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Electrochemical and Optical Methods for the Quantification of Lead and Other Heavy Metal Ions in Liquid Samples

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Abstract

Minerals and elementary compounds of heavy metals are part of the ecosystem. Because of their high density and property to accumulate in stable forms, they are considered to be highly toxic to animals, plants and humans. Continuous mining activities and industrial effluents are the major sources which are adding toxic heavy metal ions into ecosystem and biota. Hence it is of utmost importance to quantify the levels of heavy metal ions in environmental and biological samples. On the other hand, it is equally important to remove the heavy metal ions and their compounds from the environmental and biological samples. That facilitates the environmental samples to be fit for using, consumption. In this regard, promising quantification methods such as electrochemical, spectrophotometric, naked eye sensing, test strips for spot analysis of heavy metal ions are considered for discussion. The main objective of this chapter is to give the overview of the most practiced quantification approaches available in the literature. Please note that reader cannot find the pin to pin publications regarding the same and that is not the aim of this book chapter.

Keywords: heavy metal ions, quantification, electrochemical and optical

1. Introduction

Metals possess higher density, atomic numbers are considered as heavy metals. They are part of the ecosystem present in the form of minerals and also in the elemental form. Heavy metal ions [HMIs] are proved to be toxic to humans, animals and even to plants as they accumulate to form stable compounds. Over a period of exposure or accumulation to HMIs lead to serious health issues with respect to [w.r.t.] skin, neurological system, kidney etc. [1]. HMIs toxicity and its adverse effects are magnified due to the human activities such as mining, rigorous industrial activities adding HMIs to the various ecological system. Once it happens then animals and humans are prone to HMIs that is really disaster. Considering these facts seriously world health organization and environmental protection agency set the permissible levels for the HMIs in various samples [2]. Above that level that particular sample is not fit for usage or consumption. In this scenario there is a pressing need for the analytical methods through which the exact quantity of the HMI[s]

can be measured. There is a scope for the analysis of HMIs in the wide variety of samples such as water, air, food, and biological samples etc.

It is well known fact that, there exist efficient methods either individual or coupled with detection techniques for the quantification of HMIs. Atomic absorption spectroscopy, inductively coupled mass spectroscopy, inductively coupled atomic emission spectroscopy, Ion selective high-performance liquid chromatography etc. All the mentioned methods possess good linear range, sensitive down to ppb level concentration and accurate. At the same time, they are expensive, needs to be operated by skilled person, cannot be carried to field, and may require greater volume of sample. Hence, even today researchers are putting their efforts to develop analytical methods to overcome the mentioned shortcomings. There exist few techniques such as electrochemical, optical, methods based on electrical conductivity, refractive index etc. Compared to the earlier mentioned methods latter are less expensive, easy to handle and smaller in size. But there are few challenges with the latter mentioned methods such as sensitivity and selectivity. Thrust to achieve these goals is still alive, hence, one can witness lot of publications on the same topic. But, it does not mean that electrochemical, spectroscopic methods are failure. Researchers are striving to match the sensitivity and selectivity of the electrochemical and spectroscopic methods with that of earlier mentioned methods. Another improved aspect is the size. True size of both i.e. instrument and sample [volume] required for the analysis are significantly minimized. Naked eye sensing of heavy metal ions is made possible. Just addition of sample containing HMI to the reagent system in a culture tube results the color [change] that can be recognized with naked eyes. Moving a step ahead electrochemical and spectroscopic methods are miniaturized down to small paper strip. Paper based electrochemical and colorimetric methods are trending now. Important Analytical parameters for all the above discussed methods have been summarized with broader perspective in the **Table 1** for the comparison purpose [6, 7].

	Flame AAS	Graphite Furnace AAS	ICP-MS	ICP-OES	EC[*] Methods	SP[*] Methods	SF[*] Methods
Sample volume required	Large	Small	Medium	Medium	Small	Medium to Small	Medium to Small
Detection Range	nM	nM	pM to nM	pM to nM	nM to μM	μM	pM to μM
Detection limits	nM	nM	pM	pM	nM to μM	nM	pM to nM
Interference	few	few	few	More	few	few	few
Spot analysis	Not possible	Not possible	Not possible	Not possible	Possible[**]	Possible[**]	Not possible
Cost	Expensive	Expensive	Expensive	Expensive	Affordable	Affordable	Affordable
Accuracy	Good	High	Very High	Very High	Good	High	High
Precision	Good	High	Very High	Very High	Good	High	High
Recovery	Good	High	Very High	Very High	Good	High	High

[*]*EC-Electrochemical, SP -Spectrophotometric, SF-Spectrofluorimetric.*
[**]*Classical Potentiostat and Spectrophotometers are miniaturized to portable and handy devises with customized facilities especially for the spot analysis [3–5].*

Table 1.
Generalized comparison of the parameters of analytical significance of widely followed methods for HMIs quantification.

Because of this solid background HMIs quantification by electrochemical and optical methods will be a topic of interest for large group of readers. Keeping the beginners in mind discussion is focused on the fundamentals of electrochemical approaches, types of materials and strategies used for the quantification of HMIs by both electrochemical and optical methods. It must be noted that exhaustive literature citation is avoided because of the page limits and also to avoid the monotony.

2. Electrochemical sensing of heavy metal ions

2.1 Different electrochemical techniques

2.1.1 Voltammetry

Generally, in this case resultant current due to faradaic reaction [s] of the analyte is recorded by sweeping the potential between the two chosen potentials. As a result, the graph of current vs. voltage will be obtained that is referred to as voltammogram. Below are the various Voltammetric techniques commonly followed to measure the heavy metal ion[s] concentration.

2.1.1.1 Cyclic voltammetry [CV]

Current is recorded in the forward and backward directions by sweeping the potential in the fixed potential window. Faradaic reaction of the metal ion will result the oxidation and [or] reduction peaks at a particular potential where it underwent redox reaction. By referring to cyclic voltammogram

- potential required to oxidize/reduce the metal ion can be found. That information is helpful in performing amperometric measurement of metal ion samples, to decide the potential window in the other voltammetric techniques such as differential pulse voltammetry, square wave voltammetry etc.

- reversibility of the faradaic reaction can be understood.

In this three-electrode system platinum wire is used as counter electrode, calomel or Ag/AgCl electrode is used as reference electrode and glassy carbon electrode (GCE)/gold or platinum electrode/carbon paste electrode etc. is used as working electrode. Devi et al. used gold nanoparticles modified GCE as the working electrode for the quantification of Hg^{2+} ions using CV [8]. Authors exploited the well-known interaction of thiol and gold for the functionalization of gold on the GCE. Micro molar concentration of Hg^{2+} can be quantified using this CV method.

2.1.1.2 Pulse voltammetry

In this technique series of super imposing pulse of voltage are generated to result the potential sweep. Because of the applied voltage, HMI will undergo redox reaction to result the faradaic current and that is measured. Differential pulse voltammetry (DPV) is more opted out of various pulse voltammetric techniques such as normal pulse voltammetry and reverse pulse voltammetry. Xia et al. proposed DPV method for the simultaneous determination of Pb^{2+}, Cd^{2+} and Cu^{2+}. Wherein they used carbon paste electrode modified with hexagonal mesoporous silica and quercetin [9].

2.1.1.3 Square wave voltammetry [SWV]

SWV is another voltammetric technique which is also very often used to quantify the HMIs with some advantages like fast scan rate, less adsorption on the working electrode and reduced measurement time over DPV.

In the case of CV, DPV and SWV more than one HMI can be detected simultaneously.

Generally, HMIs quantification by voltammetric techniques is performed in conjunction with electrochemical deposition followed by stripping. Hence, few examples for the above mentioned voltammetric techniques are discussed under stripping voltammetry section.

2.1.1.4 Stripping voltammetry

It is a two-step procedure. First step involves the electrodeposition of the HMI[s] from the electrolyte solution onto the working electrode surface. Second, by applying any of the voltammetric techniques [discussed above], HMI[S] on the electrode will be stripped off into electrolyte solution. Based on the applied scan i.e. anodic or cathodic or during which stripping take place technique is named as anodic stripping or cathodic stripping voltammetry [10]. Following cases can be considered as an example for how stripping step is combined with various voltammetric techniques. Yao et al. proposed square wave anodic stripping voltammetry [SWASV] for the quantification of Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}. Fe_3O_4 nanocrystals of two different shapes are used as a modifier to obtain a sensitive and selective signal for the HMI [11]. **Figure 1** depicts the nature of SWASV. Serious interference of Cu^{2+} ions in the electrochemical detection of Cd^{2+} ions was effectively overcome by introducing Bi film on the GCE. As a result, stripping peaks were found to be intact even in the presence of Cu^{2+} ions for SWASV [12]. Raghu et al. developed DPASV method to achieve the quantification of Hg^{2+} ions down to picomolar concentration. Multiwalled carbon nanotubes [MWCNT] were functionalized with Fast Violet B salt through diazotization. Functionalized MWCNT then drop casted onto GCE to sense Hg^{2+} ions by DPASV in drinking water and industrial effluents [13]. Pandurangappa Malingappa and coworkers have published few exemplary works in which stripping voltammetric analysis has been systematically utilized for the analysis of HMIs from the various samples [14–16].

2.1.2 Amperometry

It is a potentiostatic technique. Electrochemical measurements are carried out at a fixed potential to measure the resultant current due to the redox reaction at the
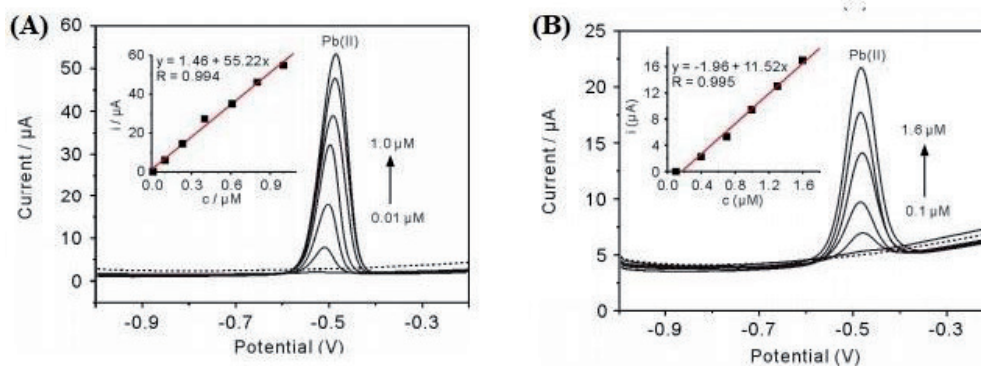

Figure 1.
SWASV recorded for the (A) octahedral and (B) cubic Fe_3O_4 modified electrodes in the presence of varied concentration of Pb^{2+} ion (reprinted with permission from [11] copyright 2014 American Chemical Society).

electrode electrolyte interface. Based on the analyte, here a particular metal ion, to be detected value of the potential needs to be applied will be decided. Hence, the measured current will be exclusively due to faradaic reaction of that particular analyte. To quote the recent example, Sannegowda and his coworkers developed iminephthalocyanine based amperometric sensor for the quantification of Pb^{2+} ions. That exhibited the linear range and detection limit in the nanomolar Pb^{2+} ion concentration [17]. Amperometric biosensor based on the urease was developed for the detection of Pb^{2+} and Hg^{2+} ions in river water samples also exhibited the analytical figures of merits closer to nanomolar levels [18]. Simultaneous quantification of more than one HMI is not possible i.e. the drawback of this method.

Another similar work can be quoted here. This case acridono-crown ether played a role of ionophore and. Poly(vinyl chloride) membrane again acted as a host. The potentiometric sensor works in a range of pH 4-7 but suffered a much-required sensitivity [19].

2.1.3 Potentiometry

Developed potential or electromotive force (EMF) is measured without applying external current. Experimental setup required for the potentiometric measurements is inexpensive. But, sensitivity of this technique is not appreciable when the routine electrodes are used. Efforts are in progress to improve the sensitivity by making use of electrodes constructed out of advanced materials such as graphene, CNT, and nanomaterials or reducing the size of the electrode itself i.e. nanoelectrodes [20, 21]. Ionophore is a corner stone of the potentiometric experimental setup that decides the selectivity and sensitivity of the procedure. Xin-Gui Li et al. developed a ionophore based on conducting copolymer microparticles. Poly[vinyl chloride] membrane acted as a platform to host the ionophore. Presence of functional molecules such as $-NH-$, $-N$, $-NH_2$, and $-SO_3H$ in the microparticles resulted high selectivity towards Pb^{2+} ions. It's worth mentioning that potentiometric sensor exhibited sub micromolar detection limit towards Pb^{2+} ions [22]. Another similar work can be quoted here. This case acridono-crown ether played a role of ionophore and poly[vinyl chloride] membrane again acted as a host. The potentiometric sensor works in a range of pH 4-7 but suffered a much-required sensitivity [23].

2.2 Electrochemical preconcentration

Generally, concentration of HMIs is very low in drinking water, food and biological samples. In addition to that, sample matrices will be complex in nature and many other ions and molecules will be present. In this regard it is very important to separate the HMI[S] from the sample matrix by enriching the same on to the working electrode surface. There by the interference from various electrochemically active species can be overcome and sensitivity can be significantly enhanced. Below two important electrochemical preconcentration methods are discussed in brief.

2.2.1 Electrochemical deposition

Electrochemical deposition is done by taking sample solution containing the HMI[s]in a three-electrode electrochemical cell. Then, suitable potential is applied to working electrode (most of the times modified working electrode) w.r.t. reference electrode. As a result of the applied potential metal ion will get reduced to metal atom and simultaneously deposited onto the working electrode. Prior to electrochemical deposition cyclic voltammetric experimental data will be helpful in

deciding the deposition potential. Suitable buffer solution and pH are necessary to fine tune the selective deposition of the particular HMI(S) [24].

2.2.2 Electrochemical adsorption

As the HMs exist as ions in the solution same nature can be exploited to achieve the electrochemical adsorption. It works on the electrostatic force of attraction principle. Basically, the working electrode will be modified with a material which has got sufficient opposite charges w.r.t. HMIs or its compounds. In addition to this material which also got greater surface area, hence, more charges on it will be preferred. It is obvious that nanomaterials are the competent candidates for this purpose. First comes the carbon nano substrates such as graphene, CNT, graphite flakes etc. Reason is twofold; Inertness of the carbon substrate hence it can just act as a platform for the HMIs adsorption and for the same reason it can be used for the construction of electrode as well. Ease with which the charge bearing functional groups can be covalently bonded on to it. There exist well-established procedures to introduce various functional groups such as carboxylic acid, amine etc. onto the carbon substrates. Now the materials, functionalized graphene or CNT, having greater surface area and also charge on it are suitable for the electrodeposition of the HMIs. Apart from these qualities, defects introduced during the functionalization process and their inherent good electrical conductivity have the added advantage for this application [25–27]. Likewise, nanomaterials other than carbon substrate can also be used. Positive or negative potential is applied to the electrode to enhance the rate of adsorption.

2.3 Different materials based electrochemical sensors

2.3.1 Carbon substrates

Graphitic carbon, glassy carbon, can be considered as the bulk form, itself has got good conductivity, stability have been used as an electrode material for a long time. Nanomaterials (NMs) derived out of graphite's single or few layers resulted in graphene, CNT, fullerene, carbon nanoflakes, etc. possessed extraordinary conductivity, excellent electrocatalytic property. Each carbon NM has been extensively studied for the electrochemical sensing of HMIs either in their pristine or modified form or as composite. Considering few examples out of large number of articles each carbon NM is discussed below.

2.3.1.1 Graphene

Two-dimensional single atomic thick monolayer is metallic in nature which inherited large surface area and very high conductivity [28]. In addition, hydroxyl and carboxylic groups originally present to a more or less extent depending on how the material is synthesized. If not present, those functional groups can be introduced on its surface with ease by following well established methods. Mentioned functional groups facilitate the interaction between the graphene and HMIs through either coordination or electrostatic or both. On the other hand, these inherent functional groups are exploited to introduce organic molecules, NMs etc. to enhance the sensitivity and selectivity. Li et al. reviewed the synthesis protocols and analytical applications of the graphene with exhaustive literature [29]. GCE modified with fluorinated graphene oxide was used to detect four HMIs such as Cu^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+} simultaneously [30]. Nafion is used in many of the reported works to assemble the graphene onto the electrode i.e. it acts as a binder. At the same time,

it also plays a role of ion exchange membrane hence, interference can be considerably overcome. Combination of the duo lead to many methods for the simultaneous determination of HMIs [31–33]. Simultaneous analysis of Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} was exhibited by a composite nafion, graphene and in situ prepared mercury film. Distinct SWASV peaks were observed for the mentioned HMIs [34]. It is worth mentioning that despite the mentioned synergetic advantages of the nafion & graphene there is problem of restacking of the graphene layers due to van der Waals force of attraction and also irreversible adsorption of HMIs onto the film was observed [35]. Gong et al. developed a strategy to overcome the restacking a graphene layers by introducing Au nanoparticles in between them. In addition, Au nanoparticles improved the analytical figures of merit for the sensing of Hg^{2+} ions [36]. In a similar approach SnO_2 and reduced graphene oxide composite lead to simultaneous determination of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} as shown in **Figure 2** [37]. Composite of reduced graphene oxide with cysteic acid lead to highly sensitive DPASV method for Ag^+ ion with detection limit of 1 nM [38]. Jingbo Chang et al. exclusively reviewed the sensing strategies of HMIs using graphene and its composites their more examples on this topic can be found [35].

2.3.1.2 CNTs

Properties, modification strategies discussed w.r.t. graphene holds good for CNTs. Since CNTs can be considered as rolled up structure of graphene and carbon atom is sp^3 hybridized in both the cases. CNTs are supposed to be equally competent for the analysis of HMIs compared to graphene but there are minor differences [39]. But, hybrid of graphene and CNTs yielded much better results compared to CNTs alone. Three-dimensional structure of graphene and CNT was able to simultaneously analyze pb^{2+} and Cd^{2+} ions [40]. CNTs are used in combination with bismuth film for the detection of HMIs [41]. CNTs and Pt nanoparticle together resulted in a highly sensitive electrochemical method for the ppb to ppt level As^{3+} determination [42].

2.3.2 Nanoparticles

As is well known, large surface area, more exposed catalytic sites, enhanced conductivity, greater electron & mass transport and faster electrode kinetics attracts
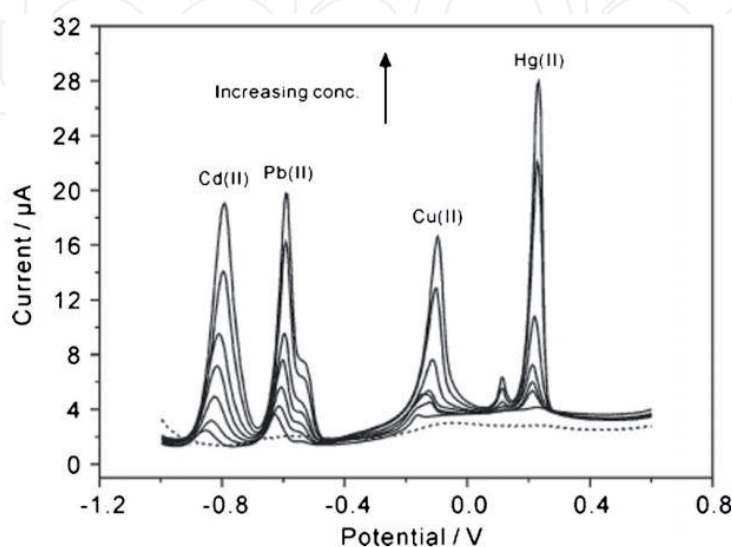

Figure 2.
SWASV peaks recorded in the presence of HMIs for SnO2-reduced graphene oxide modified electrodes (reprinted with permission from [37] copyright 2002 American Chemical Society).

the scientists to modify the working electrode with nanomaterials (NMs) for the better electrochemical sensing of HMIs. Though wide verity of NMs have been reported in the literature but metal and metal oxide nanoparticles are considered for discussion as their contribution is major among other NMs.

2.3.2.1 Metal nanoparticles

Gold nanoparticles and its derivatives have been extensively investigated as a transducer material for sensing HMIs because of its excellent conductivity, catalytic properties and inertness. There is a one more property i.e. affinity of gold towards thiol. This one property lead to plenty of works which all played around the triangular interaction between gold-thiol molecules-HMIs. As it can be observed gold component is common in below discussed cases but based on the material with which it is composed, capping agent, functionalized molecule and other experimental conditions sensitivity and selectivity towards HMIs will be totally different. Bin Zhang et al. modified carbon nanofibers with gold nanoparticles' size around 15 nm. That material was used on the GCE to simultaneously detect Cd^{2+}, Pb^{2+} and Cu^{2+} by SWASV [43]. Whereas the same Au nanoparticles capped with tannic acid modified GCE lead to highly sensitive and selective electrochemical sensor for Hg^{2+}down to 100 fM in the presence of Zn^{2+}, Al^{3+}etc. [44]. Handful number of articles can be found in which Au nanoparticles are used for the estimation of HMIs [45–47]. Inspired by the excellent electrochemical results two noble metals are combined to obtain the bimetallic composite. Same has shown promising results for the estimation of Hg^{2+} ions in the ppb range with the limit of detection down to ppt [48].

Earlier mercury electrodes were used to detect the HMIs because of the amalgamation reaction between the two. Thanks to the multicomponent alloy formation property of the bismuth and antimony with the HMIs. Because, highly toxic mercury electrodes were successfully replaced by the bismuth and antimony film modified electrodes. Nanoparticles of bismuth and antimony are proved to be an environmentally friendly and efficient platform for the quantification of HMIs [49–52]. Even the experiments were carried out to understand the effect of different morphology of the bismuth nanoparticles on the HMIs detection [53].

2.3.2.2 Metal oxide nanomaterials (MONMs)

Come into focus as a result of finding an inexpensive alternative for the noble metal nanoparticles in spite of their excellent electrochemical results as the latter are highly expensive. Other technical reasons are being as same as that any nanomaterials such as greater surface area and hence greater adsorption of HMIs, enhanced electrocatalytic activity etc. Oxides of iron, nickel, magnesium, manganese, zirconium etc. have been extensively studied for the quantification of HMIs. Majority of the reported methods are focused on experimenting with the morphology of the MONMs. Generally wide variety of morphologies can be achieved through hydrothermal synthesis. Then the MONM powder will be drop casted onto GCE for the electrochemical sensing of HMIs. Problem with this approach is modified electrode will not be sufficiently robust. Abdul Waheed et al. discussed the same with detailed literature in their review [54]. To overcome this, Lie et al. electrochemically deposited Co_3O_4 nanoparticles onto the indium tin oxide electrode followed by annealing. As prepared modified electrode is further used for the electrochemical sensing of Pb^{2+} ions in the presence of various divalent ions [55].

2.3.3 Mesoporous materials

Ordered mesoporous silicas (OMSs) can be considered as a representative candidate for mesoporous materials and their application in HMIs sensing. Because OMS exhibit uniform pore size, highly ordered pore, high volume and surface area which was explored by Mobil oil corporation [56, 57]. OMS provide a better platform for the physisorption of HMIs. As the OMS can be synthesized through various approaches different functional groups are inherently present on their surface. Out of which silanol is often present and most useful because of its reactive nature. Wide variety of organic molecules can be introduced through silanol group to result hybrid OMS. Because of the newly introduced organic molecules chemisorption of HMIs is achieved in addition to physisorption onto the hybrid OMS [58]. In majority of the reported methods particular OMS is combined with graphitic powder and mineral oil to obtain the modified carbon paste electrode to sense the HMIs. Thiol self-assembled monolayers on mesoporous supports [SAMMS] are used to prepare the carbon paste electrode for simultaneous analysis of Pb^{2+} and Hg^{2+} ion in 0.2 M HNO_3 [59]. Glycinylurea-SAMMS lead to SWASV method for the detection of Pb^{2+} with a detection limit down to 1 μg/L. It must be noted that detection can be performed over a wide range of pH 4.5 to 6.5 without using any specific buffer solution [60]. Yantasee et al. developed advanced remote accessible automated DPASV coupled with flow injection analysis of Pb^{2+} ions using Phosphonic-SAMMS [61]. Detailed literature on synthetic approaches and analytical applications of mesoporous materials can be found elsewhere [62].

3. Optical sensing of heavy metal ions

## 3.1 Spectrophotometric/ Fluorometric methods

Wide range of materials including organic molecules, nanomaterials, hybrid of earlier two, and quantum dots are used to sense HMIs by generating either color or fluorescence signal. Simultaneous signal generation for multiple HMIs is more often observed in electrochemical sensing. Whereas in case of optical methods, generally, signal will be generated exclusively due to target HMI. Hence, below are the sections categorized w.r.t. type of the material used for sensing. Lead i.e. Pb is considered as an example to explain the commonly followed strategies for the optical sensing of HMIs.

3.1.1 Cyclodextrins

In the year 1996 Czarnik et al. proposed a bench mark work for the fluorescence sensing of Pb^{2+} ions using a small molecule, heteroatom containing ligands. On complexation with Pb^{2+} ions proposed ligand exhibited enhanced fluorescence signal for about 15-fold [63]. Cyclodextrin molecule in binary solvent system exhibited 20-fold enhancement in the fluorescence signal after the addition of Pb^{2+} ions [64]. Similar cyclodextrin molecules are proposed by Chen et al. and Hayashita et al. for fluorometric sensing of the HMI as shown in **Figure 3** [65, 66].

3.1.2 Organic molecules

Color resulting dibromo-p-methyl-methylsulfonazo molecule was explored by Li et al. for spectrophotometric detection of the Pb^{2+} ions [67]. Inspired by this strategy Meng et al. worked out similar organic molecule for the colorimetric sensing of HMI [68].
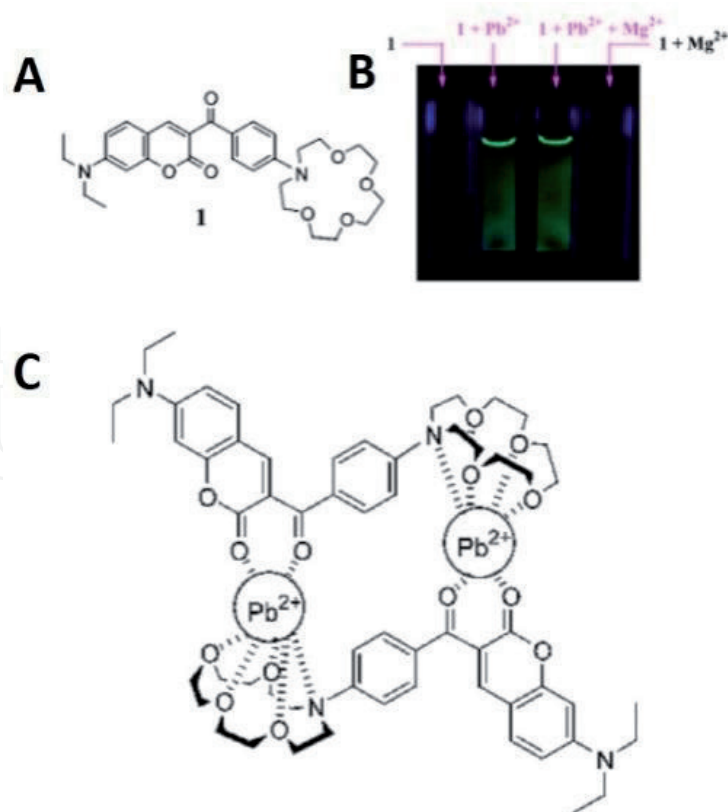
Figure 3.
(A) Representation of the structure of the ligand. (B) Image of the fluorescence response of the proposed ligand. (C) Binding mechanism of the Pb^{2+} ions with the proposed ligand (reprinted with permission from [65] copyright 2002 American Chemical Society).

3.1.3 Rhodamines

Rhodamine family molecules and its derivatives have been utilized extensively for the optical sensing of not only Pb^{2+} ions but most of the HMIs. Majority of such works result the optical signal through spirolactum ring opening or forming mechanism after interaction between the rhodamine and HMI. Yoon et al. reported rhodamine B derivative for both fluorometric and colorimetric sensing of Pb^{2+} ion in methyl cyanide medium [69].

3.1.4 Calixarenes

Calixarene family molecules are another category contributed significantly for the HMIs sensing. Calixarene structures generally from a dative bond with HMI through the functional groups to result an optical signal. Calix [4] arene derivatives are reported for the Pb^{2+} ion sensing can be observed as a regular method [70]. Switchable i.e. on–off–on fluorescent sensor observed due to the binding capacity of the calixarene molecule with two different cations i.e. Pb^{2+} and K^+ as shown in **Figure 4**. Observed phenomenon is due to the interaction of the K^+ ions with the molecular orbitals whereas that is absent in the Pb^{2+} ions case [71].

Apart from the above-mentioned categories there exist another variety of organic and bioorganic molecule extensively studied for the HMI. To name a few polymers based, peptide based, DNAzyme based sensors.

3.1.5 Carbon quantum dots

Carbon quantum dots (CQDs): Again, inherent functional groups on its surface and their deceptive role in anchoring desired molecules, nanoparticles etc.
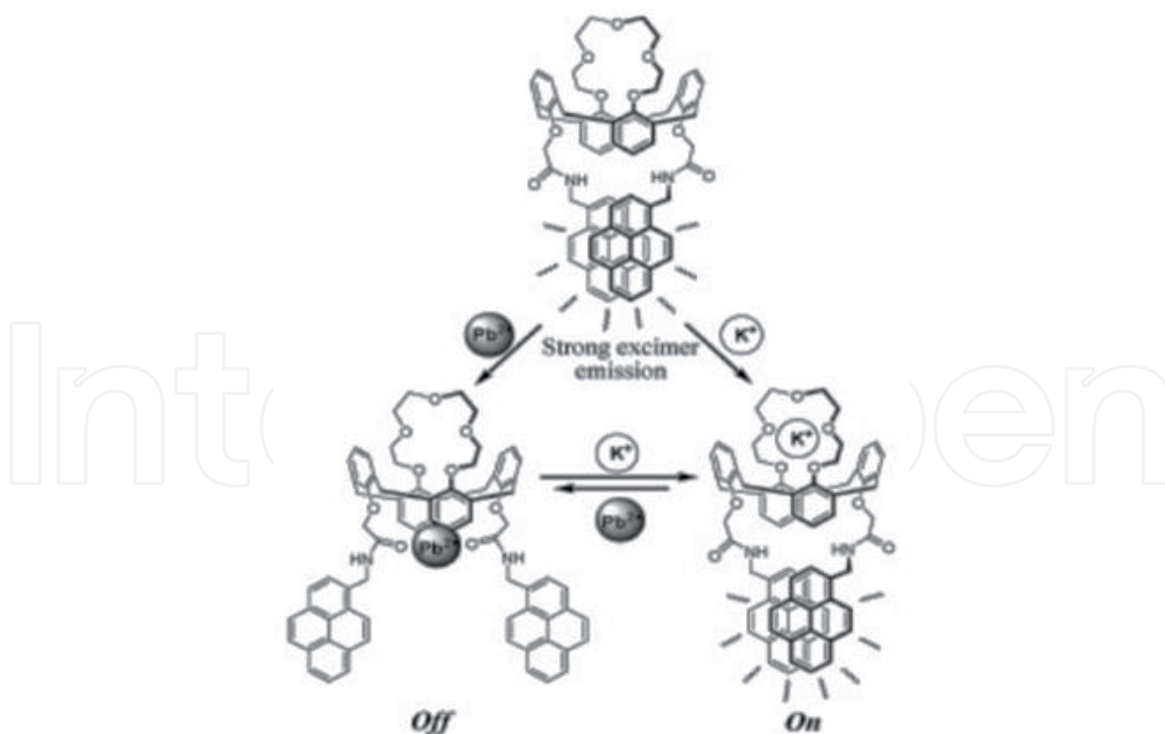
Figure 4.
Representation of the switchable fluorescence of the calix [4] arene derivative and its binding mechanism with Pb²⁺ and K⁺ (reprinted with permission from [71] copyright 2004 American Chemical Society).

made CQDs as emerging optosensors for HMIs. It is prerequisite to understand the mechanism of sensing of HMIs using CQDs before considering the individual articles on the same. Interaction between the light (electromagnetic radiation) of suitable wavelength and CQDs leads to the generation of charge carriers i.e. due to the excitation of electron from valence band to the conduction band. Generated charge carriers are utilized in the sensing of HMIs depending on the interaction of HMI with the ligand on the CQDs surface. Photo induced charge transfer, fluorescence enhancing/quenching, inner filter effects, phosphorescence etc. [72]. Sodium citrate and polyacrylamide sodium citrate resulted blue fluorescent CQDs which was quenched upon the addition of Pb^{2+} ion. By adding pyrophosphoric acid to the quenched solution, fluorescence was regenerated. This fluorescence off–on method was able to detect the Pb^{2+} of the order of 4.6 nM [73]. CQDs synthesized from the green approach using *Lantana camara* berries were exhibited sensitive and wide linear range up to 200 nM Pb^{2+} ion concentration [74]. CQDs synthesized from chocolate source also exhibited nanomolar HMI detection [75]. Household sugar was used to prepare the CQDs and found to be sensitive and selective for the naked eye sensing of Pb^{2+} ions in water [76].

3.1.6 Nanoparticles

Nanoparticles forms an interesting domain for the HMIs sensing. Though there exist a wide range of metal nanoparticles majority of the work has been done on Ag and noble metals Pt, Au nanoparticles in spite of their costly affair. Surface plasmon resonance is the corner stone of the optical sensing of HMIs using Ag, Au, and Pt. Hupp et al. used 11-mercaptoundecanoic acid capped Au nanoparticles as color generating agent for the detection of Pb^{2+}, Cd^{2+}, and Hg^{2+} ions [77]. Thomas et al. proposed quite a different approach wherein they started with Au^{3+}/Ag^+ ions and gallic acid solution. After the addition of Pb^{2+} Au/Ag nanoparticles are formed to result pink or red color respectively [78]. Non-aggregation-based sensor is developed by Huang et al. Originally Gold nanoparticles surrounded by thiosulphate and

2-mercaptoethanol in a solution. After the addition of Pb^{2+} due to the formation of Pb-Au alloy gold nanoparticles dissolved into solution and hence Surface plasmon resonance is decreased [79]. Opposite to that, i.e. aggregation based, sensing method was developed by Su et al. using glutathione modified Au nanoparticles. Upon the addition of HMI Au nanoparticles aggregate to result a color change from red to blue [80]. Theme of this work is summarized in the **Figure 5**.

Above discussed category of organic molecules, bioorganic molecules, nanoparticles have also been extensively used for the sensing of remaining HMIs. Functional moieties in the sensing molecules are different for different HMIs. But, conceptual wise it will be a repetition if the discussion is extended for the other HMIs. Ha Na Kim et al. has reviewed all the above discussed type of materials except CQDs for HMIs with an exhaustive literature survey and detailed discussion [81]. One can get more details and literature on CQDs for HMIs sensing in the review article presented by Pooja Devi et al. [72].
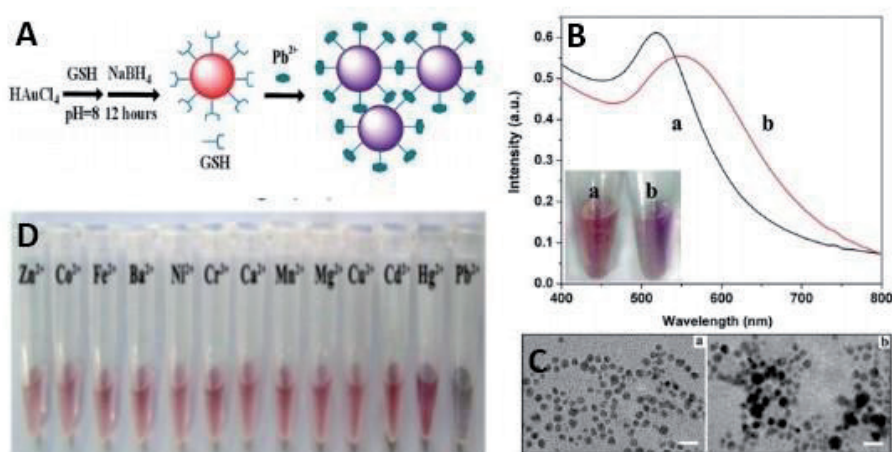

Figure 5.
(A) Scheme represents the preparation of glutathione capped Au nanoparticles. (B) Uv–Vis spectra, inset shows the images, (C) TEM images of Au nanoparticles in the absence (a) and presence of Pb^{2+} ions (b). (D) Images of the Au nanoparticle in the presence of various metal cations and Pb^{2+} ions (reprinted with permission from [80] copyright 2010 American Chemical Society).

4. Paper based optical and electrochemical sensing of HMIs

It is striking from the above discussions that both electrochemical and optical methods are good enough to quantify HMIs from various sample matrices. Selectivity, sensitivity and reproducibility of the most of the methods are sufficient enough i.e. can be used to quantify the HMIs within the permissible limits fixed by the world health organization. Apart from this there are some shortcomings for both the methodologies. It must be noted that both the instruments i.e. classical potentiostat and spectrophotometer cannot be carried away to the place at which the samples have to be analyzed. Hence, spot analysis of the HMIs is quite not possible using these methods. Also, both the instruments are expensive. Keeping these shortcomings in mind researchers are working out nonconventional methods. As it is already mentioned in **Table 1** miniaturized potentiostat and spectrophotometers are developed for spot analysis. Affordable and mobile phone installable softwares are developed to readout the color intensity on the spot [82]. On the other hand, sample holders i.e. electrochemical cells and cuvettes are replaced by paper strips. Below is the glimpse of such non-trivial methods.

4.1 Paper/strip

Making use of paper for the spot analysis of copper can be observed way back to 1945 [83]. Lateral flow through capillary action is the basis for the development of test strips not only for HMIs but various analytes. Pioneering work was published by Whiteside's group in the year 2007. In which photolithography was used to pattern the paper for the bioanalysis on the spot [84]. Paper based analytical device (PAD) is modified with resorufin thionocarbonate-based dye and it can detect µM concentration Hg^{2+} ions by using buffer solution of pH 8 [85]. 3,3′,5,5′-tetramethylbenzidine (TMB) and gold nanoparticles were used to develop a PAD for semiquantitative analysis of Hg^{2+} ions. Based on the enzyme like action of the gold and mercury nanoparticles TMB will give blue color [86]. In a similar work, platinum nanoparticles and TMB combination is used to detect Hg^{2+} ion using PAD. In this case decrease in the color intensity indicates the concentration of HMI. Enzymatic activity of the platinum nanoparticles to turn the TMB to blue is inhibited by the Hg^{2+} ions in this case [87]. Many such PAD based naked eye detection of HMIs can be found in literature [88–90]. Paper based electrochemical sensors (PESs) are coined as they inherit the simplicity and advantages of the PADs with better sensitivity. Whiteside's group developed PES by adopting the commercial electrochemical readers [91]. In case of PES electrodes are printed on a paper with carbon inks (working and counter electrodes), silver-silver chloride inks (reference electrode). These electrodes connected to a respective terminal of the electrochemical reader to measure a signal. Mariana Medina-Sánchez et al. developed PES for the quantification of Pb^{2+} and Cd^{2+} ion in a range 10 to 100 ppb. Developed sensor was reagent free and ecofriendly [92]. Two substrates i.e. plastic film and paper were used to coat graphene and polyaniline composite for the simultaneous detection of Zn^{2+}, Cd^{2+}, and Pb^{2+} ions [93]. Going one step ahead Poomrat Rattanarat et al. came up with a multi-layer-based device capable of producing both optical and electrochemical signal for iron, nickel, copper, chromium, lead and cadmium ions [94]. Iron, nickel, copper, chromium can be detected using optical signal whereas lead and cadmium ions are detected by electrochemical output as shown in **Figure 6**.
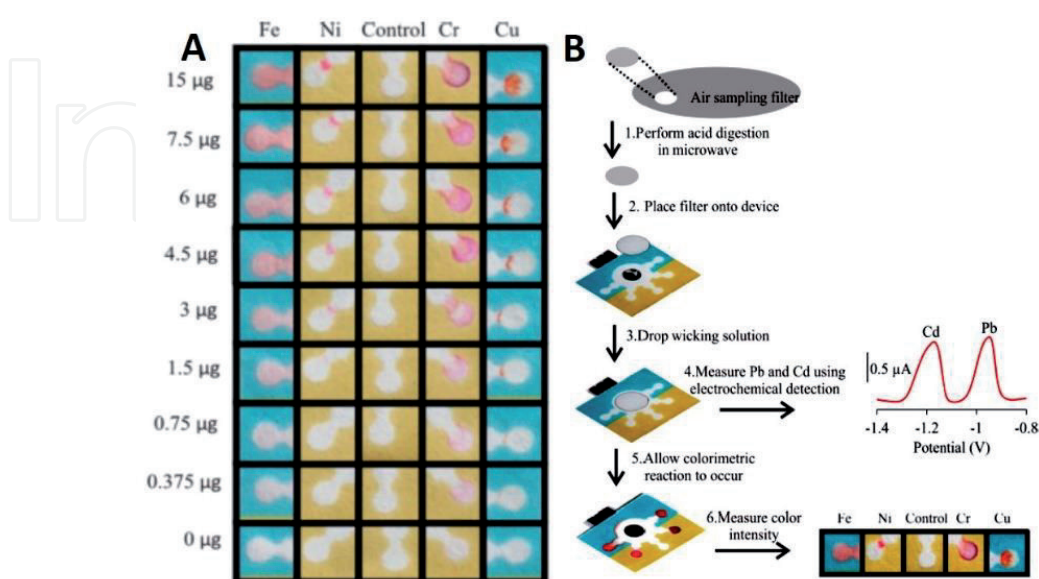

Figure 6.
(A) Image of the multilayer paper-based device's color changing response for the given HMIs. (B) Flow diagram details the preparation, electrochemical, and colorimetric response of the multilayer device (reprinted with permission from [94] copyright 2014 American Chemical Society).

5. Conclusions

Importance of HMIs quantification is stated followed by efficient methods and their drawbacks. No doubt that electrochemical and optical methods are promising alternatives. Because of the advantages such as user friendly, economical and competency, electrochemical and optical methods are further considered for the discussion. Different electrochemical techniques followed for the HMIs quantification are described with the fundamentals and reasoning in brief. Among them stripping voltammetric techniques are found to be efficient. Many electrochemical methods are reported to be capable of sensing HMIs down to ppb level and few can detect down to pico molar concentration. Another advantage of the electrochemical methods is the simultaneous analysis of multiple HMIs. Electrochemical methods are yet to be adopted for the field [spot] analysis. On the other hand, optical methods in particular colorimetric methods are metamorphosed to naked eye sensing of HMIs which will help in field analysis. PADs are coined to further simplify and miniaturize both electrochemical and optical methods. Alternatives for the often-used expensive color inducing materials such as gold, platinum and silver are still need to be explored in case of PADs for optical sensing of HMIs. It can be concluded that PESs are highly sensitive and selective but cannot be carried to field. Whereas PADs used for optical sensing are sensitive and can be used for field analysis are semiquantitative.

Acknowledgements

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