Spectroscopic Techniques and Electrochemical Sensors Technologies for Heavy Metal Ions Detection: A Review

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Abstract—*Water is an essential compound for us to sustain as it is a great source of many elements but provides some undesirable substances when to gettingpolluted which effects human health in such a manner that cause many dangerous diseases. This paper presents a review of three different techniques used for heavy metal analysis in potable water.In the first part of paper, various conventional analytical techniques are discussed in detail and a brief comparison is also made. The second part of the paper explains electrochemical methods, which produced rapid, convenient, and reliable decentralized monitoring of trace metals. In the last section,a review on impedance spectroscopy, which is used for characterization of a wide range of materialsis reported.*

***Keywords—Analytical techniques, Electro analysis, Heavy metals, Impedance Spectroscopy*.**

I. INTRODUCTION

Quality water determined the quality life as it plays a vital role in good health[1]. In developing countries like India, where finding quality water is the difficult task. As per the official data, more than 1 billion people in the world do not have access to safe drinking water and about 2.5 billion do not have access to adequate sanitation services. Although, there are many water related diseases, who kill on an average more than 6 million children each year and with an average of 20,000 children a day [2].

The real problem lies with heavy metal which makes ground water contaminated and it is one of biggest environmental issues even at all level [3]. Heavy metals generally are those who is having a specific density of more than 5 g cm^{-3}. The main problems to human health, with regard to the factum of heavy metal, are very serious in nature as exposure to cadmium, mercury, lead, cobalt, manganese, chromium and arsenic, but in addition to that there are others 19 elements known as HM: bismuth, antimony, cerium, chromium, copper, gallium, cobalt, gold, iron, nickel, manganese, platinum, silver, tellurium, tin, thallium, uranium, zinc and vanadium.

Heavy metals are having a negative effect on the environment and when they get mixed in the biosphere and enter living creatures via alimentary chain there by destroying human health. Heavy metals become poisonous when they not metabolized by the body and gathered in the soft tissues. It's dangerous effect is because of a bond making of metals with the thiol group of proteins which goes to the cell, amends the biochemical lifecycle [4].

International bodies such as the WHO played a great role in conducting a proper survey and reviewed effects of heavy metals on human health from time to time.

Some of the heavy metals are essential to present in drinking water to carry through cellular functions, upto desirable limit. If the concentration range of metals is more than permissible limit then are poisonous for human beings. A comparison of drinking water standards for some heavy metals according to the agencies like the Bureau of Indian Standards and the World Health Organization has been made in Table 1.

Table 1: A comparison of BIS, WHO, and USEPA guideline values of heavy metal ions for drinking water [5]

Heavy Metals	BIS: 10500 (mg L^{-1})	WHO (mg L^{-1})	USEPA (mg L^{-1})
Arsenic	0.05	0.01	0.01
Cadmium	0.003	0.003	0.005
Mercury	0.001	0.006	0.002
Chromium	0.05	0.05	0.1
Manganese	0.3	NM	0.05

NM: not mentioned

II. TECHNIQUES FOR HEAVY METAL IONS DETECTION IN POTABLE WATER

There are different techniques available for the detection of heavy metal ions in water samples and measuring their concentration. These techniques are divided broadly into three categories:

- Analytical Techniques

- Electrochemical Techniques
- Impedance Spectroscopy

A detailed description of all the three techniques and their types is explained in the section below.

III. ANALYTICAL TECHNIQUES

In the last few years, different types of analytical techniques have been used to analyze the heavy metal ions in water [6]. These determination techniques of metal ions are available on the basis of their basic principle, sensitivity, specificity, limits of detection, mono-multielement detection, ease of use, costs, etc. Various types of analytical techniques are illustrated below:

3.1 Atomic Absorption Spectroscopy (AAS): Atomic absorption spectrometry is widely used technique for the determination of trace heavy metal ions in all kinds of samples .In AAS, a light beam is passed through the sample and some amount of the light is absorbed based on the concentration of the elements present, different amount of lights is absorbed by the elements. By comparing the original beam intensity and of the beam after passing the sample, the concentration of the element can be calculated. This method is used for the determination of only one single element per analysis [7-8].

3.2 Inductively Coupled Plasma Spectrometry (ICP): Inductively coupled plasma spectrometry is subdivided into two techniques i.e inductively coupled plasma - optical emission spectroscopy (ICP-OES) and inductively coupled plasma - mass spectrometry (ICP-MS). ICP is a multi-element analysis technique. The ICP-OES is a spectroscopic technique in which plasma source is used to excite the atoms in samples. These excited atoms emit light of a characteristic wavelength, and a detector measures the intensity of the emission corresponding to the concentration of the element detected. But in a case of ICP-MS, the plasma source is used to atomize the sample, and mass spectrometer detects the ions according to their atomic mass-to-charge ratio [9-10].

3.3 Laser Induced Breakdown Spectroscopy (LIBS): Laser-induced breakdown spectroscopy is a versatile technique as it performs rapid analysis of heavy metals in water and as well as allows online monitoring. LIBS is a kind of emission spectroscopy that uses a laser pulse of high energy. The focused laser pulses beam are applied to form a plasma, which atomizes and excites the samples and final elemental analysis is done by the spectrometer. The elements in water is identified by their unique spectral signatures [11-12].

3.4 X-Ray Fluorescence(XRF): X-ray Fluorescence is an elemental analysis technique which uses primary excitation source, provided by X-rays tubes, which cause sample elements to emit X-ray photons of a characteristic wavelength and detectors are used to detect and analyze the secondary radiation (X-ray photons). The sample elements are identified by the wavelength of the emitted X-ray photons and the intensity of the X-ray photons determine the concentrations [13-14].

3.5 Neutron Activation Analysis (NAA): Neutron Activation Analysis is a highly sensitive procedure for determining the concentration of different metals based on sensitivities. NAA technique is based on neutron activation process, therefore, the sample is bombarded with neutrons, causing the elements in the sample to form radioactive nuclei. Using this information, concentration of the elements is determined by studying the spectra of the radioactive sample emissions [15].

3.6 Ion Chromatography: Ion chromatography is a simple technique for the simultaneous analysis and quantification of ions in the solution. It is an HPLC technique in which ion exchange resins are applied for simultaneous determination of many ionic species in aqueous solutions on ppm (mg/L) and ppb (µ/L) level. IC offers an advantage over the spectroscopic techniques for cation analysis in the area of metal speciation [16].

3.7 UV/VIS spectrometry: This spectrometry is based on molecular absorption concept and applied for the determination of low concentration of anions and cations, difficult to determine with the use of atomic absorption spectrometry. This technique provides an easy, simple and rapid determination of heavy metal ions in low to high concentrations at the cheap cost [17].

Conventional analytical techniques for heavy metals detection are precise, sensitive, versatile since they are suited for a large group of elements and their limit of detection in the femtomolar range. However these techniques suffer from many drawbacks such as expensive instruments needed to carry through the multi-step sample preparation, difficult sample pretreatment and involve complex analytical procedure, which are unsuitable for online monitoring applications.

IV. ELECTROCHEMICAL TECHNIQUES FOR HEAVY METAL IONS DETECTION

For metal analysis the two principal electrochemical techniques used are potentiometry and voltammetry [18]. These two techniques can be distinguished on the basis of controlled variable that is voltage or current. One of these variables in applied to solution containing the analyte species and the other variable is measured. Information is determined regarding the concentration and identity of analyte species in solution, from a plot of the measured variable versus the applied variable.

4.1 Potentiometric Technique [19]

- It is a classical technique in which information about the composition of the sample is provided through the potential appearing between two electrodes.

- Ion-selective electrodes (ISEs) provide rapid and selective potentiometric techniques for the determination of the major cations (metals) in water samples.
- Limit of detection in the nanomolar range (or even lower).

4.2 Voltammetric Technique [20]

- It is a method in which information about the composition of electrolytic solutions is provided by measuring the current as a function of applied potential.
- Stripping analysis is one of the most sensitive voltammetric method, which makes possible to determine a very small concentrations of analyte (subnanograms); i.e an analysis of 10^{-10} M solution.
- Limits of detection in the picomolar range.

These techniques are recognized as powerful techniques and versatile because in contrast to conventional analytical techniques, the electrochemical methods are much cheaper, quicker and simpler for carrying out a detection of heavy metal ions in water samples.

V. IMPEDANCE SPECTROSCOPY FOR HEAVY METAL IONS DETECTION

5.1 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) or ac impedance methods have seen an immense increase in popularity in recent years.EIS is a non-destructive method used for detecting and determining the target species concentrations based on electrical impedance changes at the sensor analyte interface [21]. It is a highly sensitive characterization technique used to study a variety of electrochemical systems because EIS can give accurate error-free kinetic and mechanistic information using a variety of techniques and output formats.

5.2 Principle of Operation

EIS is a modulation technique in which impedance is measured by applying a small amplitude sinusoidal excitation signal to the system under study (electrochemical system) and measuring the corresponding response signal. The response to the sinusoidal potential excitation is a current signal of the same frequency but phase-shifted with respect to the applied potential [22].

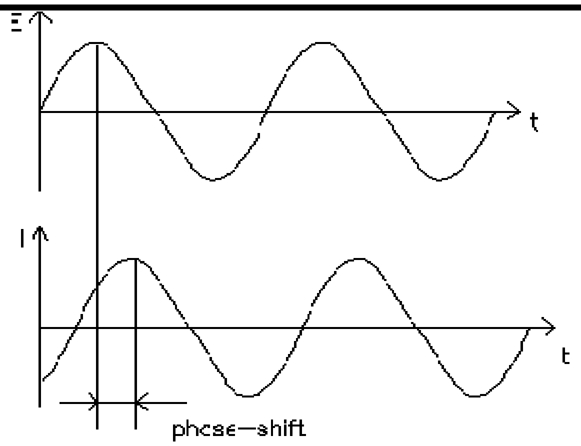

Fig.1: AC Waveforms for an Applied Potential and a Resulting Current

The impedance of the system is then represented as a complex quantity,

$$Z(\omega) = \frac{E\ (\omega)}{I(\omega)} = Z_o \exp(j\varphi) = Z_0(cos\varphi + jsin\varphi)$$

The magnitude and a phase shift of the impedance depend on the applied signal frequency. The real component represents resistance and the imaginary component is represented by combined capacitance and inductance.

Impedance measurement provides a large amount of information about the several processes occurring on electrode surfaces, the conductivity of the solution and numerical expression of the ability of an aqueous solution to carry electric current.

To interpret electrochemical systems, impedance result are then correlated to the Randles equivalent circuits consisting of resistors and capacitors. The Nyquist plot obtained from these equivalent circuits gives a visual insight into the system dynamics and qualitative interpretations are done. The circuit elements are used to describe impedance phenomenon within EIS systems.

Table 5: Electrochemical Impedance Spectroscopy Advantages and Disadvantages summarized below [23]

S.No.	Advantages	Disadvantages
1.	In EIS technique, small amplitude signals are used without disturbing the properties being measured	Large time is required to obtain a full impedance diagram when modification is done in the specimens under study
2.	The equivalent circuit can be obtained from	Impedance data is difficult to interpret, as it requires a level

	resulting EIS data and contribution of different components to the total impedance can be studied	of mathematical skills that is not commonly held by electrochemists

5.3 EIS Applications in various fields

Electrochemical Impedance Spectroscopy techniques can be used in numerous research areas for a wide range of applications as it is a simple method for translating complicated chemical responses to an electronic mode that can be interpreted and utilized in future studies.

- EIS is a useful tool to detect the corrosion protection of stainless steel [24]. In corrosion research area its application is in three areas that are for rate determination, passive layer investigations and inhibitor and coatings.
- EIS has been extensively used in the analyses of lithium battery systems [25] to study the state-of-charge, electrode design, and materials selection.
- It is used to investigate the quality of coatings in the paint industry [26]. In coatings evaluation research area its application is in dielectric measurements and corrosion protection.
- EIS is also used to analyze and characterize different food products. It acts as effective tool in the testing of metal packaging material [27], to control the quality of food packaging.

VI. SUMMARY

Electrochemical Impedance Spectroscopy is a powerful, rapid and accurate non-destructive method as it resulted in robust measurements in contrast to other techniques. EIS method does not involve a potential scan, so measurements can be performed in low conductivity solutions where dc techniques suffer from potential-control errors problem. Contrary of that electrochemical techniques, particularly voltammetric methods are simple, time-saving, selective and more sensitive for the simultaneous determination of metal ions as well as large linear dynamic range, with relatively low-cost instrumentation. In comparison to electrochemical methods, typical detection techniques for heavy metals are selected due to their wide applicability and offer high accuracy but suffer from drawbacks. Depending on the application area one of the techniques can be selected out of three different techniques discussed or the combination of techniques can be applied for detection of heavy metals in water samples.

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