UPPER AND
CHARACTERIS

)-CHEMICAL
R, A BASELINE

STUDY

MOHD AZIM BIN ABDUL HALIM

Report submitted in partial fulfilment of the requirements for
the award of Bachelor of Applied Science (Honours) in
Industrial Chemistry

Faculty of Industrial Science & Technology
UNIVERSITI MALAYSIA PAHANG

2012

ABSTRACT

A study is carried out on physico-chemical characteristics, anions and heavy metal concentration in several upper and lower sites of Pahang River. Jelai River, Tembeling River, Temerloh, Kampung Belimbing, Kampung Temai and Pekan were chosen as the sampling site. Sampling activities is done once in two weeks for three months period. The physical and chemical characteristics analyses includes six water parameters including pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), ammoniacal nitrogen and dissolved oxygen (DO). Common heavy metals such as lead, copper and cadmium are determined spectroscopically. Six anions are used as standard including fluoride, chloride, bromide, nitrate, phosphate and sulphate to determine the presence of anions in the samples. Phosphate is the only anion which is not detected in all the samples. In heavy metals analysis, only copper is detected in the samples while cadmium and lead are not detected. The values of BOD and COD are increasing due to increasing demand of oxygen as the river flows to the lower part before discharging to the sea. Tembeling River shows the lowest value of TSS as the river is less turbid than other five rivers. DO in all water samples are decreasing due to decreasing of oxygen solubility in the lower parts of Pahang River.

ABSTRAK

Satu kajian telah dilakukan berkaitan ciri-ciri fiziko-kimia, anion dan kepekatan logam berat di beberapa tempat di hulu dan hilir Sungai Pahang. Sungai Jelai, Sungai Tembeling, Temerloh, Kampung Belimbing, Kampung Temai dan Pekan telah dipilih sebagai lokasi pensampelan. Aktiviti pensampelan telah dilakukan sekali dalam dua minggu berterusan selama tiga bulan. Analisis ciri-ciri fizikal dan kimia termasuk enam parameter air iaitu pH, BOD, COD, jumlah pepejal terampai (TSS), NH_3-N dan oksigen terlarut. Logam berat termasuk kuprum, plumbum dan kadmium ditentukan melalui spektroskopi. Enam standard anion seperti fluoride, klorida, bromida, nitrat, fosfat dan sulfat telah digunakan untuk menentukan kehadiran anion dalam sampel air. Fosfat merupakan satu-satunya anion yang tidak dikesan dalam semua sampel air. Dalam analisis logam berat, hanya kuprum dikesan terdapat dalam sampel air manakala plumbum dan kadmium tidak dikesan. Nilai BOD dan COD bertambah kerana kehendak oksigen juga bertambah semasa sungai mengalir ke hilir sungai sebelum dilepaskan ke laut. Sungai Tembeling menunjukkan jumlah TSS yang paling sedikit kerana sungai ini kurang keruh berbanding lima sungai yang lain. Berlaku pengurangan DO dalam semua sampel air kerana berkurangnya larutan oksigen di hilir Sungai Pahang.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS & SYMBOLS

AAS	Atomic Absorption Spectroscopy
BOD	Biochemical Oxygen Demand Interim
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
GC-MS	Gas Chromatography Mass Spectrometry
IEC	Ion Exchange Chromatography
INWQS	National Water Quality Standards for Malaysia
ND	Not detected
TDS	Total Dissolved Solids
SS	Suspended Solids
TSS	Total Suspended Solids
UV-Vis	Ultraviolet-Visible Spectroscopy
WQI	Water Quality Index

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Surface water resources have played an important function throughout the history of human civilization. About one third of drinking water requirement of the world is obtained from surfaces sources like rivers, canals and lakes (Das and Acharya, 2003). Nevertheless, these sources seem to have been used for the discharge of industrial, agricultural and domestic wastes.

Pahang River, with the length of 459 km, it is the longest river on the Malay Peninsula. The river begins at the confluence of Jelai and Tembeling rivers on the Titiwangsa Mountains and drains into the South China Sea. Like any other parts in the world, Pahang River has played an important function for the people who live around it. Nowadays, Pahang River seems to have been used for the discharge of domestic and agricultural wastes.

1.2 PROBLEM STATEMENT

Over the past five decades, rapid development and conversions of forest land into urban land around Pahang River have led to water related problems such as solid wastes problems and degradation of water quality. As far as Pahang River is concerned, no researches have been done in determining physico-chemical characteristics, anions and heavy metals analysis of this river so far. In addition, industrial and agriculture is developing especially at Pekan which is the lower river of Pahang River. Domestic wastes may also contain in the water sample due to

dependence of people along Pahang River. These activities may resulting heavy metals contains in the water samples.

1.3 HYPOTHESIS

Based on physico-chemical characteristics, upper parts of Pahang River are suitable for water conservation while the lower parts of Pahang River needed conventional treatment. At the end of this proposal, it is expected that water samples from lower river of Pahang river will contain higher heavy metal compare from water samples from upper river. Anions will also present in water samples caused by natural occurrence and anthropogenic sources.

1.4 SCOPE OF STUDY

Along the 459 km river length, we choose six water sampling sites for the physical and chemical analysis, heavy metals and anions analysis from upper and lower river of Pahang river. In this project, the different parts of the river will be studied by means of measuring their physico-chemical characteristics. The overall results of six separate tests can be used to determine if a particular stretch of river is healthy. The WQI consists of six tests including pH, dissolved oxygen, biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammoniacal nitrogen and total suspended solids (TSS). The six resulting values are then added to arrive at an overall WQI. The highest score a body of water can achieve is 100.

1.5 OBJECTIVE

The objectives of this proposal are:

1. To study the physico-chemical characteristics of Pahang river.
2. To detect water quality changes in river water quality.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Water is the basic element of life; without it life would not exist. It is second most important resource for man, and yet it is taken for granted because water is everywhere and it flows freely when we turn on the tap. The usage of water increases as population grows until the demand sometimes overshoots the supply or availability (Kailasan, K, 2006).

Although the quantity of water on Earth is same all the time (same as in dinosaur age, 60 million year ago), the quality of water that is available has drastically changed. Every time we use water, we affect it in some way. Every watershed is affected by what takes place on the land. Once used, water flows out as quickly as it comes – down the drain and into our rivers. The gunk and grease that is flushed down into the drain unthinkingly every day will ultimately find their way to a nearby river. In other words, we are poisoning the very resource that gives us life. Therefore acquiring knowledge on ecosystem especially river basin will ensure efficient and effective management of rivers and water (Kailasan, K, 2006).

2.2 PAHANG RIVER

The Pahang River is located in the eastern part of Peninsular Malaysia. The maximum length and breadth of the catchment are 205 km and 236 km respectively. The river is about 440 km long and drains an area of 29300 km² of which 27000 km² lies within Pahang and 2300 km² is located in Negeri Sembilan. It is divided into the

Jelai and Tembeling rivers which meet at the confluence near Kuala Tembeling at about 304 km from the river mouth in the central north. Jelai River originates from the Central Mountain Range while Tembeling River has its origin at the Besar Mountain Range. The Pahang River system begins to flow in the south east and south directions from the north passing along such major towns as Kuala Lipis, Jerantut and Temerloh, finally turning eastward at Mengkarak in the central south flowing through Pekan town near the coast before discharging into the South China Sea.

The main highland areas situated within the basin are the Central Mountain Range along its western side and the East Coast Range in the north-east between Kuantan River and Tembeling River. These uplands areas are highly dissected and generally range from 1000 m to 1500m in the elevation with some peaks reaching more than 2000 m. The topography is less rugged towards the main drainage lines in the central part of the basin, where most of the land is below an elevation of 75 m and consists of low hills. The mountains areas are covered with virgin jungle while rubber, oil palm and some paddy are planted in the undulating terrains and lowlands. The eastern coastal plain is 30 to 40 km wide in the vicinity of the Pahang River. The coastal plain is flat and mostly swampy. Granite is found in the mountainous terrains in the east and west. The granitic soil in this region consists of fine to coarse sand and clay. Its depth seldom exceeds about half a metre except in areas where intense weathering has taken place and soil layer can be as deep as 9 m. In the central portion of the catchment lies a wide valley where quartize, shist, shale stone and limestone are the predominant rock types. This area, especially along the largest rivers such as Pahang River and Tembeling River is mainly covered with alluvium which varies from less than 1m to more than 18m in depth.

2.2.1 Sampling Site

As far as the sampling site is concerned, six sampling point was chosed including Jelai River, Tembeling River, Temerloh, Kampung Belimbing, Kampung Temai and finally in Pekan.

2.3 PARAMETERS

Water quality index (WQI) is a standard index to compare rivers and lakes in various parts of the country. WQI is one of the most widely used of all existing water quality procedures. The overall tests can be used to determine if a particular stretch of river is healthy. The WQI consist of six test including dissolved oxygen, pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammoniacal nitrogen and total suspended solids (TSS).

Dissolved oxygen or oxygen saturation in the environment generally refers to the amount of oxygen dissolved in the soil or bodies of water. Insufficient oxygen may occur in bodies of water such as ponds and rivers, tending to suppress the presence of aerobic organisms such as fish. Deoxygenation increases the relative population of anaerobic organisms such as plants and some bacteria, resulting in fish kills and other adverse events.

pH is a measure of the acidity or basicity of an aqueous solution. Pure water is said to be neutral, with a pH close to 7.0 at 25°C. Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are basic or alkaline.

Biochemical oxygen demand (BOD) is a chemical procedure for determining the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period.

Total suspended solids (TSS) and total dissolved solids (TDS) correspond to non-filterable and filterable residue respectively. Suspended matter consists of silt, clay, fine particles of organic and inorganic matter, soluble organic compounds, plankton and other microscopic organisms. Therefore, turbidity and transparency change seasonally according to biological activity in the water and heavy rainfall (Maitland, 1978). TSS prevents the penetration of sunlight into the water column and has a negative effect on the primary production of phytoplankton (Liu, 2005).

Ammoniacal nitrogen (NH_3-N), is a measure for the amount of ammonia, a toxic pollutant often found in landfill leachate (Aziz, H. A., 2004) and in waste products, such as sewage, liquid manure and other liquid organic waste products (Manios, T, et al, 2002).

Conductivity of the lakes generally is lower during the rainy seasons than dry season. It is due a dilution by rain and less evaporation during the rainy season, especially in lakes with short retention time (Zinabu, 2002).

Electrical conductivity (EC) is the measure of the ability of a solution to conduct an electric current. EC relates to total amount of dissolved ions in the water and has positive correlation with trophic gradient and phytoplankton abundance (Diaz et al., 2007). Sources of pollutants such as wastewater from sewage treatment plants, agricultural runoff and urban runoff increase ions in water, which leads to an increase of EC (Khan, N, 1990a). EC increases also during thermal stratification in hypolimnion due to an increase of decomposition.

2.4 HEAVY METALS

Natural water contaminant is a worldwide distributed problem which deserves large attention not only due to its environmental hazardous effects but also for the risks to the human health as well as the economical damages it produces. Between the wide diversity of pollutants affecting water resources heavy metals receive particular concern considering their strong toxicity even at low concentrations.

A heavy metal is a member of a loosely-defined subset of elements that exhibit metallic properties. Occurrence of heavy metal in water bodies can happen in two ways which is natural origin and anthropogenic. Natural occurrence of heavy metals in water bodies may be caused by the eroded minerals within sediments, leaching of ore deposits and volcanism extruded products. Iron, aluminium and tin are the examples of heavy metals which are caused by natural occurrence.

2.4.1 Copper

Copper is natural element which is widely distributed in soils, rocks and in rivers and the sea. People are most familiar with copper in its pure form as a reddish-brown metal, but in nature copper usually exists combined with other chemical elements in the form of copper compounds. Copper occurs naturally in all water sources and is therefore present in drinking water, so anybody using water for drinking, cooking, washing, bathing or going to the toilet, flushes water containing copper into the river. Copper is likely caused by industrial activities. Businesses such as textile printing works may discharge process waste containing copper directly into the river (Water UK, 2001).

2.4.2 Cadmium

Cadmium is a rare natural element which is widely distributed in the earth's crust in very small amounts. In its pure form, cadmium is a soft, bluish-white metal, but cadmium always exists in nature combined with other chemical elements in a range of chemical compounds. Cadmium is caused by domestic water supply and waste, industrial activities and runoff. Cadmium is always present in zinc metal as an impurity, so corrosion of zinc galvanised tanks used in water systems will also add trace amounts of cadmium to the water supply.

Cadmium occurs in very small quantities in many foods and so is present in all human wastes which are flushed down the toilet. Trace amounts of cadmium are present in detergents, bleach and toiletries such as shampoo, waste water from washing and bathing may therefore contain minute amounts of cadmium when it is flushed away. Cadmium compounds used in electroplating or dyeing and printing textiles may be discharged to the river by manufacturing companies. Particles of dust accumulating on roads and pavements may contain traces of cadmium derived from tyres, vehicle lubricants and exhaust fumes and from burning coal. These properties will be washed down the drains when it rains.

2.4.3 Lead

Lead is a natural element which is widely distributed in soils, rocks and in rivers and the sea. People are most familiar with lead as a dull grey metal used in water pipes and for roofing, but in nature lead usually exists combined with other chemical elements in the form of lead compounds. In industrial activities, any businesses using lead solders, working lead sheet or handling lead-acid batteries may allow particles containing lead or battery acid containing lead to get into the rivers. Lead pipes in older houses may leach small amounts of lead into the water supply and be flushed down into rivers.

2.5 ANIONS

Six anions had been chosen in this research including fluoride, chloride, bromide, nitrate, phosphate and sulphate. Anions in water samples are caused by natural occurrence and human interference. Natural occurrence is caused from interactions between water and rocks. The location of the river also can contribute to the presence of anions in water samples. Chloride, as an example, contains the highest concentration when the river is near to the sea.

Anthropogenic sources also can contribute to the presence of anions in water samples. Fertilizers runoff, domestic and industrial wastes are the main sources of anthropogenic. Bromide which is in fertilizers will flow with the rainfall into the river. Phosphate and sulphate are coming from detergents which are consumed by the people around the river. Meanwhile for industries, they use high volume of sulphate as sulphate is the most used in chemical, sulphuric acid is one of them.

CHAPTER 3

METHODOLOGY

3.1 EXPERIMENTAL DESIGN

The scope of environmental sampling can be illustrated by a sample's life with the following seven consecutive steps (Popek, 2003). Since these steps are irreversible, a mistake can be detrimental. These seven steps of a sample's life are as follows:

1. a sample is planned (conceived)
2. a sampling is identified
3. the sample collected (born)
4. the sample is transferred to the laboratory
5. the sample is analyzed
6. the sample expires and is discarded
7. the sample reincarnates as a chemical data point

3.1.1 Experimental Variables/Parameters

There are several parameters involved in this research including five water parameters of WQI which are pH value, dissolved oxygen (DO), biochemical oxygen demand (BOD) and total suspended solids. Chemical oxygen demand (COD) will also be measured in the analysis. Besides that, heavy metals and anions are also determined in the analysis.

3.1.2 Sampling Design & Methods

Samples were collected from upper and lower river along the Pahang River. Six locations are identified as the sampling site for the physical and chemical characteristic analysis. After the samples are collected, they were brought to the laboratory to be analyzed.

Samples that are not analyzed immediately must be protected from addition of contaminants, loss of determinants by sorption or other means, and any other unintended changes that affect the concentrations of determinants of interest. For this purpose, sample bottles should be chosen for long-term storage with no or as few changes to sample composition as possible. This is called sample pre-treatment. Three approaches which are refrigeration, use of proper sample container and addition of preserving chemicals are generally used to minimize such changes.

3.1.3 Data Collection (Measurement) Methods

For most types of analyses, samples must be transformed into a form that can be introduced into the analytical instrument, as only a few laboratory instruments can analyze soil and water directly. Depending on the type of analysis, this transformation may be achieved using one of the following preparation techniques:

1. Leaching of organic and inorganic compounds from soil, sediment or sludge with a buffered acidic solution
2. Digestion of soil and water for metal analysis
3. Extraction of organic compounds from soil and water with organic solvents
4. Dilution of concentrated waste products with organic solvents
5. Concentration of volatile organic compounds by the purge and trap technique
6. Distillations and digestion as part of inorganic analyses

3.1.4 Data Evaluation & Analysis Methods

From five parameters of WQI, pH and dissolved oxygen were analyzed on site while other four parameters, anions and heavy metals were done in laboratory. Analysis will be done for both upper and lower river samples in scope of WQI, heavy metals and anions analysis. The results for both upper and lower river then are compared using statistics such as minimum maximum and t test.

3.1.5 Research Plan

i.   **Flow sheet**
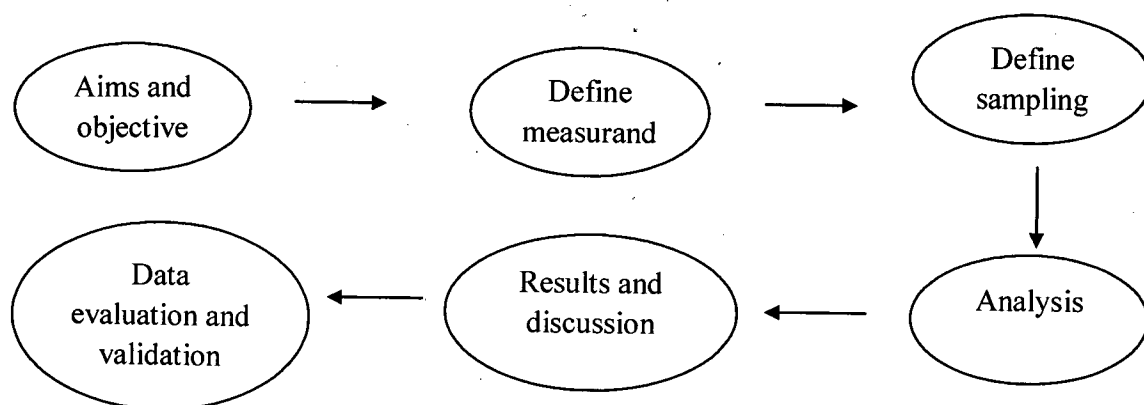
ii.   **Resources Deployment**

Once the samples is analyzed, a meeting were arranged with others students to compare the results obtained by them.

3.2 EQUIPMENTS & INSTRUMENTS

Table 3.1 Parameters and Measurement

Parameter	Measurement
Dissolved oxygen	DO meter
Biochemical oxygen demand	BOD meter
pH	DO meter
Temperature	DO meter
Total dissolved solids	DO meter
Anions	Ion Chromatography (IC)
Heavy metals	Atomic Absorption Spectroscopy (AAS)

3.3 MATERIALS

There were a number of chemical solutions involved in this research including potassium permanganate ($KMnO_4$), dichromate ($Cr_2O_7^{2-}$), distilled water, hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3), sodium hydroxide (NaOH), sodium thiosulfate ($Na_2S_2O_3$), sodium carbonate (Na_2CO_3) and potassium hydrogen phthalate ($KHC_8H_4O_4$).

3.4 PROCEDURES

3.4.1 Biochemical Oxygen Demand (BOD) (*Refer EPA Method 4051*)

Scope and application

1. The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges and allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD test are used for the development of engineering criteria for the design of wastewater treatment plants.

2. The BOD test is an empirical bioassay-type procedure which assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environment conditions of temperature, biological population water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to steam oxygen demands.

Summary of method

1. The sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

3.4.2 Chemical Oxygen Demand (*Refer EPA Method 410.1*)

1. Place several boiling stones in the reflux flask, followed by 50.0 mL of sample or an aliquot diluted to 50.0 mL and 1 g of $HgSO_4$. 5.0 mL of concentrated H_2SO_4 is added, and swirl until the mercuric sulphate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0

mL of 0.025 N $K_2Cr_2O_7$. Now add 70 mL of sulphuric acid-silver sulphate solution to the cooled reflux flask, again using slow addition with swirling motion. Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser.

2. Apply to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.

3. Allow the flask to cool and wash down the condenser with about 25 mL of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 mL Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 mL with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator to the solution and titrate the excess dichromate with 0.25 N ferrous ammonium sulphate solutions to the end point. The colour change will be sharp, changing from a blue-green to a reddish hue.

4. Blank- Simultaneously run a blank determination following the details given in but using low COD water in place of sample.

Calculation

$$COD, ppm = \frac{(A - B)N \times 8000}{S}$$

Where:

A = mL of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank

B = mL of $Fe(NH_4)_2(SO_4)_2$ solution required for of the sample

N = normality of $Fe(NH_4)_2(SO_4)_2$ solution

S = mL of sample used for the test

3.4.3 Total Suspended Solids (TDS) (*Refer EPA Method 160.2*)

1. Preparation of glass fibre filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

2. Preparation of evaporating dishes: If volatile residue is also to be measured heat the clean dish to 550 ± 50°C for one hour in a muffle furnace. If only filterable residue is to be measured heat the clean dish to 180 ± 2°C for one hour. Cool in desiccators and store until needed. Weigh immediately before use.

3. Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 mL to the funnel by means of 100 mL graduated cylinder. If total filterable residue is low, alarger volume may be filtered.

4. Filter the sample through the glass fiber filter, rinse with three 10 mL portions of distilled water and continue to apply vacuum for about 3 minutes atfer filteration is complete to remove as much water as possible.

5. Dry the evaporated sample for at least one hour at 180± 2°C. Cool in desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight is less than 0.5 mg.

Calculation

1. Calculate filterable residue as follows:

$$\text{Filterable residue, mg/L} = \frac{(A-B) \times 1000}{C}$$

Where:

A = weight of dried residue + dish in mg

B = weight of dish in mg

C = mL of filtered sample used in Ml

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 ANIONS

In anions analysis, the presences of six anions in water samples are determined. Fluoride, chloride, bromide, nitrate, phosphate and sulphate are used in this analysis. As sources of fresh water, rivers are generally low in fluoride, but many factors affect the concentration of fluoride in them such as temperature, pH and the nature and porosity of the rocks and soils over which they pass. Determination of Limit of Detection (LOD):

$$\text{LOD}: \frac{\text{Standard Concentration} \times 3(\text{Standard Deviation})}{\text{Mean}}$$

4.1.1 Fluoride (Standard solution of 1001 ± 2 ppm)

Table 4.1 Concentration (ppm) vs Peak Area (mV s^{-1}) of Fluoride Ion

Concentration of standard solution (ppm)	Peak Area (mV.S)
0	0
0.99	156.735
2.00	331.233
5.00	874.946