CHAPTER 1

INTRODUCTION

(1) INTRODUCTION

1.1 WATER USAGE

As we all know, water is one of the most important element for the living things, including the human beings. Without it, all the living organisms can not survive at all. Ninety-seven percent of the world's water is found in the oceans (Reference 1).

In normal life, the water can be used to do a lot of things for us. It can be used for human beings as follow:

(a) Drinking;

In fact, all the organisms need to drink the water all the time. If not, we will feel thirsty.

(b) Domestic, agricultural, industrial supply;

Water is needed for domestic, agricultural, industrial sectors all the time to provide us foods, goods and services.

(c) Effluent disposal;

All the wastes, including: human beings, industry, domestic, agricultural and so on are needed to undergo the water treatment, in order to maintain the environmental quality in satisfied condition.

(d) Recreation;

Water also can be used for recreation purpose. The rivers and lakes can be used for boating, water skiing, fishing, and so on. Meanwhile, the seas can use for diving, swimming, navigation, sailing and so on.

(e) Power production;

Water is one of the cheapest power supplies because it is naturally available, so we can get it easily and yet it is not harmful for us. It can use for supplying us the electricity very convenient.

(f) Habitat.

All the aquatic organisms are depend on the water for their foods, transport, and homes. Without it, non-of them can be survived at all.

1.2 WATER POLLUTION

Since, we know that how much important the water to us, so we need to improve or at least maintain the water quality at the satisfied condition for us all the time, so that the water is safe for us to consume. If not, the water in no longer useful for us when it is polluted.

Recently, the water pollution is already become an important issue to be concerned. It is due to the water pollution becomes more serious as time goes by. Water pollution is always caused by human's activities, such as: industries, agricultural, domestic uses and the others. The water from all the human's activities just dispose into the water bodies without any appropriate water treatment until deteriorates the water quality by introducing the water pollutants.

The water pollutants are those compound, such as: biological, physical or chemical, which are present beyond the levels of the regulation until hazard to the living things and not safe. The biological compounds are liked bacteria, viruses, and microorganisms, which can cause disease to organisms. The physical compound is usually the heat, which is discharged from the factory for the cooling system. The temperature of the heat is usually much more higher than the normal water bodies temperature. Meanwhile, the chemical compounds are those metal ions, organic and inorganic compounds, and radioactive compounds, which are introduced by human's activities. The following Table 1.1 is taken from (Reference 1). This table shows the types of chemical pollutants with their sources and effects to organisms.

Table1.1: *Major chemical pollutants in the hydrosphere*

Pollutant	*Typical sources*	*Comments*
Radioactivity	Accidental discharges from nuclear industry, transport of nuclear material and nuclear tests.	Emotive subject. Health effects are frequently debated.
Organic chemicals	Agricultural use of herbicides and pesticides. Industrial and domestic wastes. Marine oil pollution from oil-tanker accidents.	A wide variety of chemicals are discharged (petroleum hydrocarbons, pesticides, detergents, *etc.*). Potentially harmful effects on human health and aquatic ecosystems.
Heavy metals	Wastes from industry, agriculture, urban drainage and domestic households.	Many metal pollutants can have potentially harmful effects on human health and aquatic ecosystems (*e.g.* mercury, lead, cadmium).
Acids	Drainage from mines, wastes from industry and acid deposition from the atmosphere.	Can harm aquatic ecosystems (*e.g.* sulfuric acid, nitric acid) by mobilising toxic metals.
Nutrients	Agricultural use of fertilisers and sewage.	May cause eutrophication (*e.g.* phosporus and nitrogen compounds). Nitrates may affect human health.

Source: Practical Environmental Analysis (1998).

1.3 WATER CONSTITUENTS

In natural environmental water, such as: ground waters, surface waters (rivers, lakes), seawaters and coastal waters, and wastewaters. Usually, the constituents in the natural water will be liked following:

(a) Insoluble solid material;

(b) Soluble or colloidal compounds;

(c) Dissolved gases;

(d) Ions from inorganic salts or metals.

(a) INSOLUBLE SOLID MATERIAL;

The term 'solids' is referred to the quantity of solid matter remaining in a water sample after drying or igniting at a specified temperature (Reference 1). The solids are come from decaying plant material and also might formed into inorganic solid particles from either sediments or rocks by the process weathering. The rain and those weather processes, such like wind and erosion are those typical sources for the solids. The high concentration of the solids in natural water can cause the serious water pollution by depositing the sludge and intensive anaerobic condition.

(b) SOLUBLE OR COLLOIDAL COMPOUNDS;

The soluble or colloidal compounds are always formed by the decaying organisms, such as: decomposition of the plants or other organisms. These categories include some soluble inorganic salts and organic materials.

(c) DISSOLVED GASES;

The dissolved gases in natural water are included oxygen, carbon dioxides and the other gases. But, the gas oxygen is the most important dissolved gas for the aquatic life. The plant and fish need the gas oxygen to undergo the process respiration to produce energy, carbon dioxides and water, such like following chemical reaction (Reference 2).

$$\underset{\text{glucose}}{C_6H_{12}O_6} + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

But, on the other hand, the aquatic plant will use the gas carbon dioxides for process photosynthesis to produce food and gas oxygen, such like following chemical reaction (Reference 2).

$$6CO_2 + 6H_2O + h\nu \longrightarrow C_6H_{12}O_6 + 6O_2$$

The concentration of dissolved oxygen can be measured by a few of established methods, such like: Winkler method. The organic substances in water will use the dissolved oxygen for oxidation process. All these oxidisable organic substances are usually come from the waste from sewage.

(d) IONS FROM INORGANIC SALTS OR METALS.

The ions which are formed by inorganic salts are liked the ions of sodium, calcium, chloride, and sulphate. The following Table 1.2 (Reference 2) shows some of the concentrations of cations and anions in natural river water.

Table1.2: The concentration range for cations and anions in river water.

Concentration range in natural river water (mgl^{-1})	Cations	Anions
0-100	Ca^{2+}, Na^{+}	Cl^{-}, SO_4^{2-}, HCO_3^{-}
0-25	Mg^{2+}, K^{+}	NO_3^{-}
0-1	Other metal ions	PO_4^{3-}, NO_2^{-}

Source: Environmental Analysis (1994).

Meanwhile, the metal ions which are usually those transition metal ions, such as iron(II), copper(II), manganese, cobalt, and so on. These metal ions might come from ore refining industry, leaching from mineral, industrial effluents and the others. The metal ions can be analyzed by spectrometry methods and electrochemical methods.

1.4 HEAVY METALS

1.4.1 INTRODUCTION TO HEAVY METALS

The definitions for heavy metals are listed like the following:

(a) Heavy metals have defined as those having specific gravities of 5 or greater (Reference3).

(b) It has also been showed that any metal beyond calcium in the periodic Table of Elements should be considered as “heavy” (Reference 4).

(c) Heavy metals also means that all metals and metalloids other than the alkali and alkaline earth elements (Reference 5).

(d) Heavy metals are defined as those metals with densities greater than 5 gcm^{-3} (Reference 1).

(e) "Heavy metals" is a general collective term, which is applied to the group of metals and metalloids with an atomic density greater than 6 g/cm (Reference 6).

But, there are some conflicts in the literal meanings arise where the light metals and metalloids such as: Be, Al, As, Se, etc. are often included in some of the environmental studies dealing with toxic heavy metals (Reference 7).

Since, the concentrations of the heavy metals are present at very low levels in the waters compared with those alkaline and alkaline earth elements or other major ions, so the heavy metals are usually referred as trace metals. The "trace metals" also becomes a term that is widely used in many environmental analyses. But, the heavy metals analysis are usually placed at the second only to pesticides in environmental importance (Reference 25). The levels of analysis the heavy metal ions always from μg/L to mg/L concentration. The examples of the heavy metals are liked Aluminium (Al), Copper (Cu), Lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), tin and so on.

According to Practical Environmental Analysis (Reference 1), the metals can be classified as:

(a) Total metals – metals from unfiltered samples (dissolved + suspended).

(b) Dissolved metals – metals in unacidified samples, which have filtered through a 0.45μm membrane filter.

(c) Suspended metals – metals retained on a 0.45μm membrane filter.

1.4.2 SOURCES OF HEAVY METALS

There are two types of sources for the input of heavy metals into the water bodies, which are the natural sources and the anthropogenic sources. The natural sources for the heavy metals are liked the those natural processes, which are always happened in the ecosystem all the time, such as: process weathering (wind, erosion, volcanic activities), the interaction among the aquatic organisms, leaching from ore deposition, and so on.

On the other hand, the anthropogenic or man-made sources for the heavy metals are liked the following:

(a) Industrial wastes, which always dispose from the various types process, metal finishing, metal polishing, etc.

(b) Domestic and agricultural wastewaters, which are discharged into the water bodies all the time.

(c) The acid rain produced by the effluents from the factory plants also can cause the process of acidification to the surface and ground waters until the metals leach from it and go into the water.

There are many studies or reports about the distribution and environmental impacts of the heavy metals to the aquatic environment (Reference 8 and 9). There are also a lot of database on water quality for the stations from the whole world has been reported (Reference 8).

The most serious cause for the heavy metal pollution in natural waters is caused by the anthropogenic wastes, including industrial, agricultural, domestic and so on. The following Table 1.3 shows the anthropogenic input of heavy metals into the aquatic ecosystem (Reference 16).

Table 1.3: World Anthropogenic Input of Heavy Metals into Aquatic Ecosystem.

Metal	Total Input	Median Value
Cadmium	2.1 -17	9.4
Lead	97 – 180	138
Zinc	77 – 375	226

Values in million kg per year
Source: Nriagu and Pacyna (1988).

1.4.2.1 METALS FROM INDUSTRIAL WASTE

The industrial waste is the primary source of heavy metals pollution in water. According to Nriagu and Pacyna (1988) (Reference 16), there is 25% if the heavy metals from industries are discharged into the waters. So, this process results the concentration of certain metals are increased, such as: 90 ng/L for mercury, 180 ng/L for cadmium, 2,200 ng/L for copper and nickel, and also 2,500 ng/l for zinc (Reference 16). All these concentrations are much more higher for the level of unpolluted waters. The following statements are listed a few examples of industries, which are contributed the heavy metal pollution:

1) Electroplating industry contribute high concentration of heavy metals, such as: Cu, Cd, Ni, Cr (Reference 17).
2) The steel mills, electronic industry, chemical manufacturing, and power stations also discharge a lot of heavy metals into the river and coastal waters (Reference 18).

1.4.2.2 METALS FORM MINING

The activities of mining and metal smelting also contribute to the heavy metals pollution. There is high concentration of heavy metals inside the mine effluents. Usually, the mine effluents will discharge into the drainage streams.

The solid wastes from mining activity can contribute the sulfide minerals (pyrite) to oxidize in atmosphere to form the sulfates, which can cause the pH of water down to 2 to 3 (Reference 17).

1.4.2.3 METALS FROM SURFACE RUN-OFF

The surface water is a major component for the water budget in many water systems, especially in remote areas. Yet, the surface run-off also contributes the deposition of heavy metals in agricultural or silvicultural areas (Reference 19). Meanwhile, in urban area the storm water run-off is one of the important non-point sources of heavy metals and subsequently discharged into the river waters.

1.4.2.4 METALS FROM SEWAGE WASTEWATERS

Usually, the heavy populated areas always become the important sources of heavy metals (Reference 20 and 21). Many of the heavy metals (Zn, Cu, Hg, Ag, Cd, Pb), which are discharged from sewage into the seawater are present as insoluble sulfides, while some heavy metals (Ni, Mn, Co) are relatively soluble (Reference 22).

The input of the sewage waste into the stream can disturb the distributions of the metals in the water bodies. This process can result the high concentration of certain types of heavy metals, especially those always presence in the sewage waste. For example: the metropolitan sewage inputs of heavy metals into the Hudson River estuary contribute the sewage discharge until 30% of the total input into the river water (Reference 23).

1.4.2.5 METALS FROM SUSPENDED PARTICULATES

The anthropogenic activities, such as: mining, industry, sewage discharge and the others can discharge a lot of heavy metals into the water bodies, so this process can contribute the high proportion of the dissolved metals in rivers. It is due to the heavy metals pollution is always happened together with other types of pollution, such as: acidification. Most of the heavy metals are discharged into the water as the form of suspended particulate matters and deposited in the bottom of the water, so sometimes the bottom sediments in the water can considered as the important sink of heavy metals. There are a lot of studies are done on sediment core have shown that the long-term effects of the input of contaminants into the river and marine waters (Reference 24).

(a) LEAD

Lead can occur naturally in the water and present as the contaminant for aquatic organisms. The sources of lead are such like the following:

1) Lead has used as the petroleum additive in the form of the tetraalkyllead. The mixture of tetramethyl- and tetraethyllead also is added to the petrol. But, all of this organometallic lead will convert into the inorganic lead during the process of

combustion. The following statement is shown how the emitted organometallic lead is degraded until the inorganic lead in the environment (Reference 1):

$$R_4Pb \longrightarrow R_3Pb^+ \longrightarrow R_2Pb^{2+} \longrightarrow Pb^{2+}$$

Where R is alkyl groups (methyl or ethyl).

2) The paint that we used for our houses or buildings also contains lead.
3) The pipes which are used to pump water to whole buildings, especially in older houses also are made of lead.
4) The accidental spillages of organolead into the sea during the transportation.

(b) CADMIUM

The average abundance of cadmium in the earth's crust is about 0.16 ppm; in soils is from 0.1 to 0.5 ppm; in rivers is about 1 µg/L, and in groundwaters is in the range of 1 to 10 µg/L (Reference 14). The concentration of cadmium in the water is depending on the carbonate equilibrium, water hardness or alkalinity. The major source of the cadmium is come from the industries, such as: electroplating, paint pigments, alloys and batteries manufacturing.

(c) ZINC

Zinc is always present in the environment in the form of the oxide, sulphide or carbonate. Zinc can form complexes with other organic and inorganic ligands. The ambient level for zinc concentration in unpolluted marine water is about order of 10 µg/L (Reference 15).

The average abundance of zinc in the earth's crust is estimated as 76 ppm; in soils is ranged from 25 to 68 ppm; in rivers is 20 μg/L, and in groundwaters it is < 0.1 mg/L (Reference 14).

The natural sources of the zinc into the water bodies are atmospheric fallout, waste dumping, discharges from anthropogenic activities. The concentration of zinc in natural waters is controlled by adsorption on mineral surfaces, organic complexes, carbonate equilibrium and so on.

Meanwhile, the anthropogenic sources for zinc are come industries for manufacturing alloys (bronze and brass), pigments, fungicides and batteries.

1.4.3 TOXIC EFFECTS OF HEAVY METALS

Many of the heavy metals are toxic to the organisms, including human beings if they exist excess of certain level. For example: many of the disease caused by the toxic heavy metals previously, such as: Minamata (1953-1960) is caused by mercury, Niigata (itai-itai) disease (1965) is caused by cadmium, according (Reference 10 and 11). All these diseases are already caused a lot of human lives death.

Unfortunately, the heavy metals can not degrade in the environment by process biological or chemical, as well as the organic pollutants. Yet, the metals might react with some compounds which are available naturally and result on the metals become more toxic, e.g.: methylation of mercury. In addition that, some of the organisms can tolerate with the metals and accumulate them into the bodies until achieve high concentration. Hence, the toxic metals can bioconcentrate in the food chain until the last predators in the chain (wildlife and human), which can have the concentration much more than in the water originally.

(a) LEAD

If the concentration of Lead is too high, it can cause hazard to organisms within a few hours or days, such as: the biological processes for exchanging the salts and oxygen inside the body are seriously disturb or impairment. The toxicity of lead also causes a numerous problems to the aquatic organisms such as: fish. The following Table 1.4 is shown the acute and chronic toxicity of lead to the different types of fish (Reference 13).

Table 1.4: Summary of the published acute lethal concentrations for freshwater fish

Species	Water hardness ($mg/l\ CaCO_3$)	Lead concentration (mg/l)	Effect
Rainbow trout	32	1.17 D	96-h LC50
	385	1.32 D	-
	290	1.47 D	-
	105	8.0 T	-
Brook trout	44	3.36 D	96-h LC50
Brown trout	Soft	0.300 ?	Approx. 30h lethal concn.
Fathead minnow	20	2.4 T	96-h LC 50
	20	5.58 T	-
	20	7.33 T	-
	360	482.0 T	-
Bluegill sunfish	20	23.8 T	-
	360	44.2 T	-

T = total; D = dissolved.

Source: Proposed Environmental Quality Standards For List II Substances In Water Inorganic Lead (October, 1984).

Lead is one of the unessential elements for living organisms (plants and animals). It becomes toxic when we ingest it and bioaccumulate inside the bodies.

(b) CADMIUM

Cadmium, Cd is one of elements in Group IIB of the periodic table. It has 48 for atomic number and atomic weight is 112.41 with 2 valence (Reference 14).

Cadmium is also one of the nonessential elements for living organisms (animals and plants). But, it can become tremendously toxic to our organ system, such as: liver and kidney. The bioconcentration of the cadmium inside our bodies can lead to the dysfunction of the kidneys; even the concentration is not too high.

(c) ZINC

In periodic table, zinc, Zn is placed on the first place in Group IIB. It has the characteristic liked (Reference 14):

1) Atomic number – 30;
2) Atomic weight – 65.38;
3) Valence – 2.

Unlike lead and cadmium, zinc is one of the essential elements for growth for living organisms (plants and animals). But, at certain levels, it might become toxic to aquatic organisms. The ambient level for zinc is the order 10 μg/L in unpolluted waters (Reference 15).

The tolerance of element zinc by marine animals when the zinc is ingested controls by the ability of the them to regulate the zinc concentration, types of habitats, mechanisms of feeding, and so on. The different types of species in zinc uptake in the marine ecosystem are demonstrated by Bryan (Reference 26).

1.4.4 THE CONCENTRATION OF HEAVY METALS INSIDE RIVERS

The concentration of the types of heavy metals in the rivers is strongly dependent on the formation of drainage basin and weathering regime formation. This is usually considered as the 'Background levels' of the heavy metals.

For example: the surrounding place with metal-bearing rock available always can contribute the high input of heavy metals into water and sediments. Usually, the level of the heavy metals is present in the region of low ppb until sub-ppb.

(a) LEAD

In normal freshwater, the main forms for lead species are the carbonato species, such as: $PbCO_3$ and $Pb_2(OH)_2CO_3$ (>90%) (Reference 27). Meanwhile, in seawaters the main forms of lead species are liked carbonato complexes (83%) and chloro species (11%) (Reference 27).

Lead has strong affinity to absorb on the inorganic rather than organic ligands in pH above 7, such as: iron oxide. In seawater, most of the soluble lead is present as inorganic colloid (40% to 80%), but in lower-pH (pH 6.0) for freshwater the main form of lead species is inorganic molecular species, e.g. $Pb_2(OH)_2CO_3$ according Batley and Gardner (Reference 28).

(b) CADMIUM

In river water, the main form for cadmium is inorganic species, such like: ion cadmium (Cd^{2+}) and $CdCO_3$ (carbonate). On the other hand, the cadmium is present as $CdCl^+$ and $CdCl_2^0$ complexes (92%) in seawater (Reference 27).

Normally, a very few portion of the cadmium is present as pseudocolloids. It is due to the cadmium ion can only absorbed onto the colloidal particles at the high pH. Furthermore, the cadmium also presents as $CdHS^+$, which is nonlabile in anoxic water.

(d) ZINC

In freshwater, the main forms of zinc are inorganic forms, such as: zinc ion, Zn^{2+} (50%) and zinc carbonate, $ZnCO_3$ (38%) (Reference 27).

The water of the ocean contribute 10 ng zinc per litre (trace) from the surface (Reference 27), even though the rivers input and sewage outfalls into the seawater is about 0.5 to 2 μg zinc per litre (Reference 27).

1.4.5 THE TRANSPORTATION OF THE HEAVY METALS IN WATER

The main forms of the heavy metals are transported inside the water bodies are consisted of the dissolved and particulate matters. The fate of transportation of heavy metals has been used to study the environment pollution. Basically, there are three major phases for heavy metals to transport inside the river water, such like: the insoluble phase (suspended particulate compounds), the soluble phase (dissolved compounds) and deposition as the bottom layer for sediments.

The factors which are used to control the distribution of the heavy metals in these three phases are liked (Reference 29 and 19):

1) Physico-chemical processes – precipitation, adsorption, complexation, ion exchange, hydrolysis, coagulation, and oxidation-reduction.
2) Biological uptake by the aquatic organisms.

All these three phases are reversible and the magnitudes of the transfer metal are strongly depend on the environmental conditions, such as pH, dissolved oxygen, redox potential (Eh), different forms of suspended particulate matters, complexing ligands, the biological processes influence, and the others (Reference 30).

In the normal natural water environment, most of the heavy metals are only dissolved slightly. The levels of the heavy metals in water is depending on the solubility of the salts for the metals, such like: hydroxides, sulfates, carbonates, sufides and the others. The following Table 1.5 shows the solubility product constants for various types of salts in pure water (Reference 32).

Table 1.5: Solubility Product Constants for Solids in Pure Water

Metal Ion	Carbonate	Sulfate	Sulfide	Hydroxide
Cd(II)	13.74	-	27	14.4
Pb(II)	13.13	7.6	27.5	15.1
Zn(II)	10	-	24.7	16.5

All values expressed as $-\log K_{sp}$
Source: Stumm and Morgan (1981)
Pankow (1991)

There are various types of transportation pathways for the metals, which are based on the dynamics system of delivering the metals to the oceans are studies (Reference 33). According to Turekian (1977) (Reference 33), every single step of the transportation heavy metals is required the certain particles to play as the sequestering agent for those reactive elements. These essential particles are made up of the active organic particles on lithosphere and sea, the organic colloids in estuaries (flocculating metal), precipitated solid oxides (manganese and iron).

There are large amounts of the metals transport in major rivers around the world by association with suspended particles. But, the amounts of association between the metals and suspended particles are decreased inside the polluted water. The following Table 1.6 is shown the percentage of particulate associated heavy metals (leads, cadmium, zinc) in major rivers around the world (Reference 17).

Table 1.6: Percentage of Particulate – Associated Heavy Metals Discharged by Major rivers in the world.

Metal	Amazon River (a)	Mississippi River (b)	Polluted U.S River (b)	Polluted F.R.G Rivers (b)	Rhine (Netherland) (b)
Cd	-	88.9	-	30	45
Zn	-	90.1	40	45	37
Pb	-	99.2	84	79	73

Source: (a) Gibbs (1977)
(b) Forstner and Prosi (1979)

The association of heavy metals with the suspended particulates and sediments is depend on several factors, such like: the water pH, chemical composition of the suspended particulate and sediments, the size of the particles. For example: the adsorption capacity of iron oxyhydroxide surfaces for certain types of heavy metals (Cd, Cu, Zn) can change by nearly 100% along the pH range about 2 units (Reference 36), the cationic surfactants in water can reduce the adsorption of heavy metals on clay. But, the precipitation of metal-surfactant compound can caused by the presence of anionic surfactants (alkyl benzene sulfonate).

In addition, the partition of the metal, especially manganese and iron are always affected by the redox potential, either oxidizing or reducing conditions. If the oxide of metals is soluble, then the heavy metals can release from the absorbed oxide surfaces in the reducing condition. Furthermore, in very low redox potential, the bacteria can reduce the sulfate to sulfite and cause the metals can mobilize in water.

1.4.6 HEAVY METALS IN MALAYSIA WATER SYSTEM

The studies of heavy metals in Malaysia water system are always done in river and coastal water. Normally, the Klang River will be chosen as the sampling station for the water monitoring because it is one of the highest density of population and various types of industries in Malaysia.

The distribution of heavy metals along the Klang River has divided by Chan *et al* (1978) (Reference 37). The levels of arsenic in the soluble form is quite high (>40 μg/L), but the concentration of the other heavy metals, such as: Co, Cu, Ni, Pb, and Cd were relatively low (<10 μg/L), and were quite constant all along the river except for manganese which increase in the downstream direction (Reference 30).

Another useful study on the distribution of arsenic in the Klang River has been done by Gian and Tong (1977) (Reference 38). The report shows that the range of concentration of arsenic is from 14 to 120 μg/L (Reference 38). It is due to the rubber and oil palm estates used a large amount of arsenic during 1950's and 1960's. Hence, according to Gian (1978) (Reference 39), the concentration of arsenic in the soil samples, which are taken from two estates is from 30.6 μg/g to 74.9 μg/g, compare with the concentration of arsenic in garden soils is ranged from 11.6 μg/g to 12.2 μg/g.

The other types of heavy metals in Klang River have reported by Law and Sigh (1986) (Reference 40). This report (Reference 40) has studied the concentration of the heavy metals in water and sediments, such as: Mn, Fe, Cu, Pb and Zn. According this report (Reference 40), the dissolved metals (Cu, Pb, Zn) have the mean concentration about 4.3, 1.6 and 3.9 μg/L. Another report from Law and Sigh (1987) (Reference 41) has studied on the mercury's concentration is about 1.69 μg/L in water and 0.2 mg/kg in sediments.

The distributions of 12 types of heavy metals have reported by Sukiman (1989) (Reference 42) in the Langat River. This river is responsible for drainage the adjacent area of Klang River. According this report (Reference 42), the highest concentration of metals in suspended particulate are liked As, Cd, Co, Ce, Sc, Sb, and Zn; while the highest concentration of metals in the bottom of sediments are liked Cr, Rb and Th. Furthermore, the concentration of arsenic is tend to increase along the downstream, but the rest of metals are constant. Moreover, the concentration of arsenic is found higher in suspended particulate and sediments, compare with garden soils. It shows that the arsenic has introduced anthropogenically into the Klang River.

However, there are only a few studies of distribution of heavy metals in aquatic system in Malaysia. Yet, among these studies, many of them are concentrated on the heavy-metal pollution in river and coastal waters. But, non-of them are used to provide the information about anthropogenic sources with the heavy metals pollution. The study on interaction between the physico-chemical conditions in water also limit, such as: water pH, dissolved gas, redox potentials, water hardness, salinity, suspended particulate matters and so on.

1.5 METHODS AVAILABLE FOR TRACE METALS ANALYSIS

1.5.1 TRACE METAL ANALYSIS

Recently, the trace metal analysis has become more important as time goes by. The application of trace metal analysis can be found in trace metal pollution, elucidation of the roles of trace metals in biologic function, characterization of ultrapure materials for technological advances or scientific evidence for forensic investigation (Reference 43). For the trace metal analysis, we need to know some of the behaviours of the metals, such as toxicity, transportation, reactivity, complexation, absorption and the others.

According to Vydra *et al.*(1976) (Reference 44):

> Trace analysis requires the successful solution of three problems: (1) achieving sufficient sensitivity of the method i.e. a sufficiently high signal-to-noise ratio; (2) achieving the selectivity required to determine trace components of the system in the presence of other substances at concentrations several orders of magnitude higher; this problem is not, in many cases, soluble without the use of preliminary separation methods; (3) obtaining sufficiently pure chemicals and mastering work with very dilute solutions in which the amount of dissolved substances diminishes through adsorption on the walls of the vessel, hydrolysis, etc.

The range concentration for analysis of metal ions is usually in the μgL^{-1} to $mgL^{-1.}$ But, for trace metal analysis, the concentration of metal can down to ppb. Normally, there only few types of metals are present naturally in mgL^{-1} level, such like iron, manganese, zinc. But, the other metals are usually existed only at the very low concentration (trace), such as cadmium, lead, mercury, and the others.

1.5.2 GENERAL ANALYTICAL METHOD

For environmental analysis, we need to apply a lot of different types of analytical methods, so that the results will be more valid and reliable. Usually, we always measure the bulk properties of the specific individual ions or compounds, such as concentration, acidity, water hardness, dissolved gas, and the others.

There are two categories of the analytical methods are available for the environmental analysis, which are included the classical methods and instrumental methods.

The classical methods are such liked volumetric methods and gravimetric methods. The volumetric methods is also known as titration methods. These methods can provide fast and accurate results, simple alignment, inexpensive operation. It can use to measure the water hardness until below mg/L. The gravimetric methods are usually used to compare the accuracy of the data, which are obtained by other methods. This technique can provide the results with high accuracy. But, this is a slow technique because it requires the sample pretreatment, such as precipitation, extraction, filtration, and drying. Yet, these methods very easy to interfere by other species.

Meanwhile, the instrumental methods are always subjected for trace analysis (low concentration). The range of the measurements is in mg/L, which is near to the environmental concentrations. The instrumental methods are included chromatographic zinc. But, the other metals are usually existed only at the very low concentration (trace), such as cadmium, lead, mercury, and the others.

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Meanwhile, the instrumental methods are always subjected for trace analysis (low concentration). The range of the measurements is in mg/L, which is near to the environmental concentrations. The instrumental methods are included chromatographic methods, electrochemical methods, and spectrometric methods. The instrumental methods can provide the results in short time and can be automated. But, these methods need sample preparation and instrument calibration.

1.5.3 ANALYTICAL METHODS

There are a few types of analytical methods can be used for metal analysis, which are listed like below:

(a) Atomic spectrometry;

(b) UV-Visible spectrometry;

(c) Electrochemical methods;

(d) Chromatography methods.

(a) ATOMIC SPECTROMETRY

There are two types of atomic absorption spectrometry (AAS), either the Flame atomic absorption spectrometry (Flame AAS) or Flameless atomic absorption spectrometry (Flameless AAS). The diagram for a FAAS is shown in the following (Reference 2):

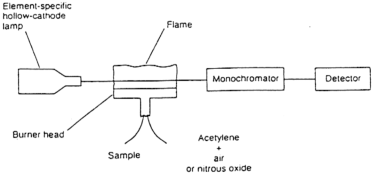

Figure1.1: *Diagram of a flame atomic absorption spectrometer.*
Source: Environmental Analysis (1994).

*PRINCIPLE:

The flame is used to aspirate and then atomize the sample. After that, there is a light beam will direct into the monochromator through the flame and lastly reach to the detector. The detector is used to measure the intensity of the absorption light of the sample. Each of the metal uses different source lamp because each of them has their own characteristic wavelength. So, this method is quite free from other interferences. The amount of light absorbed is proportional to the concentration of the atomized element over a linear range.

*ADVANTAGES:

- AAS is a sensitive method.
- AAS can use for trace metal analysis, but need to preconcentration.
- AAS is a simple technique.
- AAS require a short time for analysis.
- The cost for instrument is relatively low.

*DISADVANTAGES

- AAS is influenced by chemical interferences. For example: the sample is not atomized completely because of the flame is hot enough.
- AAS need to do the background correction because the solid particles in the flame will cause the light scattering and molecular absorption and result in high background noise.
- The sensitivity of AAS for trace metal analysis is quite low.

- There is a possibility of the contamination of sample.

The following Table 1.7 is shown the various concentration ranges of the metals is analyzed by atomic absorption spectrometry (Reference 14).

Table 1.7: ATOMIC ABSORPTION CONCENTRATION RANGES WITH DIRECT ASPIRATION ATOMIC ABSORPTION

Element	Wavelength *nm*	Flame Gases*	Instrument Detection Limit *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Ag	328.1	A-Ac	0.01	0.06	0.1-4
Al	309.3	N-Ac	0.1	1	5-100
Au	242.8	A-Ac	0.01	0.25	0.5-20
Ba	553.6	N-Ac	0.03	0.4	1-20
Be	234.9	N-Ac	0.005	0.03	0.05-2
Bi	223.1	A-Ac	0.06	0.4	1-50
Ca	422.7	A-Ac	0.003	0.08	0.2-20
Cd	228.8	A-Ac	0.002	0.025	0.05-2
Co	240.7	A-Ac	0.03	0.2	0.5-10
Cr	357.9	A-Ac	0.02	0.1	0.2-10
Cs	852.1	A-Ac	0.02	0.3	0.5-15
Cu	324.7	A-Ac	0.01	0.1	0.2-10
Fe	248.3	A-Ac	0.02	0.12	0.3-10
Ir	264.0	A-Ac	0.6	8	-
K	766.5	A-Ac	0.005	0.04	0.1-2
Li	670.8	A-Ac	0.002	0.04	0.1-2
Mg	285.2	A-Ac	0.0005	0.007	0.02-2
Mn	279.5	A-Ac	0.01	0.05	0.1-10
Mo	313.3	N-Ac	0.1	0.5	1-20
Na	859.0	A-Ac	0.002	0.015	0.03-1
Ni	232.0	A-Ac	0.2	0.15	0.3-10
Os	290.9	N-Ac	0.08	1	-
Pb^+	283.3	A-Ac	0.05	0.5	1-20
Pt	265.9	A-Ac	0.1	2	5-75
Rh	343.5	A-Ac	0.5	0.3	-
Ru	349.9	A-Ac	0.07	0.5	-
Sb	217.6	A-Ac	0.07	0.5	1-40
Si	251.6	N-Ac	0.3	2	5-150
Sn	224.6	A-Ac	0.8	4	10-200
Sr	460.7	A-Ac	0.03	0.15	0.3-5

Ti	365.3	N-Ac	0.3	2	5-100
V	318.4	N-Ac	0.2	1.5	2-100
Zn	213.9	A-Ac	0.005	0.02	0.05-2

* A-Ac = sir-acetylene; N-Ac = nitrous oxide-acetylene

[+] The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.

Source: Standard Methods for the Examination of Water and Wastewater, 20th Edition (1998).

Since, the atomic absorption spectrometry is not so suitable for analysis many types of elements in big samples and various ranges of concentration, so we can use emission spectroscopy. One of the methods is applied the emission spectroscopy is the inductively coupled plasma (ICP). The ICP developed at the mid-1960's to overcome the difficulties face by AAS.

*PRINCIPLE:

The ICP source is made up of a stream of argon gas. There is a radio frequency (27.1 MHz) is used to ionize the argon gas. The plasma is surrounding by a water-cooled coil. The nebulizer has used to generate the sample aerosol and introduced into the spray chamber through injector tube. The high temperature in the plasma (about 6000 to 8000°K) is used to atomize and excite the element, so that the element will emit light. The emitted light will pass through monochromator or polychromator and reach to the detector.

*ADVANTAGES:

-The technique can use for simultaneous multi-element analysis.

-The linear range for ICP is wider than the AAS.

-The analysis time is rapid, normally 5 seconds per element.

*DISADVANTAGES

-The ICP can be influenced by many types of interferences, such as: spectral interference and non-spectral interference (physical and chemical).

-The sensitivity of ICP is a bit lower than graphite furnace AAS, but still can detect the trace metal down to 1 µgL^{-1} (Reference2).

The following Table 1.8 is shown the wavelengths, detection limits, alternate wavelengths, calibration concentration and the upper limits for various metals by using the ICP method.

Table 1.8: Suggested Wavelengths, Estimated Detection Limits, Alternate Wavelengths, Calibration Concentration, AND UPPER LIMITS

Element	Suggested Wavelength *nm*	Estimated Detection Limit *µg/L*	Alternate Wavelength* *nm*	Calibration Concentration*mg /L*	Upper Limit Concentration+ *mg/L*
Aluminum	308.22	40	237.32	10.0	100
Antimony	206.83	30	217.58	10.0	100
Arsenic	193.70	50	189.04++	10.0	100
Barium	455.40	2	493.41	1.0	50
Beryllium	313.04	0.3	234.86	1.0	10
Boron	249.77	5	249.68	1.0	50
Cadmium	226.50	4	214.44	2.0	50
Calcium	317.93	10	315.89	10.0	100
Chromium	267.72	7	206.15	5.0	50
Cobalt	228.62	7	230.79	2.0	50
Copper	324.75	6	219.96	1.0	50
Iron	259.94	7	238.20	10.0	100
Lead	220.35	40	217.00	10.0	100
Lithium	670.78	4s	-	5.0	100
Magnesium	279.08	30	279.5	10.0	100
Manganese	257.61	2	294.92	2.0	50
Molybdenum	202.03	8	203.84	10.0	100
Nickel	231.60	15	221.65	2.0	50
Potassium	766.49	100s	769.90	10.0	100
Selenium	196.03	75	203.99	5.0	100
Silica (SiO_2)	212.41	20	251.61	21.4	100

Silver	328.07	7	338.29	2.0	50
Sodium	589.00	30s	589.59	10.0	100
Strontium	407.77	0.5	421.5	1.0	50
Thallium	190.86++	40	377.57	10.0	100
Vanadium	292.40	8	-	1.0	50
Zinc	213.86	2	206.20	5.0	100

[*] Other wavelength may be substituted of they provide the needed sensitivity and are corrected for spectral interference.

+ Defines the top end of the effective calibration range. Do not extrapolate to concentration beyond highest standard.

++Available with vacuum or inert gas purged optical path.

s Sensitive to operating conditions.

Source: Standard Methods For The Examination Of Water And Wastewater, 20th Edition (1998).

(b) UV-VISIBLE SPECTROMETRY

The visible spectrometry technique involves the element of interest to form the complex with colour-forming complexing agents. The selectivity of the analysis can increased by two different ways (Reference 2):

(1) Solvent extraction

The solvent extraction can use to increase the sensitivity and selectivity. For example: chromium is react with complexing agents to form dipenylcarbazide complex after extraction by trioctylamine/chloroform solution. This method can provide detection limit about 5 μg/L.

(2) Colour-forming complexing agent.

The selectivity of the analysis can increase by the choice of suitable colour-forming complexing agent. So, this method no need to use the solvent extraction procedure. The few examples are shown like the following:

Table1.9: The various colour-forming complexing agents with detection limits for different types of metals.

Metal	Reagent	Limit of detection ($\mu g l^{-1}$)
Iron(II)	2,4,6-Tripyridyl-1,3,4-triazine	60
Manganese	Formaldoxime	5
Aluminium	Pyrocatechol violet	13

Source: Environmental Analysis (1994).

(c) ELECTROCHEMICAL METHODS

There are some electroanalytical methods have used for the determination of the metals concentration in environmental analysis, such as polarography and voltammetry techniques. The electrochemical methods manage to provide the high sensitivity and quantify the metal in inorganic and organometalic compounds efficiently.

(1) Polarography

There are two types of polarography, including the differential pulse and square wave modulation. Since, the abundance of the most metal in environment is in the range 10^{-10} to 10^{-8} M, so the polarography is not sensitive enough to detect the element of interest. It is because the concentration of polarography is limited to 10^{-7}M (Reference 27).

(2) Anodic Stripping Voltammetry (ASV)

Since, the polarographic is not sensitive enough for environmental analysis, so the ASV has introduced to overcome this problem. ASV has been applied widely for the determination of trace metals in water analysis. It is due to ASV manages to provide very high sensitivity until the concentrations of the metals less than 10^{-11}M (Reference 27).

(3) Cathodic Stripping Voltammetry (CSV)

Another types of voltammetry technique are the CSV. The CSV technique involves the cathodic stripping of an insoluble film, usually the mercury salt of the analyte (HgL) deposited on the working electrode like the following (Reference 27):

Deposition: $Hg + L^{2-} \longrightarrow HgL + 2e$
Stripping: $HgL + 2e \longrightarrow Hg + L^{2-}$

The CSV technique is started with the adsorption of an organic ligand on the mercury electrode. Then, the metal ion will react with the adsorbed ligand to form the metal complex and result the cathodic stripping form the film and produce the metal amalgam.

The other CSV technique is used to determine the total and reactive metal in water. The technique is used to measure the reduction of the adsorbed ligand, but not the metal in the metal complex.

But, there is a problem where the natural organic matter in water will compete with the metal ion to adsorb on the electrode for the adsorption sites. According to Wang *et al.* (Reference 45), this problem can be overcome by protecting the glassy carbon electrode with a layer cellulose acetate coating. This layer only allows the smaller particles (complexing ligands) but not the larger molecules (e.g., humic acid) to pass through it.

This technique can detect until 10^{-10} M within a short deposition time. This technique also can use to differentiate the labile and inert metal species in water by their reactivity with the organic ligand.

(4) Potentiometric Stripping Analysis (PSA)

This PSA technique involves the deposition of the metal into the Thin Mercury Film Electrode (TMFE) at certain potential. There is a chemical oxidant (O) in solution has been used to oxidize and strip the metal. The potential for working electrode is worked as the function of time. The process are shown in the following (Reference 46).

$$\text{Deposition: } M^{2+} + 2e \longrightarrow M^0(Hg)$$
$$\text{Oxidation: } M^0(Hg) + O \longrightarrow M^{2+} + R^{2-}$$

The metals are always oxidized by the chemical oxidants, such like dissolved oxygen or mercuric ion, so that we can get the potential-time step, which is separated efficiently. Compare with ASV, the PSA is less sensitive to the adsorbed organic. Yet, the analysis of PSA won't have the problem of interfere by any redox compounds.

(5) Pseudopolarography

According to Brown and Kowalski (Reference 47), the pseudopolarography technique can be used to determine the arsenic, cadmium, and lead in many types of natural waters.

The pseudopolarography technique can produce a pseudopolarogram with a plot of ASV stripping peak current versus the deposition potential. In a pseudopolarography, the peak height will increase with deposition potential until produce a classical polarographic shape.

(6) Modulation Waveforms

We can increase the sensitivity of the ASV by modulating the DC voltage ramp in waveforms. In nowadays, there are two types of the modulation waveforms are available, such as differential pulse and square wave. But, the AC and staircase waveforms are less commonly used.

The square wave and staircase voltammetry can provide the fast scan rate, up to $2Vs^{-1}$ with a square wave frequency of 200 Hz, so the complete voltammogram can obtain less than 2 s and in a single drop of mercury (Reference 48). But, the differential pulse voltammetry cannot have the scan rate faster than $5\ mVs^{-1}$ (Reference 49).

A problem for pulse and square wave techniques is that these techniques are more sensitive to the substances adsorb on the mercury electrode than linear scan voltammetry. The adsorbed layer can cause the multiple redox reactions happen at the electrode during the deposition step. The different modulation waveforms will produce different results for the determination of labile or inert species by ASV.

(d) CHROMATOGRAPHY METHODS

The liquid chromatography is used when the atomic spectrometry is not suitable for the analysis. Those types of situations where atomic spectrometry is not ideal are liked following (Reference 2):

(1) Complex matrices;

The AAS often require the extraction steps for the complex matrices, in order to remove the interfering substances. So the analysis time will be longer.

(2) Analysis of the mixture;

AAS needs to use different lamp sources for different elements. So, sometimes the unexpected elements are not detected. But, the liquid chromatography can determine the elements with the suitable column and eluent.

(3) Quantification of different chemical forms of the ions.

AAS is not managing to differentiate and separate the different chemical forms of the ions. On the other hand, we can separate and quantify the different chemical forms of ions by using ion chromatography.

The chromatographic methods, such as ion chromatography and HPLC are also used for metal analysis. Among these, the 'chelation ion chromatography' has found as the most sensitive method for the determination of transition metals. The detection limits for this technique are 0.2-1 $\mu g l^{-1}$ with a 20 ml of sample (Reference 2).

1.6 THE ELECTROCHEMICALS METHODS USED FOR THE DETERMINATION OF TRACE METALS IN RIVER WATERS.

1.6.1 BASIC VOLTAMMETRY

The voltammetry techniques have applied for the determination of the trace metals in this work. Voltammetry is one of the electroanalytical techniques, which are used to measure the potential as a function of waveform at the working electrode.

There are three types of electrodes in voltammetry, which are the working electrode, the reference electrode, and the auxiliary (counter) electrode.

The working electrode is the place of the reaction is happened. There will a certain potential apply at this electrode to act as a driving force to lead the electrochemical reaction to occur. The electrochemical reaction will start when the elements of interest in the sample are electrolysed (oxidized or reduced) at this electrode. The proper choice of the working electrode can increase the sensitivity and reproducibility of the technique. The ideal working electrode will have the surface area, which is reproducible and the low background current. There are a few types of the working electrodes, such as the Hanging Mercury Drop Electrode (HMDE), Dropping Mercury Electrode (DME), Mercury Film Electrode (MFE) and Thin Mercury Film Electrode (TMFE).

The second major electrode is the reference electrode. This electrode is not sensitive to the composition of the solution and the potential of the working electrode, so it is used to provide the known and fix potential for the redox reactions. The types of the reference electrodes are silver-silver chloride and saturated calomel electrodes. Sometimes, the reference electrode can be leaked. To overcome this problem from leakage, we can separate it by an ultrafine porosity sintered-glass disc. The salt clogging problem also can cause the unrelated resistance.

The third electrode is the auxiliary/counter electrode. This third electrode is used to minimize the cell resistance to control the working electrode's potential. This electrode is consisted of the chemically inert conducting solution and surface area. The examples of this electrode are platinum wires and graphic rods.

There are two types of variations for the potential in the voltammetry techniques, including linear ramp or pulse train. The elements that can be electrolysed are called electroactive species. The electroactive species will be either oxidized or reduced at this electrode like the following:

$$O \rightleftarrows R - ne$$

Where O = oxidized species;
R = reduced species.

The electroactive species will control by the law of thermodynamics. According to the Nernst equation, which is written as the following:

$$E = E^0 + 0.059/n \log (C_o/C_R)$$

Where E = the applied potential;
E^0 = the standard potential;
n = the number of electrons involve in this reaction;
C_o = concentration for oxidized species;
C_R = concentration for reduced species.

The electrochemical reactions involve the electroactive species to be oxidized or reduced until produce the "faradaic current" (Faraday's law). The Faraday's law is stated that the electric charge involves in a redox reaction of 1 mole substance is equivalent to n times 96485 *C*. The faradaic current can be used as the measurement of the rate of the reaction. The faradaic current is influenced by two factors, such as (a) Mass transport – the rate of the species move from the bulk solution to the electrode. (b) Charge transfer – the rate of the electrons transfer from the electrode to the solution species and vice versa.

The result of this technique can be presented in a curret-potential plot, which is called "voltammogram". The current (vertical axis) is plotted versus potential (horizontal axis). The shape of the voltammogram can be either a wave- or peak-shaped response. The reaction takes place in the electrode will affect the shape of the response. Besides the faradaic current, there is another species is called "background current". From the voltammogram, we ca get certain types of information, such as analytic, kinetic, mechanistic and thermodynamics.

The main interference for the voltammetry technique is the dissolved oxygen. The oxygen is electrochemically active and very soluble in water. The oxygen can reduce in two steps depends the pH (Reference 51):

Step 1:
$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$ (acidic medium)

$O_2 + 2H_2O + 2e \rightleftharpoons H_2O_2 + 2[OH]^-$ (neutral or basic medium)

Step2:
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$ (acidic medium)

$H_2O_2 + 2e \rightleftharpoons 2[OH]^-$ (neutral or basic medium)

All these reduction process of oxygen can increase the background current. So, the oxygen should be removed from the sample. The removal of oxygen can be done by bubbling the electroinactive gases, such as nitrogen or argon into the solution.

1.6.2 DIFFERENTIAL PULSE POLAROGRAPHY (DPP)

In DPP, the slow continuous direct current (DC) is used to superimpose with a series of voltage pulses in a constant magnitude.

*PRINCIPLE:

The elements of interest in the solution are either oxidized or reduced at the Dropping Mercury Electrode (DME) by the potential scans. This reaction will produce a current peak at certain potential relative to the saturated calomel electrode. The peak height is measured and it is directly proportional to the concentration of the element.

The following Figure 1.2 (a) and (b) shows the common excitation signals for the DPP technique (Reference 52). The Figure 1.2 (a) is the result produce by superimposing a periodic pulse on a linear scan by using analogue instruments. Meanwhile, the Figure 1.2 (b) is the result produce by superimposing a pulse output with the staircase signal by using digital instruments.

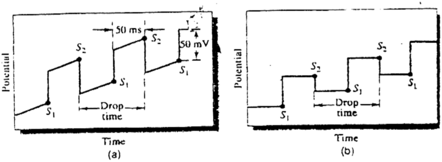

Figure 1.2: Excitation signals for DPP.
Source: Analysis of selected trace metals in water using Differential Pulse Polarography and Anodic Stripping Voltammetry (2000).

From the Figure 1.2 (b), the dc pulse is started at S_1 (16.7 ms) and is ended at S_2 (16.7 ms). The currents will be measured at this two points and the difference of these 2 currents per pulse (Δi) is recorded as the function of voltage. The differential curve will produce a peak, which is directly proportional to concentrations of the elements of interest, like the Figure 1.3 as below (Reference 52):

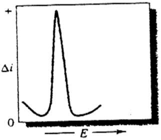

Figure1.3: Voltammogram for a differential pulse polarography experiment.
Source: Analysis of selected trace metals in water using Differential Pulse Polarography and Anodic Stripping Voltammetry (2000).

*ADVANTAGES:

- The DPP can produce the polarograms as the peak, but not the waves (classical polarography), so the sensitivity can be increased.
- The diffusion current can be increased by 7 to 10 times more than the classical polarography (Reference 53).
- The charging current can be minimized by the charge of the electrode is only changed by the difference in potential. So, the signal-to-noise ratio can be increased too.
- The concentration can be measured until 10^{-7} to 10^{-8} M (Reference 54).

1.6.3 DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY (DPSV)

DPSV is the most common stripping mode, which is used to compensate the charging current.

*PRINCIPLE:

The elements of interest will deposit on the surface of the Static Mercury Drop Electrode (SMDE) as complex with mercury under the certain potential for a specified deposition time. Then, the potential will strip the metal from the complex with mercury. This reaction will produce a current peak at specific potential relative to the saturated calomel electrode. The peak height is directly proportional to the concentration of the metal.

Like the DPP, the currents are measured at 2 times for the analysis. The first time is before the pulse is applied and the second one is just before the pulse termination. The difference of these 2 currents versus potential is plotted. This voltammogram will produce a peak-shaped response.

The total current is come from the faradaic (wanted) and charging (unwanted) currents. When we plot the faradaic and charging currents versus time, we found that the relationship $i_c \sim e^{-t/RC}{}_d$ and $i_f \sim t^{1/2}$, where t is the time, R is the resistance, C_d is the differential capacity, i_c and i_f are the charging and faradaic currents (Reference 52). These relationships show that the charging current decay faster than the faradaic current. So, the current will sample almost at the end of pulse, which is mostly the faradaic current.

The sensitivity of this technique can be increased by using the Hanging Mercury Drop Electrode (HMDE) until 1000-fold decrease in detection limit (Reference 55). According to Lund & Onshus, 1976 (Reference 56), the equation for the peak current of DPSV like the following:

$\Delta i_p = k\, n^2 r\, \Delta E\, v^{1/2}\, t_d\, C_b$
where i_p = peak current;
ΔE = pulse amplitude.

According to Batley and Florence, 1974 (Reference 57), the equation for the peak potential of DPSV is shown as below:

$$E_p = E_{1/2} - 1.1\, RT/nF - \Delta E/2$$

*ADVANTAGES:

- DPSV can improve the signal-to-noise ratio compare with DPP.
- DPSV can detect the lower concentration (ppb level) than the DPP.

*DISADVANTAGES:

- DPSV use the slow scan rate to increase the sensitivity, so the analysis time will be taken from 2 to 3 minutes.
- DPSV is more easily influence by the interferences of the surface-active materials.