrices, demonstrates great promise for use in continuous environmental monitoring.

4.3. Surface functionalization

Voltammetry is an inherently selective technique, because metals oxidize or reduce at discrete peak potentials, however in complex matrices, some analytes greatly out-concentrate others, thus some peaks will mask others present at lower concentrations. In these scenarios a much higher level of selectivity must be conferred towards analytes of interest present in trace quantities.

Modifying analysis methods and electrode surfaces with nanoparticles, complexing agents, polymers, and ionophores has emerged as an attractive approach to improve sensitivity and selectivity. However, it is crucial to consider and curb the toxicity of certain additives for this type of analysis. To avoid contamination, any coating or complexing molecule must have low toxicity and form a stable and irreversible attachment to the electrode surface.

Metal nanoparticles are used as an electrode modification material to enhance the sensitivity and limit of detection, due to the rich and porous surface area formed from the single or multilayer coverage [99e101]. A few notable examples of trace metal detection using nanoparticles include Au nanoparticle modified electrodes used to detect Hg(II) in groundwater [102] and Pt nanoparticle electrodes for differentiating inorganic As(III) and As(V) species [92].

Certain metals are particularly difficult to analyze using voltammetry; Ni(II) and Co(II) are prime examples of this because these metals do not easily preconcentrate due to irreversible reduction processes, requiring an extremely negative deposition potential (1.2 V vs. SCE). Furthermore, Ni tends to form intermetallic compounds that co-deposit and generate unpredictable matrix-dependent stripping patterns. Thus, adsorption stripping voltammetry is employed instead. Here, a complexing agent, dimethylglyoxime (DMG), that complexes Ni(II) and Co(II) with high favorability ($K_{f(Ni)}$ ¼ $10^{17.4}$, $K_{f(Co)}$ ¼ $10^{12.85}$) facilitates preconcentration onto the electrode [43,103e107]. The toxicity of DMG however makes it a controversial complexing agent for environmental analysis. Similarly, sensitivity is improved for Pb(II) and Cd(II) by incorporating a macrocyclic chelating solid to enhance analyte deposition [108], and, while most commonly used with other detection methods, the popularity of DNA, RNA, and proteins as metal complexing agents has risen for use in electrochemical sensors [109e114]. These apta-sensors are still in the early stages of characterization and optimization.

Conductive polymers have been employed to increase selectivity for metal detection, though few studies are applied in the context of rapid in situ metal monitoring. Typically, these polymers function via charge exclusion. Conductive polymers including polyaniline-poly(2,2^{0}-dithiodianiline) (PANI-PDTDA) doped with S [115] and Nafion (NA) coupled with DMG and Bi films [106,107,116] have been employed to facilitate selective and simultaneous detection of Hg(II), Pb(II), Ni(II), Co(II), Cd(II), and Zn(II) ions in aerosols and water analysis. Furthermore, ion-imprinted polymers (IIP) and polymeric nanobeads have also been explored as an option for trace metal detection in real water samples based on size exclusion [117e123]. Ion imprinted materials significantly enhance sensitivity and selectivity, however slowed diffusion through the polymer layer necessitates lengthy extraction or preconcentration times (in many cases >10 min) and limits this method's applicability [123e132].

Due to the broad peaks and poor selectivity of metal ion fast voltammetry, a novel surface functionalization method was introduced to covalently modify CFMs with a Cu(II)-selective ionophore [30]. An ionophore was synthesized and covalently bound to the carbon electrode surface via a reductive coupling of a diazonium salt and click chemistry. The top panel of Fig. 6 shows the structure of these ionophore-grafted CFMs and the bottom panel displays the enhanced selectivity of the electrodes for Cu(II) in the presence of 8 interfering divalent metals that were 10-times more concentrated. Furthermore, this surface functionalization improved the method's LOD in comparison to an unfunctionalized CFM.

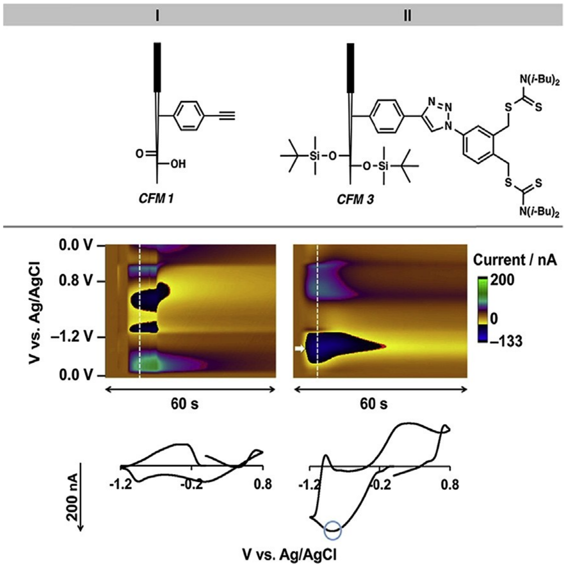

Fig. 6. (I) Unfunctionalized CFM shows non-faradaic response and (II) Ionophore Grafted CFM shows clean Cu(II) redox features in a mixed metal solution. Mixed Metal Solution: 1 mM Cu(II) and 10 mM each of Zn(II), Cd(II), Ni(II), Co(II), Ca(II), Mg(II), Pb(II), and Mn(II) all with NO_3 counter ions. Reprinted with permissions from Y. Yang, A.A. Ibrahim, P. Hashemi, J.L.Stockdill, Analytical Chemistry, 88 (2016) 6962e6966. Copyright © 2016 American Chemical Society.

4.4. Safe materials

Hg electrodes have been heavily used among metal analysis groups due to their many attractive features resulting from the stable amalgam formation between Hg and metals. The hanging drop ensures a consistent matrix for nucleation and growth, and provides a new surface for each analysis, hence greatly facilitating reproducibility. This method is highly sensitive (1 zmol with 1 s deposition) [133]. The inherent advantageous electrochemical properties of Hg sustains the community's interest in Hg for trace metal monitoring tools. Hg is still used in low concentration as a solid dental amalgam electrode or a thin film as the sensing component for portable trace metal analysis devices [134e142]. Because Hg is toxic to human and aquatic system health, electrochemists have been investigating non-Hg materials as an alternative sensing probe for in situ metal analysis.

4.4.1. Carbon electrodes

Because of its excellent electrochemical and mechanical properties, carbon has become one of the most popular solid electrode substrates, often serving as the base sensing component of surface modifications and SPEs [143,144]. The beneficial features of carbon materials include: 1) slow kinetics of carbon oxidation that causes minimal background currents compared to other electrode materials, 2) oxygen functionalities on the carbon surface that ambiently adsorb small cations, 3) ease of chemical modification, 4) a wide potential window, 5) biocompatibility, and 6) the low price and ready-availability of the material [145e148]. For environmental analysis, carbon is an excellent safe material since environmental systems contain large amounts of carbon and are thus not very sensitive to this material. Among different types of carbon materials, glassy carbon, graphite, carbon fibers and new carbon nanomaterials like magneto carbon paste, carbon nanotubes and boron-doped diamond have been employed to develop metal sensors in the last decade [58,101,116,119,146,149e154]. The choice of carbonaceous material depends on the application, the type of analyte and the analysis method. Additionally, as mentioned before, the regeneration and ease of modification of the carbon surface makes this material much less prone to fouling issues, eliminating the need to replace the sensing component between measurements, and allowing for more continuous environmental monitoring.

4.4.2. Bismuth electrodes

Bi film serves as a greener substitute electrode material for Hg for metal analysis because of the ability to form a multicomponent alloy with metal analytes, analogous to amalgam formation by Hg, that facilitates the nucleation/growth process during the analysis. Insensitivity towards dissolved oxygen eliminates a tedious de-oxygenation step and all-together makes Bi a simple and suitable replacement for Hg [155].

The efficiency of Bi electrodes is heavily dependent on the design process. Bi electrodes are prepared either by pre-plating Bi on a supporting substrate (ex situ) or by adding Bi(III) directly into the sample solution (in situ (not to be confused with in situ metal analysis as we use frequently in our discussion)) followed by a simultaneous adsorption of Bi and the target metal. Typically, carbonaceous materials are employed as substrates for Bi films including glassy carbon [156], screen-printed carbon ink [107,157], graphene [106,158] and porous carbon composites [159,160]. Additionally, the combination of Bi doped with other materials such as Sb and Ir have been explored for enhancing sensitivity [156,159,161]. Bi has proven useful in a number of environmentally relevant samples including surface [156,162], and tap waters [160,163] and shows great promise to be used in the field as a reliable material to monitor trace metals.

Although Bi exhibits versatility as a non-toxic electrode material for metal analysis, there are limitations. In particular, the narrow anodic potential window limits application for multielemental analysis and the insufficient reproducibility of ex situ bismuth electrodes necessitates improvement. For these reasons, other electrode materials are also being explored.

4.4.3. Antimony electrodes

The potential window and signals corresponding to model metal ions (Pb(II) and Cd(II)) suggest Sb and Bi alloy formation are similar processes. Consequently, Sb has gained popularity as an electrode film material for electrochemical stripping analysis of trace metal ions. Sb displays similar or slightly improved sensitivity compared to bismuth, favorable hydrogen evolution, and smaller voltammetric reoxidation than Bi and Hg films, thus lessening interferences near the anodic potential limit. It is easily integrated onto a disposable, commercially available SPE and many groups have coupled Sb film electrode and stripping voltammetry for a variety of applications including, canned foods [164] and water analysis [165e168]. Additionally, many approaches have been explored to determine the best Sb film fabrication method including in situ [167e171], and ex situ electrolytic plating [172,173], Sb nanoparticles [173], Sb sputtering [105], fabrication of a macroporous electrode [174], combination of Sb, Bi, and Sn [161,170,175e177], and a self-doped co-polymer [62].

While Sb alloys have yet to be fully characterized, many groups are attempting to understand the mechanism behind Sb's electrochemical properties to improve performance [178,179] and optimize the technique by comparison of carbon substrates as the working electrode base [169,180] and selective measurements in the presence of common interferences [167,181]. At this time, while less toxic than Hg, Sb and its compounds are listed as priority pollutants [182], thus the risk associated with using Sb electrodes for in situ environmental monitoring still needs to be assessed. Furthermore, Sb is limited to extremely acidic solutions (pH 2), requires nitrogen purging and pretreatment, and preparing ex situ Sb film is still challenging thus improvements are necessary for in situ analysis [178]. Our discussion is targeted towards portable, in situ sensing, however there is an excellent review published in 2018 on emerging “green” metals as electrode materials for trace metal analysis [183]. While in situ analysis is not highlighted, these “green” metals would be good candidates for environmental analysis.

5. Portable voltammetric instrumentation

An in situ trace metal speciation sensor should ideally satisfy all 6 S's and thereby be integrated into a portable device for on-site analysis. One commercially available portable system is the voltammetric in situ profiling (VIP) system, which incorporates microarrays and submersible sensors to make trace metal concentration measurements with high stability in the field [22]. Bulky instrumentation originally presented challenges, however, this device has been miniaturized and applied to several metal analytes in various applications [11,184e186]. Though, the VIP system is highly sensitive and robust; ongoing challenges include the necessity for an oxygen removal step and safer electrode materials.

Significant progress has also been made towards new portable voltammetric systems by integrating handheld potentiostats, solar panels or batteries, and wireless communication modules as the data acquisition and electrochemical control systems [49,68,71,137,139,187e190]. The integration of injection analysis [92,108,139,157,175,191], on-chip automatic sampling and pretreatment [48,192], and fluid transfer systems controlled by a fluidic motherboard [72] has improved the quality of electrochemical data collected in terms of stability by providing a constant flow of sample and increased mass transfer to the electrode surface. Fig. 7 illustrates a representative outline of a total electroanalysis system that is field portable, weighing less than 3 kg.

There are just a handful of reports of successful field measurements made on-site with new technology in recent years [188e190]. There is only one recent report of an apparatus capable of performing both on-site and in situ analysis, introduced by Van Den Berg et al. to study Cu(II) cycling in coastal waters [193]. The group outlined several physical constraints, including high noise, limited scope, an impractical background subtraction step for oxygen and a 300 s preconcentration period. This method clearly requires a more robust and rapid analysis component to fulfil the 6 S's, which may be met via advanced stripping voltammetry or fast-scan cyclic voltammetry but is a promising start towards determining undisturbed metal speciation in situ.

6. Towards on-site, in situ trace metal analysis

By means of summarizing the methods described in the discussion above, Table 1 compares fundamental analytical characteristics. An electrochemical sensor capable of rapid in situ trace metal monitoring and fulfilling the 6 S's does not yet exist, thus encompassed in this table are the methods that we believe are good candidates from the last 10 years for further development towards a portable in situ trace metal sensor. With the 6 S's in mind, excluded from this table are studies reporting LOD's outside of the mg/L range, greater than 5 min analysis time, and use of toxic (Hg film) electrode materials. Furthermore, ex situ Bi and Sb film electrodes are preferentially featured here, as it is not feasible to form in situ Bi or Sb films when directly submersing the electrode into a system of interest. Nearly all studies highlighted require sampling, pretreatment, and often times sample acidification or spiking, limiting electrochemical environmental sensing platforms to ex situ methods at this time.

There are still many ongoing challenges to consider when designing on on-site analysis device with an in situ capable sensing probe. In the laboratory, the optimization of delivery of analyte to the electrode has contributed to enhanced sensitivity [48] via flow injection systems [92,108,139,157,175,191,192], however this highly controlled convection is still a limitation for making truly in situ measurements because it is not possible to control the convection of dynamic environmental systems. Additionally, unpredictable fluctuations in pH, temperature, pressure, and biofouling are also

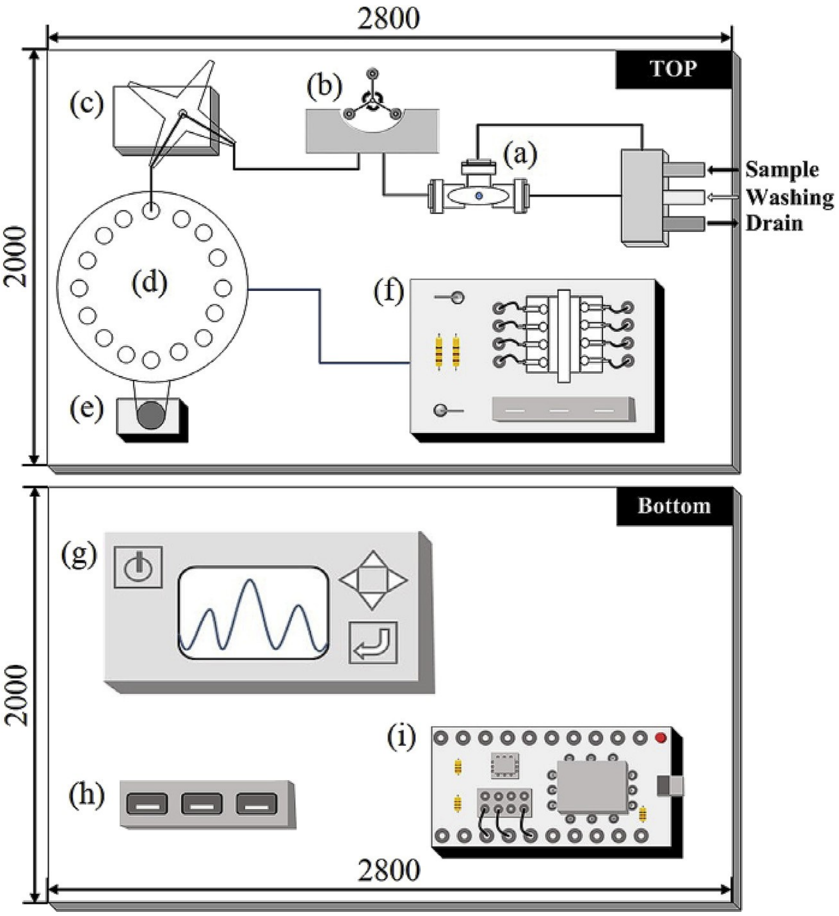

Fig. 7. Diagram of a total analysis system designed for on-site sensing: incorporating microfluidic tubing, a peristaltic pump, a rotary disc voltammetric sensor, portable potentiostat, data acquisition board, electronic controller, and USB and power inputs. Reprinted from Chemosphere, 143, Y.G. Lee, J. Han, S. Kwon, S. Kang, A. Jang, Development of a rotary disc voltammetric sensor system for semi-continuous and on-site measurements of Pb(II), 78e84, Copyright (2016), with permission from Elsevier.

ongoing issues for interpreting signals collected in the field. Finally, the sensitivity of these techniques, while suitable to confirm contamination according to US-EPA drinking water quality standards [194], for the most part are below the limit of detection for previously reported resting metal concentrations in fresh and seawater [1,195,196]. Altogether, these technological gaps necessitate advancements in the coming years for better trace metal sensing tools. We encourage those highlighted in this review and others to continue their progress towards this common goal: to create a field portable analysis device capable of in situ sensing.

7. Conclusion

Metals play important chemical roles, acting as nutrients and cofactors in biochemical and environmental processes. They can also exert toxic effects in excess. Electrochemistry has emerged as an attractive analysis strategy due to the inherent portable nature of electrodes. An electrochemical method capable of distinguishing metal speciation is highly desirable, because electrolabile metals are available to engage in chemical processes. The process of sampling and pretreatment alters metal speciation, thus it is necessary make in situ measurements. Real environmental systems however are challenging to analyze because real matrices can be chemically harsh, complex and dynamic. We identified a set of criteria for electroanalysis of trace metals, coined the 6 S's: sensitivity, selectivity, size, speed, stability, and safe materials. Progress towards developing an electrochemical probe for in situ metal analysis is discussed in this review, with focus on a promising voltammetric technique (FSCV) that satisfies our 6 criteria. Novel probe design aspects including electrode materials, configurations, and surface functionalizations are targeted in our discussion. Additionally, we report new developments in portable electrochemical instrumentation for on-site capabilities. In this review, we conclude that there is a clear gap in technology for this specific environmental application, and most techniques are still limited to ex situ measurements and analysis. We highlight studies that we believe show potential for on-site, in situ measurements, and iterate the importance of actively pursuing technology development to achieve, within the next few years, a truly robust on-site, in situ trace metal speciation sensor.

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