

CHAPTER 1

Introduction

1.1 Overview of the research

Arsenic is a naturally occurring element present in the environment in both organic and inorganic forms. Inorganic arsenic is considered to be the most toxic form of the element, and it is found in soil, groundwater and surface water as well as contaminated in many foods [1]. Depending on the environment, inorganic arsenic can exist in the two different oxidation states As^{III} and As^{V} in natural water.

Several detection methods have been developed for the determination of arsenic, including atomic absorption spectrometry (AAS), inductively-coupled plasma (ICP) spectrometry, high-performance liquid chromatography (HPLC), and electroanalytical techniques such as cathodic stripping voltammetry (CSV) and cyclic voltammetry (CV). Voltammetry is of great interest because of its high sensitivity, low limit of detection and good selectivity, in addition to the relatively low cost for its implementation [2].

Cathodic stripping voltammetry with a hanging mercury drop electrode (HMDE) is promising and features the advantages of simple and usually portable instrumentation amenable to both laboratory and field applications. Generally, HMDE is used as the working electrode, due to its fresh working electrode surface that gives high sensitivity, reproducibility and renewability [3]. Alternatively, complexing ligands can be used to form complex with arsenite (As^{III}), which is adsorptively deposited on the HMDE.

Sodium diethyldithiocarbamate (Na-DDTC) is a widely used reagent in spectrophotometric method for the determination of arsenic. In the literatures, the determination of trace amounts of arsenic employs diethyldithiocarbamate (DDTC) or diethyldithiophosphate (DDTP) as As^{III} complexing agents at the sample-preconcentration stage. Cathodic stripping voltammetry involves the electrochemical reduction of As^{III} to As^0 in the preconcentration step to form As-Cu intermetallic compound, which is the presence of DDTC or DDTP can improve the sensitivity of the

analysis [4-8]. Arsenate (As^{V}) is generally regarded to be electrochemically inactive and normally the determination of As^{V} requires its prior reduction to As^{III} before analysis as total arsenic ($\text{As}^{\text{III}}+\text{As}^{\text{V}}$) by CSV [9-10]. In this work, a square wave cathodic stripping voltammetric method for determination of trace arsenic by using the HMDE as working electrode in presence of copper and sodium diethyldithiocarbamate was developed.

The determination of arsenate by spectrophotometric or colorimetric analysis has become the most practical technique for field application. It is based on the molybdenum blue method, which involves the forming of As^{V} with molybdenum blue complexes while As^{III} could not [11]. The aim of this work is to develop the method for arsenate detection in water using glassy carbon electrode (GCE), the electron transfer reaction will occur and a measurable current can be detected by cyclic voltammetric method.

1.2 Introduction to arsenic

1.2.1 Occurrence and application of arsenic

Arsenic (As) has the atomic number 33 and an atomic weight of 74.92. It is a naturally occurring, group V element that is a semi-metallic element found in soils, groundwater, surface water, air, and some foods [12]. Arsenic is widely distributed throughout the Earth's crust, generally as arsenic sulfide or as metal arsenates and arsenides. It can be released to the atmosphere, primarily as the trioxide, mainly by high-temperature processes. In the atmosphere, it is mainly adsorbed on particles, which are dispersed by wind and deposited on land and water [13].

Arsenic can be released into the atmosphere and water in the following ways:

- natural activities, such as volcanic activity, dissolution of minerals (particularly into groundwater), exudates from vegetation and wind-blown dusts;
- human activities, such as mining, metal smelting, combustion of fossil fuels, agricultural pesticide production and use, and timber treatment with preservatives;
- remobilization of historic sources, such as mine drainage water;
- mobilization into drinking water from geological deposits by drilling of tube wells.

Arsenic is a natural component of the earth's crust, and found in all environmental media. Concentrations in air in remote locations range from < 1 to 3 ng m^{-3} , but concentrations in cities may range up to 100 ng m^{-3} . Concentrations in water are usually $< 10 \text{ } \mu\text{g L}^{-1}$, although higher concentrations can occur near natural mineral deposits or anthropogenic sources. Natural levels in soils usually range from 1 to 40 mg kg^{-1} , but pesticide application or waste disposal can produce much higher values [14-15]. In drinking water, the maximum acceptable concentration established by the U.S. Environmental Protection Agency (USEPA), and also by the World Health Organization (WHO), is $10 \text{ } \mu\text{g L}^{-1}$ (10 ppb) for total arsenic [12-13].

Arsenic can occur in the environment in several oxidation states ($-III$, 0 , $+III$, and $+V$), its compounds can be classified into three major forms: inorganic, organic, and arsine gas [16].

Inorganic arsenic may be formed with either trivalent (As^{III} , arsenite) or pentavalent (As^V , arsenate) arsenic. The most common inorganic trivalent arsenic compounds are arsenic trioxide, sodium arsenite, and arsenic trichloride. Pentavalent inorganic compounds are arsenic pentoxide, arsenic acid, and arsenates such as lead arsenate and calcium arsenate. Inorganic arsenic compounds are used in metal alloy manufacturing, electronics manufacturing (semiconductors), and as wood preservatives. They are also formed as by-products during the smelting of metals and coal combustion.

Organic arsenic compounds are formed when arsenic combines with carbon. Organic arsenic compounds may be trivalent or pentavalent. Most organic arsenic compounds found in the environment are methylated as a result of biomethylation by organisms in soil or water. Organic arsenics, such as disodium methylarsenate (DSMA) and monosodium methylarsenate (MSMA), are used as herbicides. Organic arsenic compounds are registered for use as medicinal animal feed additives. Arsenobetaine or "fish arsenic", an organic form of arsenic, is normally found in seafood and is nontoxic.

Arsine gas is formed by the reaction of hydrogen with arsenic and can have a garlic-like or fishy odor at high concentrations. Arsine gas is used commercially in the semiconductor industry, during the synthesis of organic arsenic compounds, and in the manufacture of crystals for computer chips and fiber optics. Arsine gas can be generated accidentally during the smelting and refining of nonferrous metals and in mining processes.

The numerous arsenic forms present in the environment and living organisms as shown in the Table 1.1 [17-18].

Table 1.1 Arsenicals of environmental and biological importances

Compound	Abbreviation	Chemical formula
Arsenite (arsenous acid)	As ^{III}	As(OH) ₃
Arsenate (arsenic acid)	As ^V	AsO(OH) ₃
Monomethylarsonic acid	MMA ^V	CH ₃ AsO(OH) ₂
Monomethylarsonous acid	MMA ^{III}	CH ₃ As(OH) ₂
Dimethylarsinic acid	DMA ^V	(CH ₃) ₂ AsO(OH)
Dimethylarsinous acid	DMA ^{III}	(CH ₃) ₂ AsOH
Trimethylarsine oxide	TMAO	(CH ₃) ₃ AsO
Tetramethylarsonium ion	Me ₄ As ⁺	(CH ₃) ₄ As ⁺
Arsenobetaine	AsB	(CH ₃) ₃ As ⁺ CH ₂ COOH
Arsenocholine	AsC	(CH ₃) ₃ As ⁺ CH ₂ CH ₂ OH
Arsenolopids	AsL	(CH ₃) ₃ As ⁺ CH ₂ CHOHCOOH
Trimethylarsine	TMA ^{III}	(CH ₃) ₃ As
Arsines	AsH ₃ , MeAsH ₂ , ME ₂ AsH	(CH ₃) _x AsH _{3-x} (x=0-3)

1.2.2 Toxicology of arsenic

The toxicity of arsenic varies widely based on route of exposure and chemical species. Ingestion and inhalation are the primary routes of both acute and chronic exposures; inorganic arsenic is not readily absorbed by skin. Arsine gas is one of the most toxic forms and is readily absorbed into the body by inhalation. The LD₅₀ values of various arsenic compounds in Table 1.2 show that the inorganic forms of arsenic are the most acute toxic, whereas MMA and DMA show intermediate acute toxicity, and the trimethyl and tetraalkylarsonium compounds may be considered innocuous.

Table 1.2 Toxicology of arsenic species (oral administration to mice and rats) [19]

Arsenic Species		LD ₅₀ values (mg/kg)
Arsenite	As ^{III}	15-42
Arsenate	As ^V	20-800
Monomethylarsonate	MMA	700-1,800
Dimethylarsinate	DMA	1,200-2,600
Arsenocholine	AsC	6,500
Arsenobetaine	AsB	>10,000

Toxicology quick facts about arsenic:

- Arsine gas is extremely toxic.
- Inorganic arsenics are more toxic than the organic forms.
- Trivalent arsenic compounds tend to be more toxic than pentavalent arsenic compounds.
- Metalloid arsenic is nontoxic because it is insoluble in water and body fluids.
- Arsenobetaine is the primary form of arsenic found in fish and is nontoxic.

The signs and symptoms of arsenic may vary with the route of exposure, form, the dose, the duration of exposure and the time elapsed since the exposure are summarized in the Table 1.3.

Table 1.3 Possible health-effects of arsenic exposure in adults [20]

Form	Acute	Chronic
Inorganic Arsenic	Neurologic: light-headedness, headache, weakness, lethargy, delirium, encephalopathy, convulsions, coma, sensorimotor peripheral neuropathy	Peripheral and CNS: paraesthesia, muscle tenderness, muscle weakness, peripheral neuropathy, anorexia
	Hepatic and renal: elevated liver enzymes; hematuria, oliguria, proteinuria; and acute tubular necrosis, renal cortical necrosis	Hepatic jaundice, cirrhosis, ascites
	Cardiovascular and respiratory hypotension, shock, ventricular arrhythmia, congestive heart failure, pulmonary edema	Peripheral vascular disease, acrocyanosis, Raynaud's phenomenon, endarteritis obliterans
	Gastrointestinal: severe abdominal pain, nausea, vomiting, bloody stools, gastroenteritis	Gastrointestinal hemorrhagic gastroenteritis
	Hematological: anemia, leukopenia, thrombocytopenia	Dermal; hyperpigmentation, hyperkeratosis of hands/feet
	Death	Metallic taste, garlicky breath Diabetes mellitus Mees lines Increased risk of skin, lung, liver, kidney and bladder cancers, lymphomas and leukemias
Arsine Gas	Hemolytic anemia, chills, malaise, nausea, vomiting, abdominal pain, jaundice, renal failure	Shortness of breath, general feeling of weakness

1.3 Analytical methods for arsenic determination

The analytical methods for determination arsenic have been reviewed [21-24]. At present, there are many analytical methods for the determination of arsenic, such as hydride generation atomic absorption spectrometry (HG-AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray spectrometry, neutron activation analysis (NAA), electrophoresis, chemiluminescence and electrochemistry [25-29]. The spectroscopic techniques were developed for arsenic speciation, which based on coupling with chromatographic separation. However, these methods are not suitable for use in the field. In contrast, the electroanalytical techniques such as voltammetry [30-31], potentiometry [23], polarography [32], amperometry [33] are relatively simple, inexpensive with superb sensitivity, possess capability for speciation and small-sized instrumentation which could be field deployable [34].

Voltammetry is an electrochemical technique, which current is measured as a function of the applied potential to an electrochemical cell [35], similar to that shown in Figure 1.1. A common electrochemical cell consists of a working electrode (WE), a reference electrode (RE), and an auxiliary electrode (AE). The whole system contains a voltammetric cell with various volumes capacity, magnetic stirrer and gas line for purging and blanketing the electrolyte solution.

The diffusion current (i_d) produced by the desired reaction is proportional to the concentration of analyte (C_A) under ideal conditions,

$$i_d = k \cdot C_A \quad (1.1)$$

where k is a constant [36]. Thus, the plot of i_d versus concentration can be used for calibration.

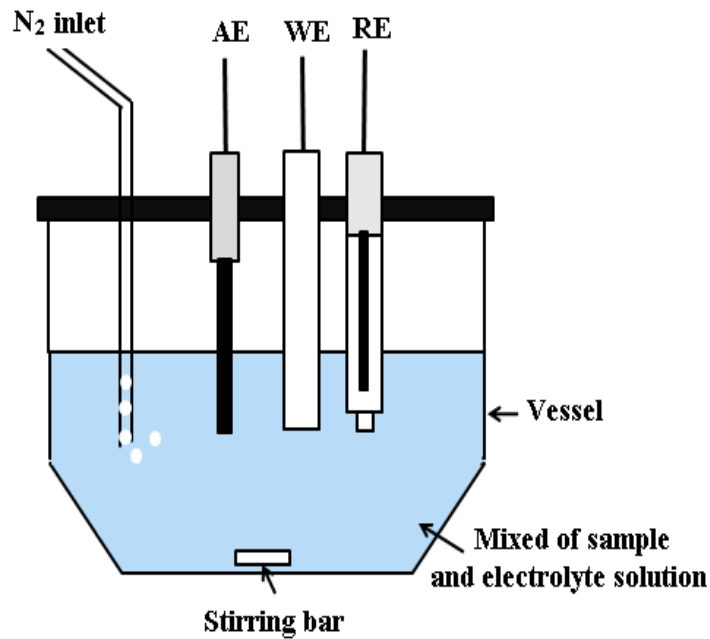


Figure 1.1 Typical electrochemical cell for voltammetry
(AE: auxiliary electrode, WE: working electrode, RE: reference electrode)

1.3.1 Cathodic Stripping Voltammetry

Stripping technique is one of the most sensitive voltammetric techniques for measuring trace metals. Stripping voltammetric method includes three steps as follows [37];

1) Deposition step:

In this step, analyte will be preconcentrated on the WE within a certain time while solution is stirred. The deposition potential imposed on the WE is chosen according to the species to be determined and is maintained for a deposition period depending on their concentration. During deposition step, the solution is stirred to facilitate transportation of ions of interest to the surface of WE.

2) Rest step:

In this step, it allows the formation of a uniform concentration of the ions of interest on the mercury, as the forced convection is stopped at the end of the deposition period.

3) Stripping step:

This step consists of scanning the potential anodically for anodic stripping and cathodically for cathodic stripping. When the potential reaches the standard potential of a certain ion of interest–metal ion complex, the particular ion of interest is reoxidised or reduced back into the solution and a current is flowing. The resultant voltammogram recorded during this step provide the analytical information of the ions of interest. The potential-time sequence in stripping analysis is shown in Figure 1.2 which shows all three steps that were mentioned earlier.

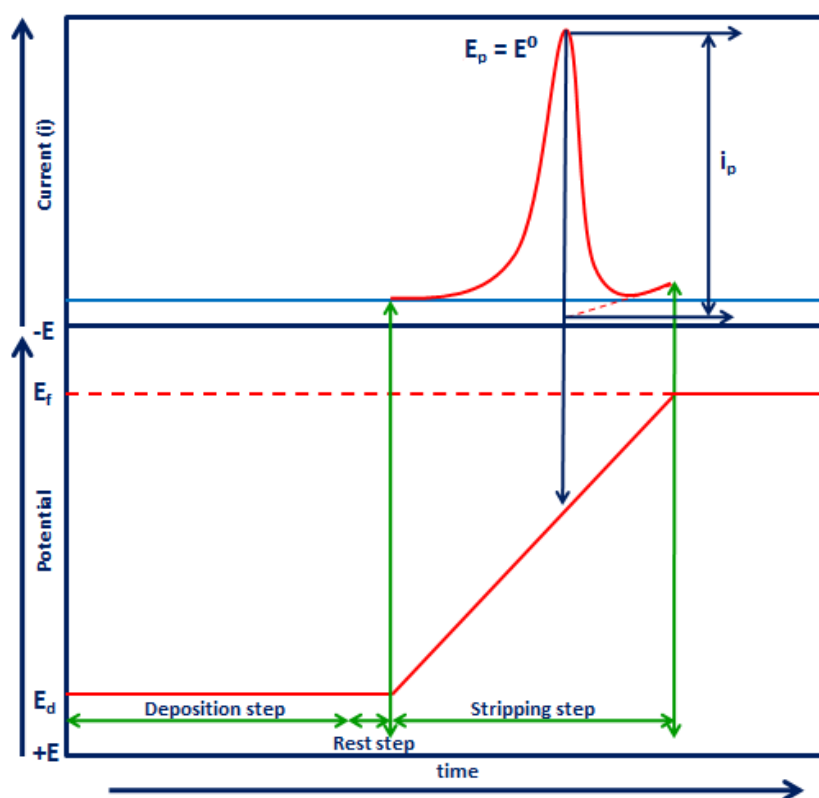


Figure 1.2 Cathodic stripping voltammetric technique: the potential-time waveform (Bottom), along with the resulting voltammogram (Top)

Stripping voltammetric technique is especially suitable for trace analysis due to the enrichment of analytes by pre-concentration, resulting in a detection limit usually at the sub- $\mu\text{g L}^{-1}$ level. Therefore, voltammetric techniques provide a quantitative and qualitative analysis.

Cathodic stripping voltammetry (CSV) using a HMDE [38-48] as a working electrode for determination of arsenic is summarized in Table 1.4. The principle of cathodic stripping for arsenic analysis is based on arsenic preconcentration in highly acidic media reacts with copper or selenium to form intermetallic complexes, that is deposited onto the WE. In the stripping step, the intermetallic compounds are reduced to arsine form by cathodically potential scan. The current measured during the stripping step can be related to the amount of the arsenic in the solution.



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Table 1.4 Cathodic stripping voltammetric methods for arsenic determination

No.	Method	Arsenic species	Detection condition	Sample	LOD ($\mu\text{g L}^{-1}$)	Ref.
1	DPCSV	As^{III} , As^{V} , MMA, DMA	HMDE, Cu^{II} , HCl, L-cysteine/HCl/70 °C, org. As: UV+S ₂ O ₈ ²⁻	tap, ground, sediment pore and stream waters	0.3	3
2	SWCSV	As^{III}	HMDE, Cu^{II} , HCl, ADDTC ligand	carrot, beet, irrigation water	0.5	4
3	DPCSV	As^{III}	HMDE, Cu^{II} , HCl, SDDTC ligand	drinking water	0.004	5
4	DPCSV	As^{III} , As^{V}	HMDE, HCl, SDDTC ligand, S ₂ O ₃ ²⁻	ground waters	As(III) 0.0001, As(V) 0.0002	6
5	AdCSV	As^{III} , As^{V}	HMDE, Cu^{II} , HCl, SDDTC ligand, S ₂ O ₅ ²⁻ /S ₂ O ₃ ²⁻ /80 °C	mineral, sea and dialysis water	As(III) 0.3 Total As: 1.05, 4.2, 15.0	8
6	CSV	As^{III}	HMDE, Se ^{IV} , H ₂ SO ₄	-	2	38
7	SWCSV	As^{III}	HMDE, Cu^{II} , HCl	river and sea waters	0.005	39
8	DPCSV	As^{III} , As^{V}	HMDE, Cu^{II} / Se ^{IV} mannital/H ₂ SO ₄	spring and mineral waters	0.52	40
9	SWCSV	As^{III} , As^{V}	HMDE, Cu^{II} , HCl, KI/ascorbic acid	mineral and sea waters	As(III) 0.7; Total As 0.6	41
10	SWCSV	As^{III} , As^{V}	HMDE, Cu^{II} , HCl, S ₂ O ₃ ²⁻	spring and mineral waters	As(III) 0.06; Total As 0.7	42
11	DPCSV	As^{III} , As^{V}	HMDE, Cu^{II} / Se ^{IV} , HCl, S ₂ O ₅ ²⁻ /S ₂ O ₃ ²⁻	tap, ground and drinking waters	0.5	43
12	LSCSV	As^{III} , As^{V}	HMDE, Cu^{II} , HBr, S ₂ O ₄ ²⁻	thermal, mineral and sea waters	As(III) 0.01; As(V) 0.02	44
13	DPCSV	As^{III} , As^{V}	copper amalgam drop electrode, Cu^{II} , HCl, S ₂ O ₃ ²⁻	natural water	0.02	45
14	DPCSV	As^{III} , As^{V}	HMDE, Cu^{II} , HCl, S ₂ O ₃ ²⁻	fresh and ground waters/SORAR	As(III) 0.5; As(V) 0.5	46
15	SWCSV	As^{III} , As^{V}	HMDE, Cu^{II} , HCl, S ₂ O ₃ ²⁻	water, soil, ores leached, ores digest	0.3	47
16	CSV	As^{III}	Hg drop, Cu^{II} , HCl,	river, stagnant, rain and tap water	0.0002	48

1.3.2 Cyclic voltammetry

Cyclic voltammetry (CV) is a very important electrochemical technique. It can be used to study the redox behaviour of compounds and probe coupled chemical reactions, in particular to determine mechanisms and rates of oxidation/reduction reactions. CV is an extension of a linear sweep voltammetry (LSV) in that the direction of the potential scan is reversed at the end of the first scan (the first switching potential) and the potential range is scanned again in the reverse direction. In the CV technique, the applied potential sweep backwards and forwards between two limits, the starting potential and the switching potentials. In this technique, the potential of the WE is increased linearly in an unstirred solution so that the measured current is limited by analyte diffusion at the electrode surface [49-50]. The resulting plot of current versus potential is called a cyclic voltammogram (Figure 1.3).

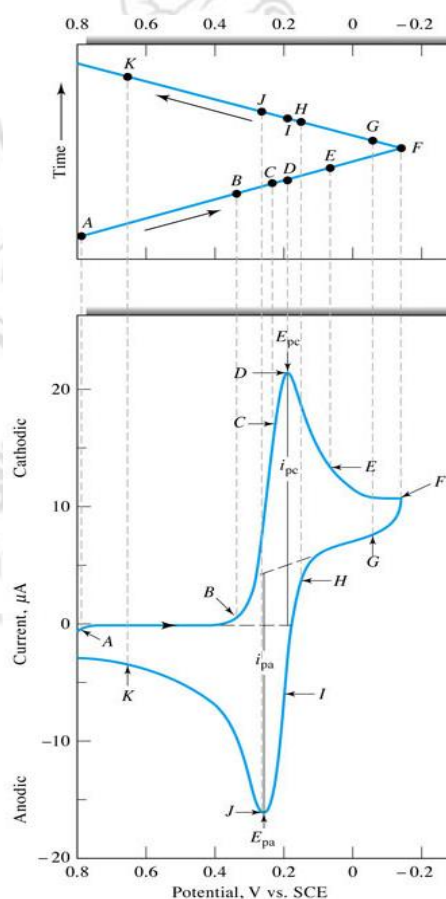


Figure 1.3 Cyclic voltammetry waveform (Top), cyclic voltammogram (Bottom) [35]

The peak current (i_p) is directly proportional to the analyte concentration (C) as described by the Randles-Sevcik equation [51-52]:

$$i_p = 0.4463nF \sqrt{\frac{nFD}{RT}} AC\sqrt{v} \quad (1.2)$$

where

- i_p : the peak current
- n: the number of electrons
- F: Faraday constant
- T: the temperature in Kelvin
- R: the gas constant
- D: the analyte diffusion coefficient
- A: the surface area of the working electrode
- C: the analyte concentration
- v : the scan rate of the applied potential

CV is the most widely used technique for acquiring qualitative information about electrochemical reactions.

1.4 Working electrodes

The working electrode is the most important component of an electrochemical cell, which used to show the response of the analyte to the applied potential. The most commonly used working electrode materials are platinum, gold, carbon and mercury.

Mercury has been a widely used electrode material such as hanging mercury drop electrode (HMDE). It displays an excellent potential window in the cathodic direction (Figure 1.4) that mercury is the best electrode material for CSV analysis of anions [30]. The use of mercury is limited due to its toxicity. As a result, the glassy carbon is electrode an alternative materials that can potentially replace mercury.

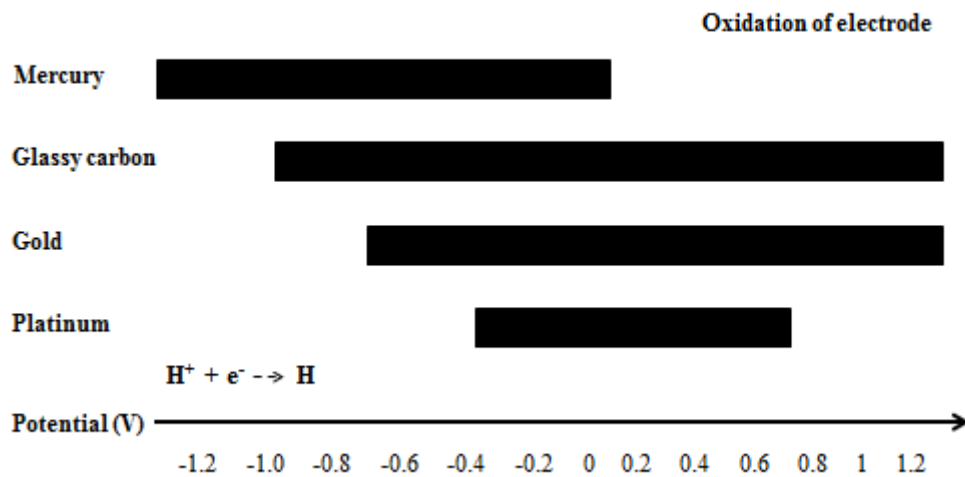


Figure 1.4 Potential ranges of the different working electrodes

1.5 Research objectives

The aims of this research can be summarized as follows:

1. To develop cathodic stripping voltammetric method for the preliminary determination of inorganic arsenic.
2. To develop cyclic voltammetric method for determination of arsenate in water samples.

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