ADSORPTIVE CATHODIC STRIPPING VOLTAMMERTRIES OF LEAD IN WATER SAMPLES USING 2, 2′-BIPYRIDYL; 1,10-PHENANTHROLINE AND NITRITE IONS

by

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AAS	Atomic absorption spectroscopy
AdCSV	Adsorptive cathodic stripping voltammetry
AdSSWV	Adsorptive stripping square wave voltammetry
AdSV	Adsorptive stripping voltammetry
ASV	Anodic stripping voltammetry
a.u.	Arbitrary units
2-APSH	2-Acetylpyridine salicyloylhydrazone
bpy	2,2'-Bipyridyl
CB	Calcein-blue
CSV	Cathodic stripping voltammetry
CTAB	Cetylpyridinium bromide hydrate
DDOB	2,2-Dipyridyl–2,4- dioxybenzoic acid
DPASV	Differential pulse anodic stripping voltammetry
DPAdCSV	Differential pulse adsorptive cathodic stripping voltammetry
DPP	Differential pulse polarography
FAAS	Flame absorption atomic spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HMDE	Hanging mercury drop electrode
2-HBBH	2-Hydroxbenzaldehyde benzolhydrazone
ICP–AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
i_p	Peak current
KHP	Potassium hydrogen phthalate

L.O.D	Limit of detection
MFE	Mercury film electrode
NAA	Neutron activation analysis
OFN	Oxygen-free-nitrogen
Oxine	8-Hydroxyquinoline
phen	1,10-Phenanthroline
R^2	Linear regression coefficients
rpm	Rotation per minute
RSD	Relative standard deviation
s	second
SDS	Sodium dodecyl sulphate
SLM	Supported system liquid membrane
SPADNS	4,5-Dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt
TPN	Thymolphthalexone
Triton X-100	T-Octyphenoxypolyethoxyethanol
UV-Visible	Ultraviolet-Visible
XRF	X-ray fluorescence

VOLTAMMETRI PELUCUTAN JERAPAN KATOD BAGI PLUMBUM DALAM SAMPEL AIR MENGGUNAKAN 2,2'-BIPIRIDIL; 1,10-FENANTHROLINADAN ION NITRIT

ABSTRAK

Kaedah baru bagivoltammetri pelucutan katod penjerapan denyut pembezaan (DPAdCSV)telah dibangunkan untuk penentuan kepekatan plumbum dalam larutan akueus. Kaedah ini berdasarkan pengkompleksan plumbum dengan gabungan dua ejen pengkompleks iaitu2,2′- bipiridil dan 1,10 fenanthrolina dengan nitritpada elektrod titisan raksa tergantung (HMDE). Pembolehubah yang mempengaruhi tindak balas seperti pH, elektrolit sokongan, masa pembersihan awal, saiz titisan, kelajuan pengacauan, potensi pemendapan, masa pemendapan dan masa keseimbangan, kadar sapuan, amplitud denyut dan kepekatan ligan telah dikaji.Pada keadaan optimum, menggunakan 2,2'-bipiridil dengan nitrit[reagen (I)]hubungan antara arus puncak dan kepekatan plumbumadalah linear diantara julat 10 - 500 ng mL^{-1}. Had pengesanan telah didapati pada 0.48 ng mL^{-1}. Sisihan piawai relatif (RSD) bagi n = 9 penentuan piawai 25 ng mL^{-1} Pb^{2+}ialahdengan 1.74% dengan pekali regresi linear (R^2) 0.9991.

Parameter yang sama seperti reagen I telah dilakukan menggunakan reagen kedua iaitu 1,10 fenanthrolina dan nitrit [reagen (II)]. Padakeadaan optimum, hubungan antara arus puncak dan kepekatan plumbum adalahlinear dalam lingkungan 7 - 500 ng mL^{-1}. Had pengesanan telah didapati pada 0.36 ng mL^{-1}. RSD bagi n = 9 penentuan piawai 25 ng mL^{-1} Pb^{2+} ialah1.84% dengan R^2 bersamaan dengan 0.9986. Kaedah DPAdCSV menggunakan kedua-dua reagen (reagenI dan II) telah digunakan untuk penentuan plumbum dalam air laut, air tasik dan air paip.Gangguan garam logam utama yang hadir dan lain-lain sebatian organik (kebanyakannya surfaktan) telah diteliti dan didapati boleh diabaikan. Kaedah ini telah disahkan dengan kaedah piawai, iaitu spektrometri penyerapan atom (AAS). Kajian ini mencadangkansatu kaedah yang peka dan mesra pengguna untuk menentukan plumbum.Dua reagen tak memilihuntuk plumbumyang biasanya ditemui dalam makmal pengajaran boleh juga digunakan untuk mengkompleks plumbum dan dijerappadaHMDEdengankehadiran nitrit sebagai agen penggaraman keluar.

ADSORPTIVE CATHODIC STRIPPING VOLTAMMERTRIES OF LEAD IN WATER SAMPLES USING 2,2'-BIPYRIDYL; 1,10-PHENANTHROLINE AND NITRITE IONS

ABSTRACT

A new differential pulse adsorptive cathodic stripping voltammetric (DPAdCSV) method was developed for the determination of lead concentration in aqueous solution. This was based on complexation of lead with combination of two complexing agents *viz* 2,2'-bipyridyl and 1,10-phenanthroline with nitrite at hanging mercury drop electrode (HMDE). Variables affecting the response such as pH, supporting electrolyte, initial purge time, drop size, stirring speed, deposition potential, deposition and equilibration times, sweep rate, pulse amplitude and ligand concentration were investigated. Using the first reagent 2,2′-bipyridyl with nitrite[reagent (I)] and under optimized conditions the relationship between peak current and lead concentration was linear in the range of 10-500 ng mL^{-1}. The limit of detection was found to be 0.48 ng mL^{-1}. The relative standard deviation (RSD) for n= 9 determinations of standard 25 ng mL^{-1} Pb^{2+} was to 1.74% with linear regression coefficient (R^2) 0.9991.

Using the second reagent i.e. 1,10-phennanthroline and nitrite[reagent (II)]similar parameters as reagent(I) was carried out.Under optimized conditions the relationship between peak current and lead concentration was linear in the range of 7- 500 ng mL^{-1}. The limit of detection was found to be 0.36 ng mL^{-1}. The RSD for n = 9 determinations of standard 25 ng mL^{-1} $Pb^{2+}$was to 1.84% with R^2 equal to 0.9986. The DPAdCSV methods using both reagents (reagent I and II) were applied to the determination of lead in sea water, lake water and tap water. The interferences of major metals salts present and other organic compounds (mostly surfactants) were investigated into and were found negligible. The methods were validated with standard method, i.e. atomic absorption spectrometry (AAS).This study showed that a relatively sensitive and user-friendly method for determination of lead was proposed. Two reagents non-selective to lead normally found in teaching laboratory can also be used to complex lead and be adsorbed on HMDE with provision that nitrite was present as salting out agent.

CHAPTER ONE

INTRODUCTION

1.1 Water pollution

Through history, the quality of drinking water has been a factor in determining human welfare.Fecal pollution of drinking water has frequently caused waterborne diseases that have decimated the populations of whole cities. Unwholesome water polluted by natural sources has caused great hardship for people forced to drink it or use it for irrigation. Although there are still occasional epidemics of bacterial and diseases caused by infectious agents carried in drinking water, waterborne diseases have in general been well controlled, and drinking water in technologically advanced countries is now remarkably free of the disease-causing agents that were very common water contaminants only a few decades earlier.

For the most part, a greater concern with water safety now is the potential presence of chemical pollutants. These may include organic chemicals, inorganic, and heavy metals from industrial, urban runoff and agricultural sources. Water pollutants can be divided among some general categories, as summarized in Table 1.1(Manahan, 2005)

Table 1.1General types of water pollutants (Manahan, 2005)

Class of Pollutants	**Significance**
Trace elements	Health,aquaticbiota,toxicity
Heavy metals	Health,aquatic biota,toxicity
Organically bound metals	Metal transport
Radionuclides	Toxicity
Inorganic pollutants	Toxicity,aquatic biota
Asbestos	Human health
Algal nutrients	Eutrophication
Acidity, alkalinity, salinity (in excess)	Water quality, aquatic life
Trace organic pollutants	Toxicity
Polychlorinated biphenyls	Possible biological effects
Pesticides	Toxicity, aquatic biota,wildlife
Petroleum wastes	Effect on wildlife,aesthetics
Sewage, human and animal wastes	Water quality, oxygen levels
Biochemical oxygen demand	Water quality, oxygen levels
Pathogens	Health effects
Detergents	Eutrophication,wildlife,aesthetics
Chemical carcinogens	Incidence of cancer
Sediments	Water quality, aquatic biota,wildlife
Taste, odor, and color	Aesthetics

Existences of pollutants in water can cause some changes to the physical, chemical and biological properties of water. Turbidity, color, taste, odor, temperature, pH, hardness and dissolved oxygen are some of the characteristics can cause problem to aquatic life and human health. Public concern for health from environmental problems arising from industrial activities is increasing so modern legislation is often obliged to impose more restrictive regulations for effluents discharges. In Malaysia, the Environmental Quality Act 1974 is established to provide legal provision for project proponents to very their standard of emission or effluents.

1.2 Heavy Metals in the Environment

Heavy metals have been excessively released in to the environment due to rapid industrialization and have created a serious global concern. lead, zinc, copper, nickel, mercury, silver, arsenic, chromium and cadmium are among heavy metals often detected in industrial wastewaters. These heavy metals can be originated from metal plating (electrolysis) mining activities, smelting, battery, manufacture, petroleum refining (Ozay et al.,2010), coal combustion, tanning, paint manufacture, pesticides, printing and photographic industries (Rajesh and Manikandan,2008). Heavy metals in the environment have become a major concern due to their toxicity, bio accumulating tendency, mobility in the ecosystems and potential threat to human life. Table 1.2 shows the types of heavy metals often found in wastewater and theirphysiological effects on humans.

Table 1.2 Types of heavy metals and their physiological effects on humans

Heavy metal	**Physiological effects of some heavy metal cations on humans**	**Reference**
Cd	Excruciating pain in the bone, kidney dysfunction, hypertension, renal disorder destruction of red blood cells, cancer	Wen et al., 2011
Hg	Nausea,vomiting,abdominal pain, depression, bloody diarrhea, kidney damage, death usually within 10 days	Gaballah and Kilbertus, 1998
Cu	Wilson 's disease	Gai et al., 2008
Ni	Nausea, vomiting, diarrhea, chest pain, inhibition of enzyme actives	Alluri et al., 2007 and Madhava krishnan et al., 2008
Zn	Corrosive effect on skin by zinc fumes and damage to nervous membrane	Alluri et al., 2007
As	Bronchitis, dermatitis, cancer	Alluri et al., 2007 and Maiti et al.,2008
Cr	Severe irritation of the gastrointestinal tract, circulatory shock and renal damages, carcinogenic	Gaballah and Kibertus, 1998
Ag	Inhibition of Na^+ and Cl^- up take, leading to ion regulatory failure in marine species	Huo et al., 2009
Pb	Mental retardation in children brain damage, seizures, affect hemoglobin synthesis, vomiting, anemia	Alluri et al., 2007 and Dwivedi et al., 2008

Unlike organic wastes, heavy metals are non biodegradableandcannot be broken down by bacterial action and they can be accumulated in living tissues, causing various diseases and disorders. Based on their harmful effects on humans and non biodegradable properties, heavy metals must be removed before discharged in to the environment.

1.3 Lead

The word lead derives from the Anglo-Saxon *leaden*, and the symbol Pb, from the Latin word for lead, *Plumbum*. Lead isby far the most abundant (13 ppm) heavy element in the earth'scrust. It is considered as a one of the few metals that can be found in metallicform in nature (rather than in compounds that have to reduce to extract metal). Lead is an earliest metal, having been famous since beforerecorded history. It is one of the oldest metals known to mankindand is mentioned in the Old Testament. In Ancient Egypt (7000–5000 b.c.), leadwas utilized in pottery glazing and the Hanging Gardens of Babylon were floored with lead slabs to guardagainst moisture. The Roman Empire used lead frequently for water pipes and plumbing, some of which is still in use today. The Romans also used lead to produce cooking utensils.Studies suggest that the Roman civilization fell largely as aresult of widespread lead poisoning. This theory is supported bydata presenting high lead concentrations in the bones of ancientRomans. In the middle Ages, the practice of "sweetening" winewith lead or lead acetate became a serious toxicological problem. In those days, the alchemists believed lead was the oldestmetal and made innumerable attempts to transform it into gold (Korn et al., 2006).

1.4 Lead properties

Lead a lustrous bluish-white metal, quite soft, highly malleable, a relatively poor conductor of electricity and ductile. It is highly corrosion resistant but tarnishes under exposure to air (Korn et al.2006). The general physicochemical properties of lead are given in Table 1.3.

Table 1.3 Physicochemical properties of lead(Lenntech,2011)

Lead	**Physical properties**
Phase	Solid
Atomic number	82
Atomic mass	207.2
Density	11.3 gcm^{-3}
Melting point	327.4°C (621.3°F)
Boiling point	1.750 – 1.755°C (3.180 – 3.190°F)
Heat of Fusion	4.799 $kJmol^{-1}$ = 23.2 Jg^{-1}
Heat of Vaporization	177.7 $kJmol^{-1}$ = 857.6 Jg^{-1}
Thermal Conductivity	35.3 $(Wm^{-1})/K$, 27°C
Specific Heat	0.129 Jg^{-1} °C = 0.031 $Calg^{-1}$ °C

1.5 Transformations of lead in the environment

One of the main problems of the modern world is the lead contamination in the environment. Our environment contains countless sources of lead, which is a natural component of soil, vegetation (Resmiaet al., 2011), water (Alonsoet al., 2004), animal life (Dietert et al., 2004) and air (Asano et al., 2010). Lead arising from a number of industrial and mining processes occurs in water in the +2 oxidant state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which at the end entered natural water system (Manahan, 2005). In fact, using lead as petrol additive (antiknock products) as a mixture of tetramethyl and tetraethyl lead leads to release of inorganic Pb^{+2} in the environment as given in Equation 1.1 (Radojevic and Bashkin,2006).

$$R_4Pb \rightarrow R_3Pb^{+} \rightarrow R_2Pb^{2+} \rightarrow Pb^{2+} \qquad (1.1)$$

Furthermore, the extensive usage of lead compoundsby industry can be responsible for adding other sources of lead in the environment as recorded in Table 1.4. In fact, levels of lead in air can be changed with the location and weather. In water, lead comes from soil and rocks, fallout, dust, and vehicular exhaust. Lead is widely distributed in foods, with widest variation in root and green vegetables. This variation probably indicates the contamination of the soil by domestic and industrial fallout. Lead in vegetables and fruit cannot be removed by using normal washing process. Lead enters human body system though air, water,

Table 1.4 Lead compounds formula and different uses(Advameg,2012)

Compound	**Formula**	**Use**
Lead acetate	$Pb(C_2H_3O_2)_2$	Dyeing of cloth, insecticides, production of gold, hair dye
Leadantimonate	$Pb_3(SbO_4)_2$	Staining of glass, porcelain and other ceramics
Leadazide	$Pb(N_3)_2$	As a primer for high explosives
Lead chromate chrome yellow	$PbCrO_4$	Industrial paints (use restricted by law)
Lead fluoride	PbF_2	make lasers, specialized optical glasses
Lead iodide	PbI_2	Photography, cloud seeding to produce rain
Leadnaphthenate	$Pb(C_7H_{12}O_2)$	Wood preservative, insecticide, additive for lubricating oil, paint and varnish drier
Leadphosphite	$2PbO. PbHPO_3$	used to screen out ultraviolet radiation in plastics and paints
Lead stearate	$Pb(C_{18}H_{35}O_2)_2$	Make soaps, greases, waxes, and paints; lubricant, drier for paints and varnishes
Lead telluride	$PbTe$	Make semiconductors, photoconductors, and other electronic equipment

1.6 Effect of lead on health

Lead is a serious cumulative body poison. It enters our body system through air, water, and food. Inorganic lead (Pb^{2+}) binds itself with the -SH group in enzymes or proteins and acts as an enzyme inhibitor.Lead interferes with the calcium metabolism and gets deposited in the bone (Bosiacka. and Hlynczak,2003). Organic Lead compounds, such as tetramethyl lead, are highly poisonous because they are absorbed readily by the body through skin and mucus membranes (Ahmed and Al Mamun, 2001).Acute lead poisoning in humans causes severe damage in the kidneys, liver, lung (Dugo, et al., 2004), brain (Patkovaet al., 2012), reproductive system, and central nervous system (Ibrahim et al., 2010), and sometimes causes death. Mild lead poisoning causes anemia, headache, and sore muscles and the victim may feel fatigued and irritable (Manahan, 2005).

The infants and children bodies have been suffered from absorb lead (Ruengsitagoon et al, 2010) more easily than adult bodies (Wanget al, 2007) as shown in Figure 1.1.Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semi-permanent brain damage in young children with ability to replace calcium in bone to form sites for long-term replaceand to absorb phosphate, and vitamin D in the body (Cortina-Ramırezet al., 2006). All these findings cause great concern regarding to public health, demanding accurate determination of this metal ion at trace and sub-trace levels.

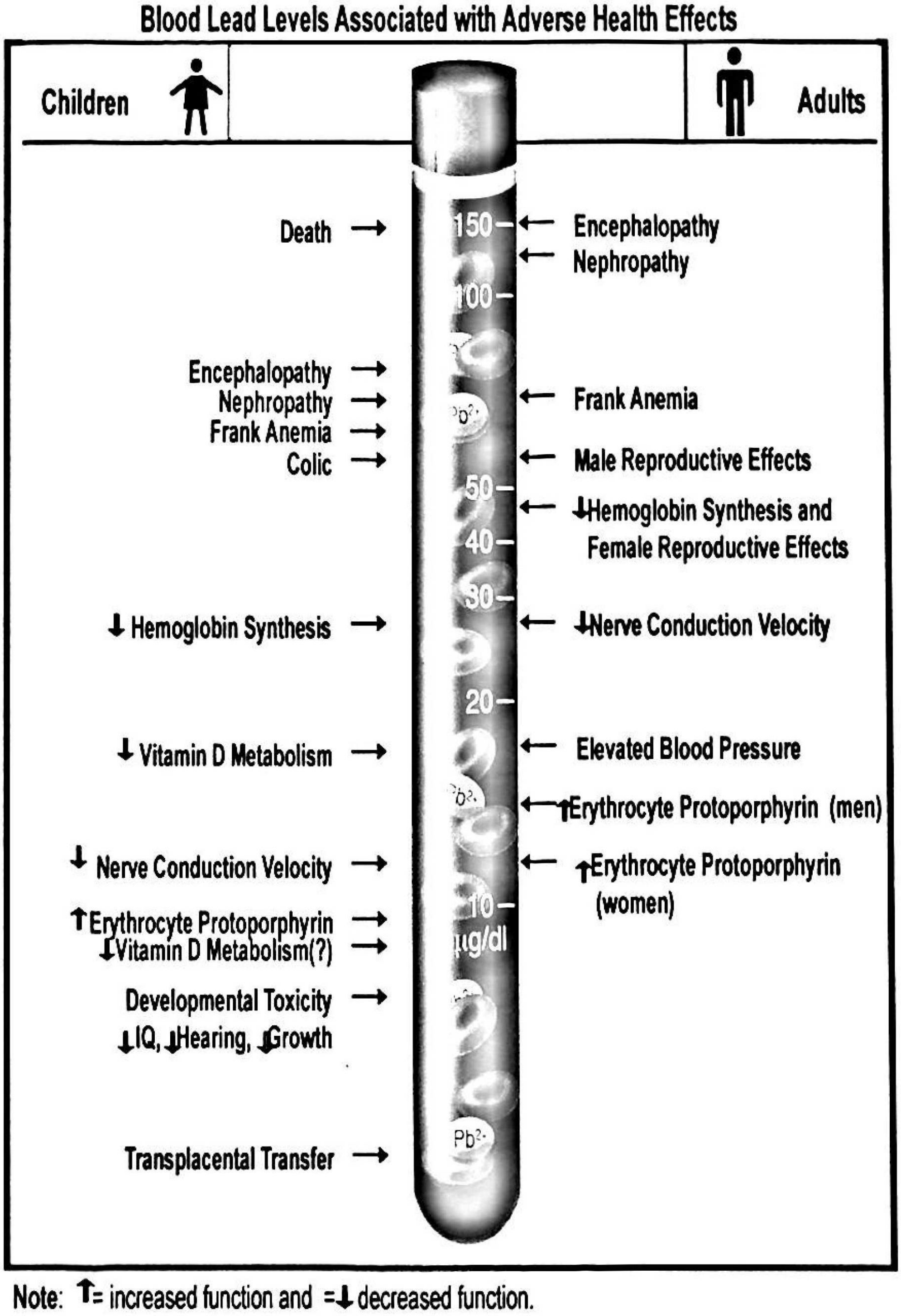

Figure 1.1 Blood lead levels associated with adverse health effects (Royceand Needelman, 1990)

1.7 Lead determination

Lead is one of the heavy metals which maximum acceptable concentration (MAC) in drinking water is 0.010 mg L^{-1} (10ngL^{-1}) (Eshaghi et al., 2011). Therefore, the analysis of lead in water has received great attention. Recently, there are various methods which have been reported for the qualitative and quantitative determination of lead in water. Among these methods, the spectrophotometry is most convenient for use due to its simplicity and low cost. On the other hand, the low sensitivity or selectivity of this method makes it not fitto determine very low concentrations of lead (1.0 μg L^{-1} or even lower) in water (Zaijun et al.,2003).

In spite of the neutron activation analysis (NAA) has high sensitivity, it is not commonly used because of the need of a neutron source, specialized technique, skills, costs and time involved (Erden et al., 2010). Other available techniques capable of multi element determination such as inductively coupled plasma mass spectrometry (ICP-MS)(Rahmiet al., 2007), inductively coupled plasma atomic emission spectrometry (ICP–AES) (Vassileva and Furuta, 2001), chromatography (Centineoetal.,2004), X-ray fluorescence (XRF) are extremely expensive apparatus, complicated operation, high cost of maintenance, well-controlled experimental conditions are required and often do not offer sufficient sensitivity for accurate determination of most elements at the trace to ultratrace concentrations usually encountered in environmental and biological samples (Inam et al., 1999).

Graphite furnace atomic absorption spectrometric (GFAAS) method is widely used due to its sensitivity and simple procedure for the qualitative and quantitative determination of metal residues in the forensic laboratories. On the other hand, many disadvantages can be detected of this technique. For instance, simultaneous analysis of more than one element by GFAAS is impractical, relatively time consuming and requires highly specialized operator, and rather expensive instrumentation (Erden at al., 2010).

For these reasons, electrochemical methods recently have been used to determine trace elements in natural waters. For instance, differential pulse polarography (DPP) determination of lead aqueous medium (Perretet al., 2000). Stripping voltammetry in particular with adsorptive collection has been widely used for determination of Pb in a natural water (Yabutaniet al., 2006). Adsorptive cathodic stripping voltammetry (AdCSV) is a very useful methods and the most favorable technique to determine heavy metal elements in natural waters because of speed of analysis, good selectivity and sensitivity, excellent accuracy and precision, low costs of instrumentation and maintenance compared with other techniques. In addition to the possibility of simultaneous analysis of mixtures and good performance with saline matrices like seawater and raining water samples (Zuman,2000).

1.8 Stripping Voltammetry

Electrochemical stripping means the oxidative or reductive removal of atoms, ions or compounds from an electrode surface by using hanging mercury dropper electrode (HMDE) or Mercury film electrode (MFE) as a main electrode (Bond,et al.,2010). The greatest advantage of mercury electrodes is the fact that new drop or new thin mercury films can be readily formed, and this cleaning process removes problems that might be caused by contamination as a result of the previous analysis (Bareket al.,2001).

Stripping analysis basically includestwo main steps technique.Firstly, deposition step or accumulation step involves the electrolytic deposition of a small portion of the metal ions in solution onto the mercury electrode to pre concentrate the metals. Secondly, stripping step (the measurement step) which involves the dissolution (stripping) of the depositmetal ions. Different versions of stripping analysis can be used depending on the nature of the deposition and measurement steps (James, A.1982). Stripping voltammetry is widely used in trace analysis because of the electrode capacity for the analyte accumulation is limited and the condition of linearity is satisfied only well below the electrode saturation and can be used for measuring simultaneously in different matrices at concentration levels down to 10^{-10} M (Wang,2006).

Anodic stripping voltammetry (ASV) is the most widely used form of stripping analysis. In this method, the metals are being preconcentrated by electrode position into a small-volume mercury electrode. The preconcentration process is done by cathodic deposition at a controlled time and potential. On the other hand, the cathodic stripping voltammetry (CSV) is the mirror image of ASV. It involves anodic deposition of the analyte, followed by stripping in a negative-going potential scan. In fact, the CSV is commonly used to measure a wide range of organic and inorganic compounds that capable of forming insoluble salts with mercury (Wang, 2006).

1.8.1 Adsorptive stripping voltammetry

The expression adsorptive stripping voltammetery (AdSV) means adsorption process utilized to concentrate analytes at the surface of HMDE electrode. It is considered as a relatively new technique involves the formation, adsorptive accumulation and reduction of a surface-active complex of the metal as shown in Figure 1.2. The voltammetric stripping scheme, with a negative-going potential scan or constant cathodic current can be used for measuring the adsorbed complex. Most procedures involve the reduction of the metal in the adsorbed complex. The response of the surface-confined species is directly related to its surface concentration, with the adsorption isotherm, providing the relationship between the surface and bulk concentrations of the a dsorbate. Consequently, calibration curves display nonlinearity at high concentrations(Wang,2006).

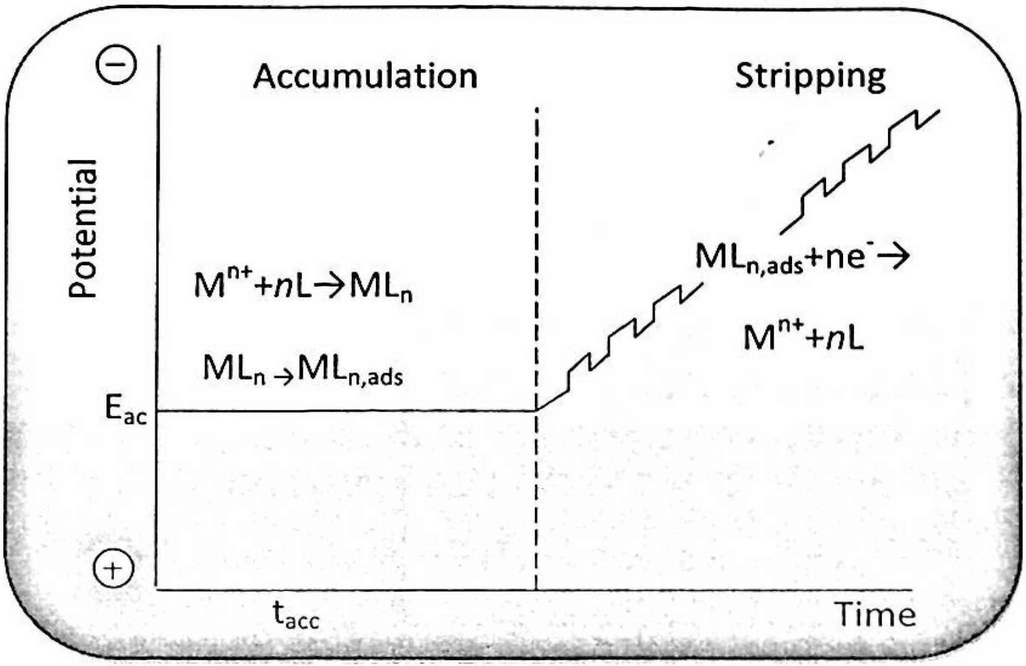

Figure 1.2 Accumulation and stripping steps in adsorptive stripping measurementsof a metal ion (M^{n+}) in the presence of the ligand agent (L)(Wang,2006).

The peak current depends on different parameters of the deposition and stripping steps, in addition to the characteristics of the metal ion and the electrode geometry and linearly on the surface, or volume, concentration of the accumulated substance. The factor of this linear proportionality is the ampere metric constant of the voltammetric technique as given in the Equation 1.2 (Kalvoda,1994).

$$I_p = K\,A\,\Gamma \qquad (1.2)$$

Where K is proportionality constant, A is electrode surface area, Γ is the surface concentration of the compound.

$$K = \frac{n^2\,.\,F^2\,.\,\nu}{4\,.\,R\,.\,T} \qquad (1.3)$$

Where n is electron exchange, F is Faraday constant, ν is scan rate, R is gas constant, T is Absolute temperature .

$$\Gamma = C_a . \left[\frac{D}{r} . t_{acc} + 2\sqrt{\frac{D}{\pi} . t_{acc}^{\frac{1}{2}}}\right] \quad (1.4)$$

Where C_a is concentration of the analyte, D is diffusion coefficient of the analyte, r is radius of the mercury drop and t_{acc} is accumulation time.

Once the electrode surface becomes saturated Γ_{max} after $t^{1/2}_{acc(max)}$ the peak current I_p increases linearly with t_{acc} and reaches a maximum (Wang, 2006).

$$I_{p(max)} = K .A .\Gamma_{max} \quad (1.5)$$

The AdCSVhave been applied in different fields as clinical materials and pharmaceutical (Perezetal., 2002), environmental, metallurgical, geological (Vyskocil and Barek,2009), vitamins (Bareket al.,2001), pollutants (Lin et al.,1999) and biological, biochemical (Ali et al.,2000). Besides, many cations have been determined by using AdCSV.

In general, the cations are complexed with surfaceactive complex agents and have been used for measuring trace elements in environmental water samplessuch as cobalt (Vega and van den Berg, 1997), copper (Jin and Gogan, 2000), cadmium (Gonzalez et al., 2003), molybdenum (Ensafi and Khaloo, 2005), tin (Li et al.,2005), arsenic (He et al., 2007) uranium (VI) (Mohdesi, 2009), selenium(IV) (Grabarczyk and Korolczuk, 2010) and Titanium (Croot, 2011). In addition to the ability of AdCSV for determining several metals simultaneously in one scan (Ghoneim et al., 2000). At the same time, it can be adopted as reliable, sensitive, and precise methods for the verification of results obtained by atomic absorption spectroscopy or some chromatographic technique (Bondet al., 2010).

1.9 Lead determination by AdCSV with different ligands

An adsorptive cathodic stripping voltammetry (AdCSV) method is becoming increasingly popular technique for the determination of trace and ultra trace levels of metal ions. Several complex agents have been studied for the adsorptive collection of complexes with lead on the HMDE to determine lead in environmental water since 2001 until now.

In this regard, Fischer and van denBerg (2001) optimized the experimental conditions to determine leadin natural water samples taken from mountain lake (the Gossenkoellensee, Austria)using Calcein-Blue (CB) (8-[N,N-bis(carboxyl-methyl)aminomethyl]-4-methylumbelliferone) ligand in Figure 1.3.

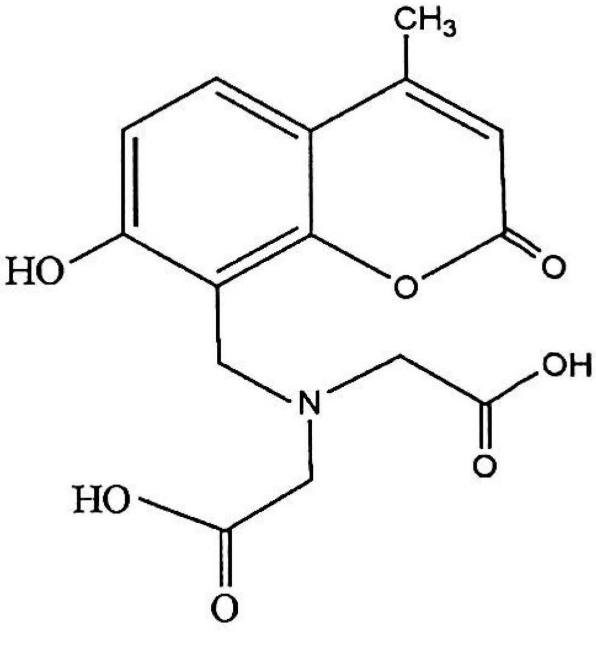

Figure 1.3 Structural formula of Calcein-blue

Zayats et al. (2002) determined the adsorption parameters of the leadon the mercury electrode in the natural water sample was taken from the ValeavMorilor Lake (Kishinev) by using 2,2-dipyridyl–2,4-dioxybenzoic acid molecular complex(DDOB)in (Figure 1.4).

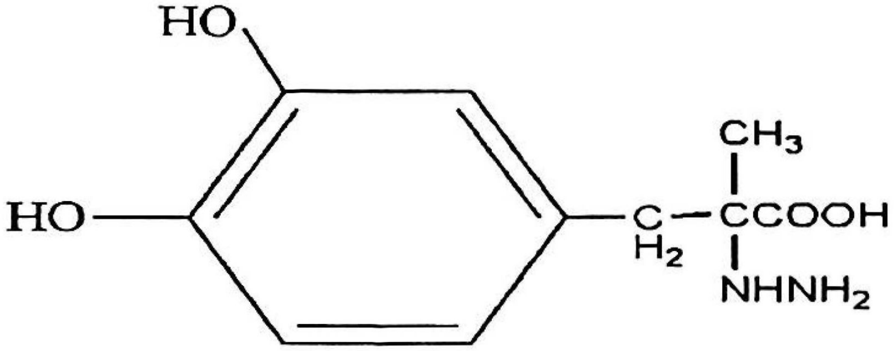

Figure 1.4 Structural formula of 2,2-dipyridyl–2,4- dioxybenzoic acid molecular complex ,DDOB

Ensafi et al. (2003) hassuccessfullydevelopeda sensitive method for determination of lead in water sample of Zayandeh Roud river and tap water (Isfahan) by using Pyrogallol red (PGR) ligand in Figure 1.5 onto a hanging mercury drop electrode.

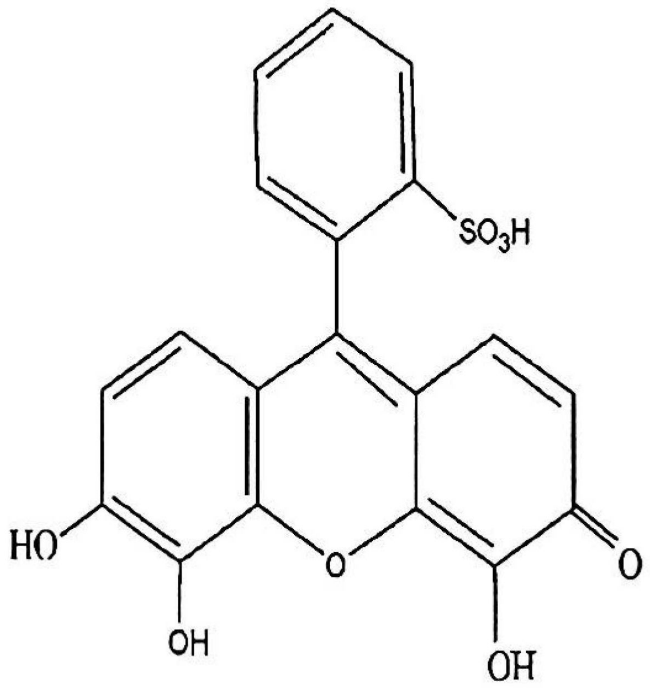

Figure 1.5 Structural formula of Pyrogallol red, PGR.

Shams et al. (2004) presented a sensitive and selective method for the simultaneous determination of group of metal ions such as copper, zinc and lead in tap-water of IASBS, Zanjan, Iran by using complexes of these elements with 2′,3,4′,5,7-pentahydroxyflavone (Morin) Figure 1.6 onto a hangingmercury drop electrode, followed by reduction of adsorbed species by voltammetric scan using differential pulse modulation.

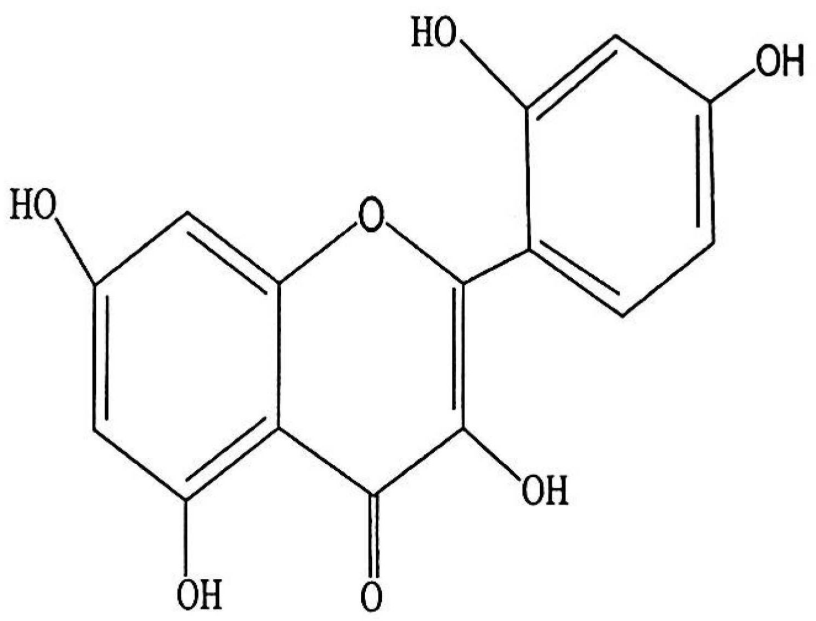

Figure 1.6 Structural formula of Morin

Babaei et al. (2006) introduced a novel and selective procedure for simultaneous determination copper, bismuth and lead in tap-water of Arak University, Arak, Iran and other synthetic samples as well by utilizing thymolphthalexone (TPN) Figure 1.7as a complexation agent of these elements onto a HMDE, followed by reduction of adsorbed species by voltammetric scan via differential pulse modulation.

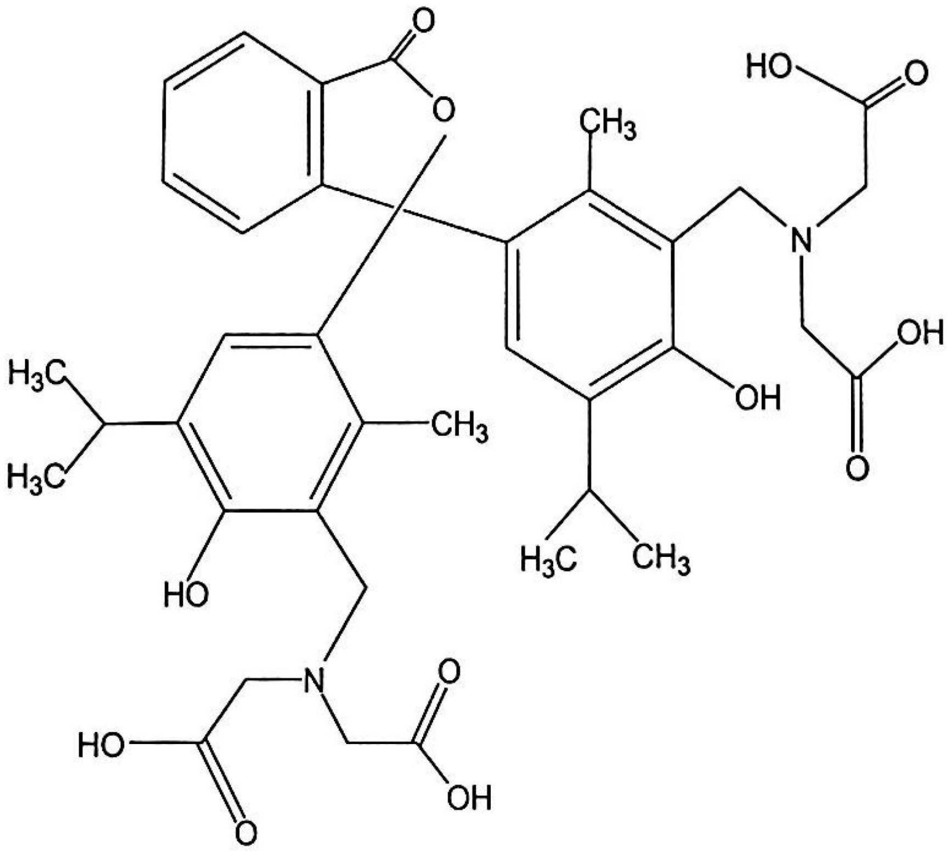

Figure 1.7 Structural formula of thymolphthalexone.

Ensafi et al. (2006) performed simultaneous determination of lead, copper and cadmium elements in the real samples taken from Zayandeh rood river water and tap-water by using xylenol orangein Figure 1.8 as a suitable complexing agent.

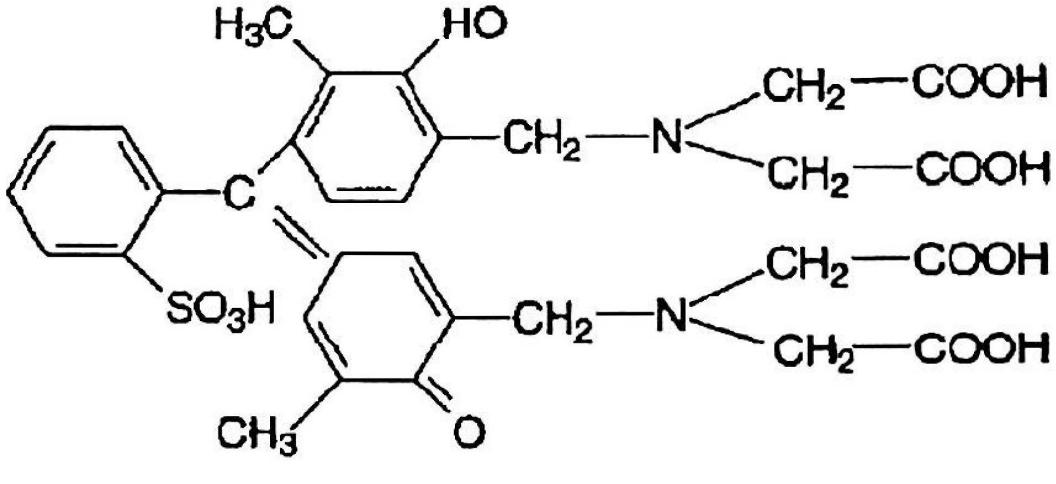

Figure 1.8 Structural formula of xylenol orange

Suren et al. (2007) determined simultaneously lead and cadmium in seawater from Dardanells, Canakkale by using 8-hydroxyquinoline (oxine) in Figure 1.9 as a suitable ligandonto a HMDE.

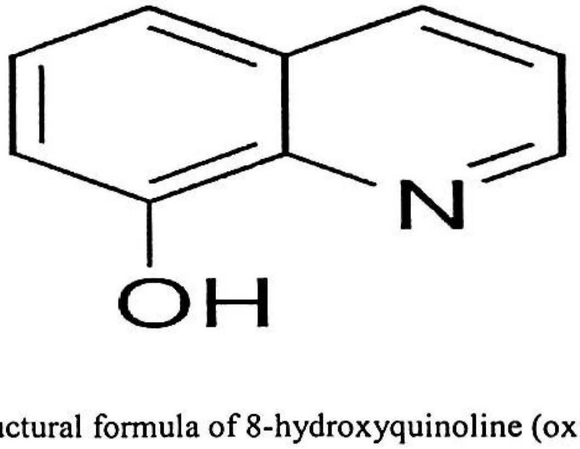

Figure 1.9 Structural formula of 8-hydroxyquinoline (oxine)

Hosseinzadeh and Abassi (2007) determined the ultra trace of lead ions in different real samples (seawater, river water, and underground) by using Carbidopain Figure 1.10 as a appropriate complex agent onto a HMDE.

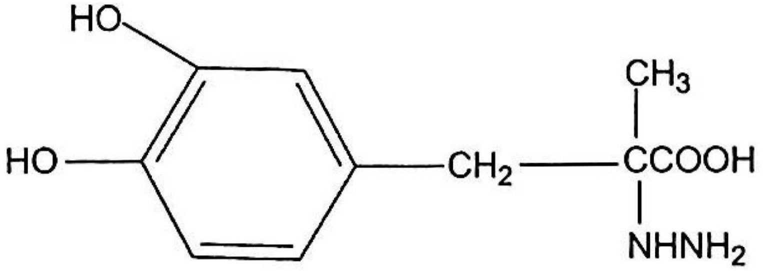

Figure 1.10 Structural formula of Carbidopa

Abbasi et al. (2009) determined the lead in edible oil and water samples using 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodiumsalt (SPADNS) Figure 1.11 as a complexation agent.

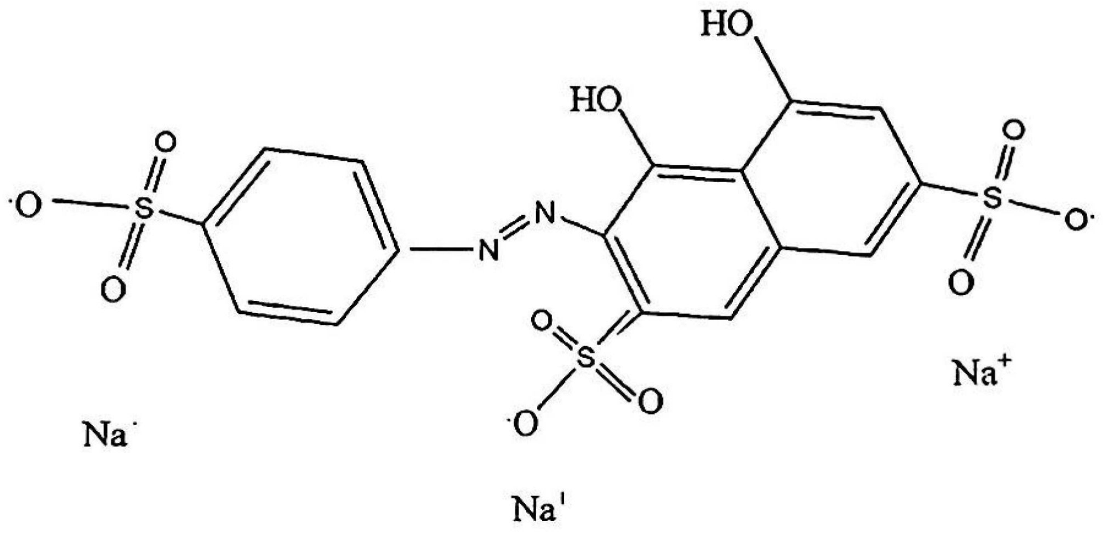

Figure1.11 Structural formula of 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalenedisulfonicacid trisodiumsalt SPADNS.

Bellido et al. (2009a) determined the lead at nanomolar levels in seawater (from Spain southwest coast) by using 2-acetylpyridine salicyloylhydrazone 2-APSH in Figure 1.12 as a complexing agent.

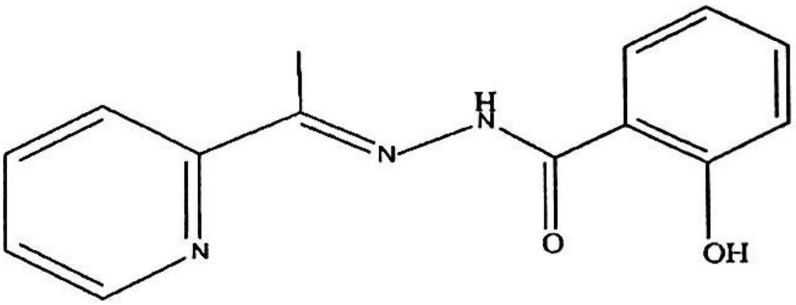

Figure1.12 Structural formula of 2-acetylpyridine salicyloylhydrazone.