CHAPTER III

EXPERIMENTS AND ANALYTICAL TECHNIQUES

This chapter presents experimental methods and analytical techniques. Experimental methods can divide to 2 parts, adsorbent preparation and adsorption process. Analytical techniques are provided in detail for analysis both adsorbent section and liquid section.

3.1 Experimental methods

This section comprises of 2 parts. The first part is performed how to prepare adsorbents. The second part is conducted to the adsorption process.

3.1.1 Preparation of Adsorbents

Adsorbents used are defined to Silica adsorbent, Nickel oxide adsorbent, Chromium oxide adsorbent, Molybdenum oxide adsorbent, Ferric oxide adsorbent, Manganese oxide adsorbent and Mix metal oxide adsorbent. These adsorbents are prepared by wet impregnation on silica support with solution of nickel nitrate, chromium nitrate, ammoniummolybdate tetrahydrate, ferric nitrate, manganese nitrate for monometallic adsorbent, and mixture of those nitrate for Mix metal oxide adsorbent. Percent of metal loaded on support are at 2.5% with respect to support weight for each of monometallic adsorbent and 2.5% with respect to support weight by the ratio of metal composition in stainless-steel type 316.

Procedure of preparation adsorbents

The following procedure is subdivided into 2 steps, impregnation technique and calcination technique. The former is conducted to prepare support covered by metal compound as indicated above. The latter is performed to convert support with metal compound covering to metal oxide support.

Impregnation technique

Impregnation method involves the use of an excess of solution with respect to the pore volume of the support. The procedure is left for a certain time under stirring, filtered and dried. The impregnation method for this study is defined below.

Approximately 10 grams of silica support, identified as support, is added to 250 mL conical flask. The flask is then evacuated, kept at pressure under vacuum pressure and heated at $120^{\circ}C$ for 3 hours. After that, the flask is cooled to room temperature. Demineralization water is damply added into the flask and held at this condition for 30 minutes. Dissolve nickel nitrate 1.2388 grams, chromium nitrate 1.9239 grams, ferric nitrate 1.3552 grams, tetrahydrate molybdate 3.221 gram and manganese nitrate 1.2017 grams into 10 mL demineralization water to provide appropriate concentration solution, calculated to 2.5% by weight to support for monometallic adsorbent. In addition, dissolve nickel nitrate 1.72 gram, chromium nitrate 0.3463 gram, ferric nitrate 0.8673 gram, tetrahydrate molybdate 0.0644 gram and manganese nitrate 0.0240 gram into 10 mL demineralization water to provide appropriate concentration solution, calculated to 2.5% by weight to support for mixed-metallic adsorbent. The solution is added into the flask for covering the support's surface. The suspension is then stirred at 300 rpm and $80^{\circ}C$ until almost dry and kept at $120^{\circ}C$ about 12 hours.


Calcination technique

Calcination method has the purpose of decomposing the metal precursor with formation of an oxide and removal of gaseous products. Besides decomposition, during the calcination a sintering of the form oxide can occur. The calcination method for this study is defined below.

The metal compound impregnated on support is reduced to elemental form by hydrogen at flow rate of 5 ml/ 3 seconds with the increasing step about $5^{\circ}C$/ 5 minutes. Reduction temperature is kept at $400^{\circ}C$ for all adsorbent, including silica support, for 3 hours. The supported adsorbent is oxidized to metal oxide form by flowing dehumidify air at $400^{\circ}C$ and at flow rate of 5 ml/ 3 seconds for 3 hours. The adsorbent is cooled and kept in desiccator, respectively.

Apparatus for preparation adsorbent are shown in Figure 3.1.
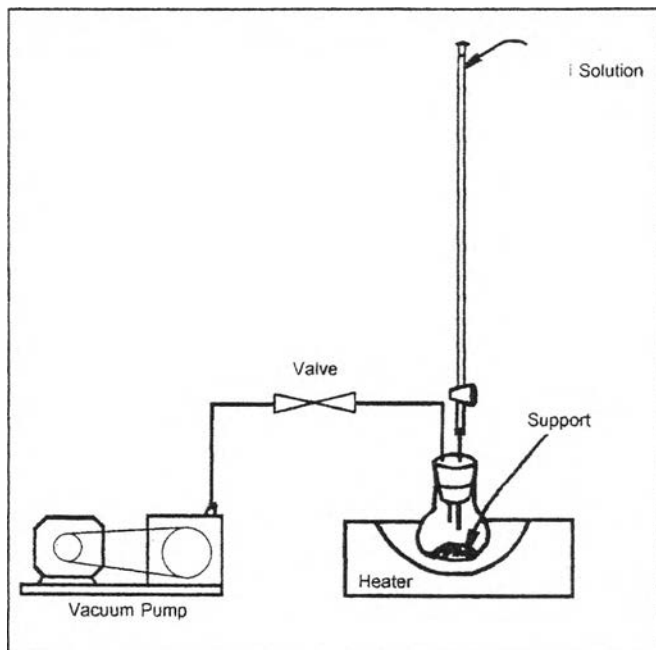
Impregnation
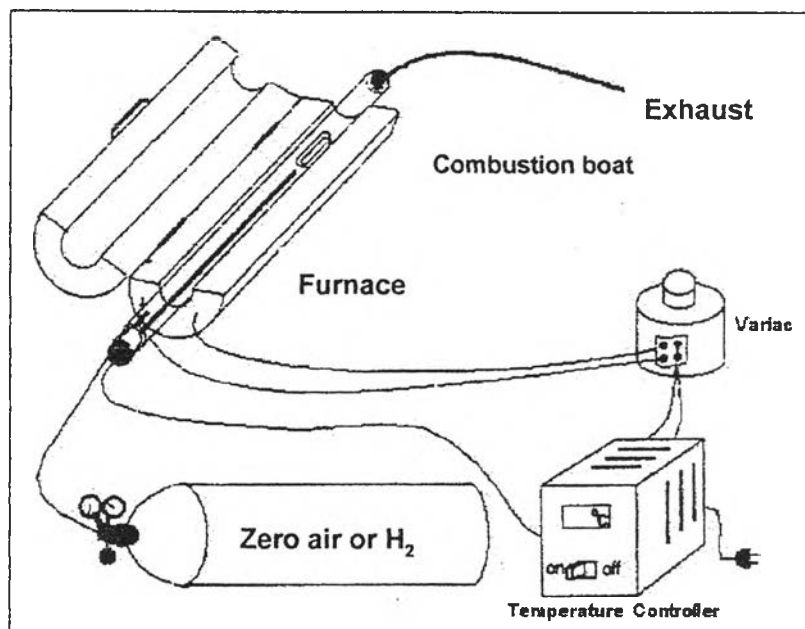
Calcination

Figure 3.1 Apparatus for adsorbent preparation

Characterization of adsorbent

Adsorbents are analyzed to specify some characteristics such as percent of metal loaded, form of metal loaded, surface area, pore volume and average pore size diameter. Techniques and procedure for adsorbent analyses is shown below. The analytical results are shown in chapter 4.

Form of metal oxide on support surface

X-ray diffraction technique can determine chemical composition on the surface of material both quantity and quality. The composition occurred on adsorbents are necessary to form sufficient crystalline content for diffracting of x-ray beam.

Adsorbents are prepared to form high content of metal so that x-ray diffraction can detect metal oxide form. The results and patterns of metal oxide adsorbents are shown in chapter 4.

Metal Content in Adsorbents

The standard test method, ASTM D1977-91, which is intended, for the determination of nickel and vanadium in catalysts is applied for determination of metal content in each adsorbent. In this experiment, the quantitative analysis of metal is carried out by use of Varian SpectrAA 300/400 atomic absorption spectroscopy.

This test method is a process by which adsorbent samples are decomposed with hydrofluoric and sulfuric acid. After complete volatilization of the acid and cooling, the sulfate salts are dilute to the appropriate concentration range for analysis by flame atomic absorption. The procedure for analyzing metal content is shown below. The results of metal contents in adsorbents are shown in chapter 4.

Procedure

Approximately 0.5 gram of adsorbent is weighed and transferred to a basin. The content of 10 mL of 48%sulfuric acid, 10 mL of concentrated nitric acid is added to each basin. The solution is evaporated by heated on the hot plate to near dryness.

After that, the basin is removed from the hot plate and cooled to ambient temperature. The content of 20 mL of 19% hydrochloric acid and 30 mL of 3% hydrogen

peroxide are added and the basin is covered with watch glass and return to hot plate. The solution is heated to boiling and continues to boil until the salts are dissolved. After dissolution is complete, the basin is removed from the hot plate and cooled to ambient temperature. The watch glass is washed in the basin and the solution is transferred to a 100 mL of volumetric flask. The solution is diluted with water to a mark and mixed. This diluted solution is quantitatively analyzed by flame AAS to determine the concentration of metal content in each sample.

Surface Area and Pore Volume

A Micromeritics ASAP 2000 is used to determine surface area, pore volume, and pore size distribution of each adsorbent. There are two operating steps, the degassing step and analysis step.

Fresh adsorbents are analyzed in order to study the variation of surface area, pore volume and also pore size distribution. The adsorbent first is heated and placed under vacuum to remove moisture and other contaminants. Temperature of degassing is carried out at $150^{\circ}C$ and vacuum pressure of 10 mmHg for 3 hours. After this step, the catalyst is weighed and the degassed sample is transferred from the degas port to the analysis port.

At the analysis port, the sample is analyzed at vacuum pressure of 15 mmHg and liquid nitrogen is used as coolant. The nitrogen gas is used as analysis gas. The volume of adsorbed nitrogen on sample will relate with relative pressure (P/P_0).

3.1.2 Adsorption process

This section explains procedure and apparatus of adsorption process. Feedstock containing mercury compound is contacted to acsorbent. Batch system is represented in the experiments.

Experimental procedure

The experiments are conducted in glassware to protect the system from mercury adsorption onto the wall. Adsorbents used are prepared by methods described above. Mercuric chloride and diphenylmercury are used as model compounds for inorganic and organic mercury, respectively. Toluene is used as a liquid hydrocarbon solvent. A schematic diagram for the system is shown in Figure 3.2.
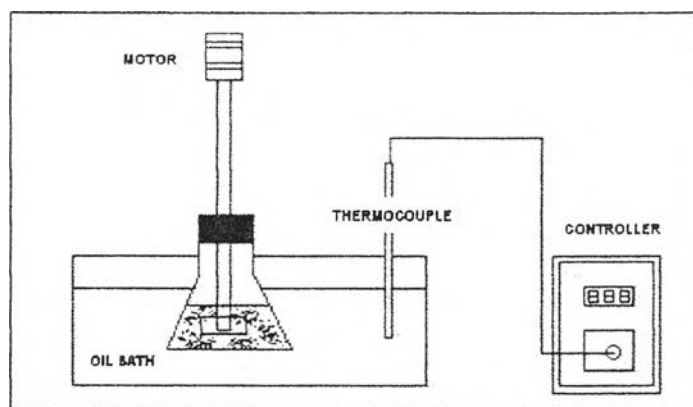
Figure 3.2 Schematic diagram of experimental apparatus

Approximately 100 g of toluene containing 0.1 µg of mercury are used as liquid feed and added into a 250mL-flask. Approximately 1 gram of adsorbent is pore-filled with exceeding fresh toluene, about 3 ml, and then added into the liquid feed. The flask is placed in an oil bath. The oil bath is set on the heating band that is connected to a temperature indicator and controlled temperature by using transformer. The suspension is stirred by a propeller connect to the speed-adjustable motor.

The system is operated at ambient pressure and at constant temperature of 30, 50 and 70°C. After 1 hour of operation time, the liquid product is filtered and prepared for analysis. Spent adsorbent obtained from each of experiment is kept and prepared for analysis too.

Analytical techniques

In each experiment, two types of samples are collected: liquid product samples and adsorbent used samples. Liquid product samples are analyzed for quantity of mercury remaining to monitor the removal efficiency of mercury for each type of adsorbent used. Adsorbent used samples are analyzed for mercury content, form of mercury compound via metal oxide, surface area and pore volume.

Liquid product characterization

Analytical methods for remaining mercury in liquid product include wet digestion and wet extraction. Wet methods oxidize mercury specie in the hydrocarbon liquid matrix to Hg^{2+} that separates to an aqueous phase. Wet digestive methods that use strong acid and heat in digestion bomb.

Digestions and extractions are treated with sodium borohydride to generate Hg^{0} and then sparge. The sparge gas is either sent directly to a detector then thermally evolved into an inert gas stream for detection. Technique and procedure in detail are shown as the following.

Mercury content by cold vapor Technique

Atomic Absorption Spectroscopy (AAS) is an effective method for determination of metal content in solution. There are many techniques using for determining metal content such as flame atomized, cold vapor and furnace graphite. Since mercury shows poor sensitivity when it is determined by conventional flame AAS, cold vapor technique is commonly used for detecting mercury content.

A characteristic of the cold vapor technique is that only inorganic mercury in the sample is measured. Organomercurials did not response to this technique. As a consequence, organic mercury compounds must be converted to inorganic mercury prior to determination. Otherwise, digestion of sample is necessary in order to obtain the ionic form and reduce analytical interference. The sample digestion used in this study is based on ASTM D-3223 that is a standard method for determining of total mercury in water. To generate mercury vapor, the VGA-76 that is a hydride generation unit, is attached with Varian SpectrAA 300/400. The detection limit of this technique is 0.2 ppb.

Procedure

100 grams of liquid sample is transferred to 250 mL flat round flask. 5 mL of concentrated sulfuric acid and concentrated nitric acid are added and mixed after each addition. Then, 15 mL of potassium permanganate solution is added to each flask. The mixture is stirred virgously for at least 15 minutes. After that, 8 mL of potassium persulfate is added to the flask. The flask at the top is equipped with a reflux condenser and

subsequently heated in oil bath at 95°C for approximately 2 hours. The flask is then removed from the oil bath and cooled to ambient temperature. The content about 6 mL of sodium chloride-hydroxylamine hydrochloride solution is added to the flask and the flask is shaken for a few seconds. The solution is transferred into 250 mL separation funnel and shaken virgously. After the water-phase is added to a 100 mL volumetric flask. The solution in the funnel is still washed with 10 mL of distillated or deionized water. This water is also added to the flask until the flask is filled up to the mark. Then the obtained aqueous solution is shaken and transferred to a sample bottle. The mercury content in the digest solution is determined and recorded.

3.1.3 Adsorbent used characterization

Adsorbent used samples are analyzed to identify mercury content by using method of determining metal content in adsorbents as indicated above. Although the surface area, pore volume and pore size distribution are analyzed by the given method above.

Mercury compound via metal oxide form is analyzed by x-ray diffraction technique. The detection limit is quite high for x-ray diffraction technique with the result that adsorbent has been repeatedly adsorbed by high concentration mercury compound to form high content of mercury compound via metal oxide form.

3.2 Experimental and Instrumental error

This chapter is also provided blank test experiments and results, instrumental error, error from digestion and error from repeatability. The experiments are studied mercury removal without using any adsorbents and attest to accept some errors as indicated before. The results are shown as the followings.

3.2.1 Blank test experiment

This part was studied removal of mercury on glassware without using of any adsorbents. The temperatures were varied at 30°C, 50°C and 70°C in the procedure and apparatus shown before. The initial concentration of mercury compounds was 1 ppm of mercuric chloride and diphenylmercury for each experiment. The results are shown in Figure 3.3 and Table 3.1.
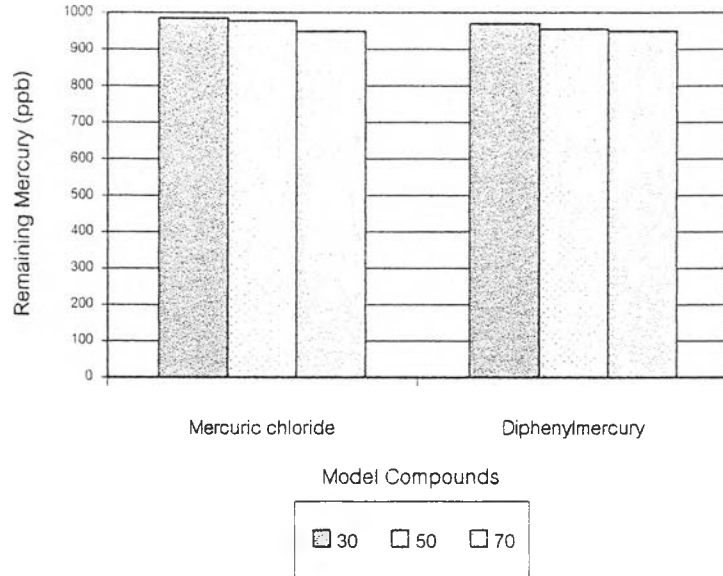
Figure 3.3 Remaining Mercury in the Study on Blank test at various Temperatures

Table 3.1 Percent loss of mercury compounds from feedstock at various

temperatures

| Mercury type	Average Percent Loss (%)		
	30 °C	50°C	70°C
Mercuric chloride	1.5	2.2	5
Diphenylmercury	2.9	4.5	5.1

The remaining concentration in product is shown in Figure 3.3 and Table 3.1. It is found that the final concentration is nearly the same as the initial, in range of 5% losses, for both mercuric chloride and diphenylmercury. It indicated that glassware can remove a few contents of mercury compounds and can be considered that glassware cannot adsorbed by mercury compounds.

Instrumental error

This part is claimed about error by analysis and error by experimental procedure. Analysis error by using AAs technique can be determined as error from repeatability. Furthermore, experimental procedure is provided error from digestion. The results are shown below.

Error from repeatability

The repeatability experiments were conducted to study a deviation of mercury compound removal after repeating experiments. The experiments were operated at various temperatures of $30\,^{\circ}C$, $50\,^{\circ}C$ and $70\,^{\circ}C$, and adsorbent used was silica support. In addition, both mercuric chloride and diphenylmercury, at initial concentration 1000 ppb, were represented in the experiments. The weight of adsorbent used was 1.0 gram for each experiment. The experiments were repeated for 5 times at the same temperature and mercury compound. Experimental results are illustrated in Figure 3.4 to 3.5. Average concentration and deviation data are shown in Table 3.2.
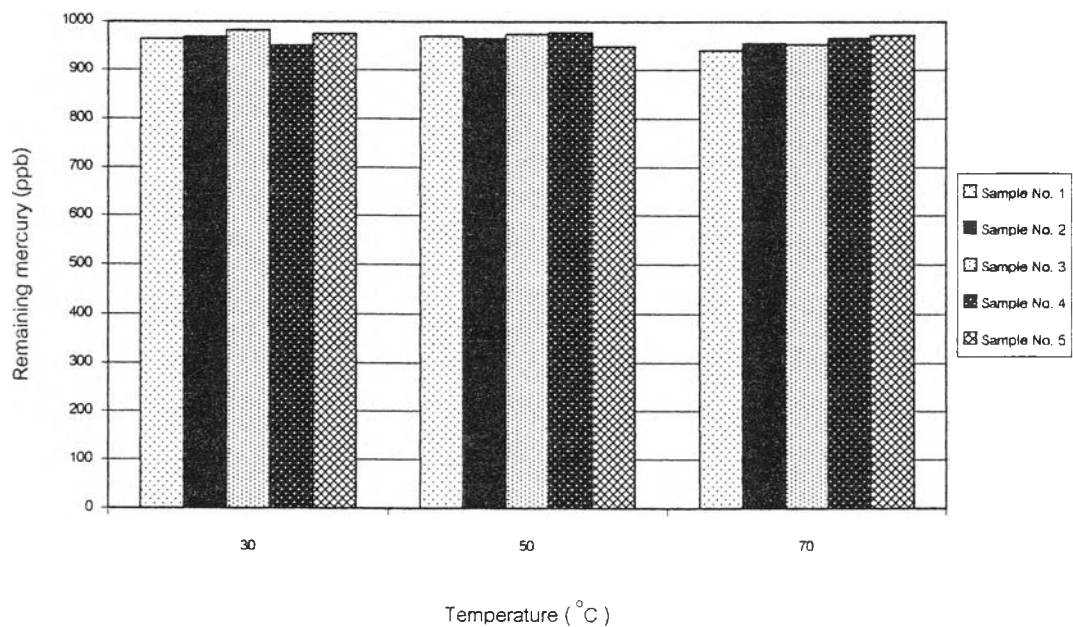
Figure 3.4 Remaining Mercury in study on Error from Repeatability of Mercuric Chloride at various Temperatures
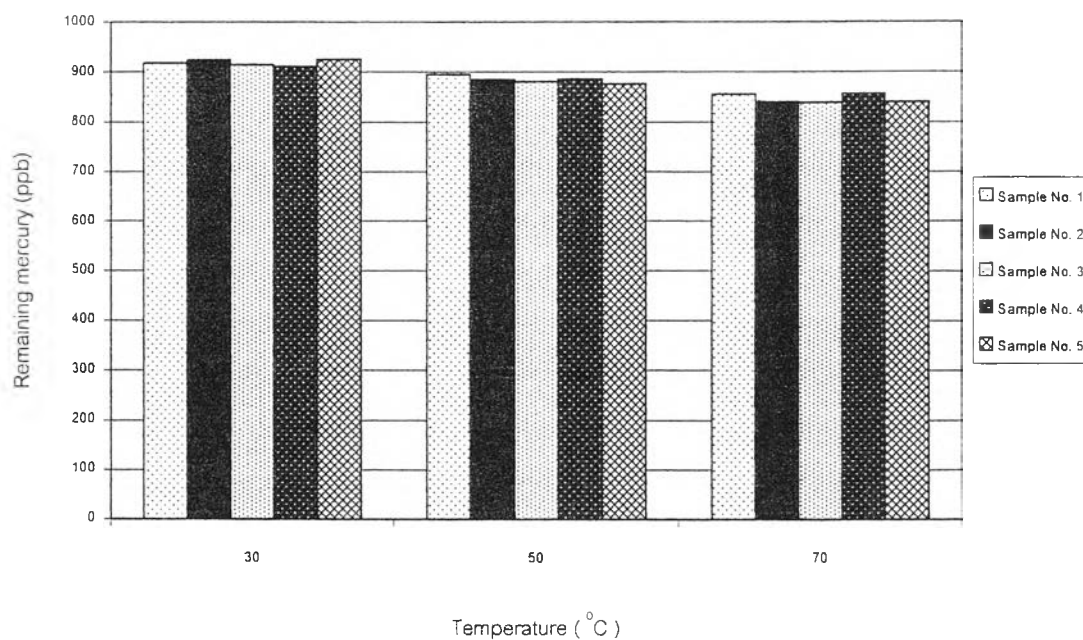
Figure 3.5 Remaining Mercury in study on Error from Repeatability of
Diphenylmercury at various Temperatures

Table 3.2 Average Value of Concentration and Percent of Deviation Range of
Mercury Compounds in repeatability study.

Mercury Type	Temperature (°C)	Sample Con. (ppb)					Average Value (ppb)	% of Deviation Range
Mercuric Chloride	30	964	968	982	950	975	968	-1.84 to +1.47
	50	970	965	974	977	948	967	-1.94 to +1.06
	70	940	955	953	966	972	957	-1.80 to +1.55
Diphenylmercury	30	918	925	914	911	926	919	-0.85 to +0.78
	50	895	885	881	886	876	885	-0.97 to +1.18
	70	855	840	839	857	840	846	-0.85 to +1.28

From results above, it certain that the value of remaining concentration for both of
mercury compounds seem nearly constant. Table 3.1 shows percent of deviation range that
is low, in range of 2% deviate, and can be neglected for both of mercury compounds.

Error from digestion

The experiments were conducted to study deviation from digestion error. The experiments were digestion of feedstock, both mercuric chloride and diphenylmercury, concentration about 1 ppm. The experiments were repeated at the same prepared-sample for 5 times. Experimental results are plotted in Figure 3.6. Deviation data are shown in Table 3.3.
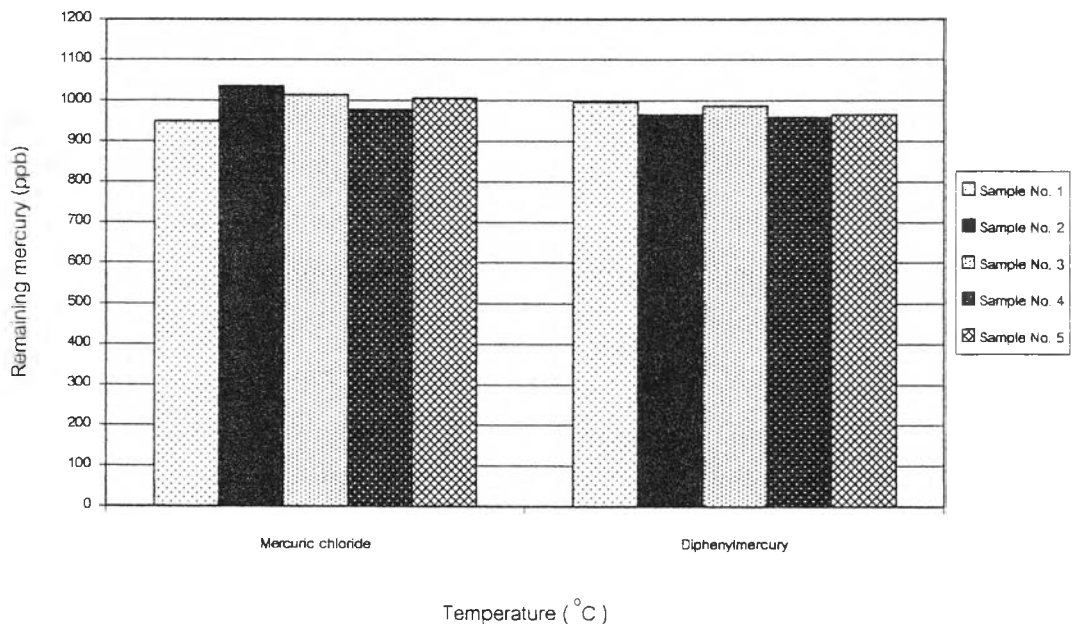

Figure 3.6 Concentration of Mercury Compounds in study on Error from digestion

Table 3.3 Average Value of Concentration and Percent of Deviation Range of Mercury Compounds in digestion study.

Mercury Type	Sample Conc. (ppb)					Average Conc. (ppb)	% of Deviation Range
Mercuric Chloride	950	1035	1014	977	1005	996	-4.64 to +3.89
Diphenylmercury	996	965	986	958	966	974	-1.66 to +1.21

From results above, it certain that the value of concentration after repeating digestion for both of mercury compounds seem nearly constant. Table 3.2 shows percent of deviation range that is in range of 5% and 2% deviate from average concentration of

mercuric chloride and diphenylmercury, respectively. That can consider to be neglected the error from digestion for both of mercury compounds.

Error from Analysis by AAs

The studies were conducted to consider the deviation from analysis error. The experiments are detecting the samples, both mercuric chloride and diphenylmercury, concentration of samples before dilution and digestion about 1 ppm. The analyses were repeated at the same prepared-sample for 5 times. Experimental results are plotted in Figure 3.6. Deviation data are shown in Table 3.2.
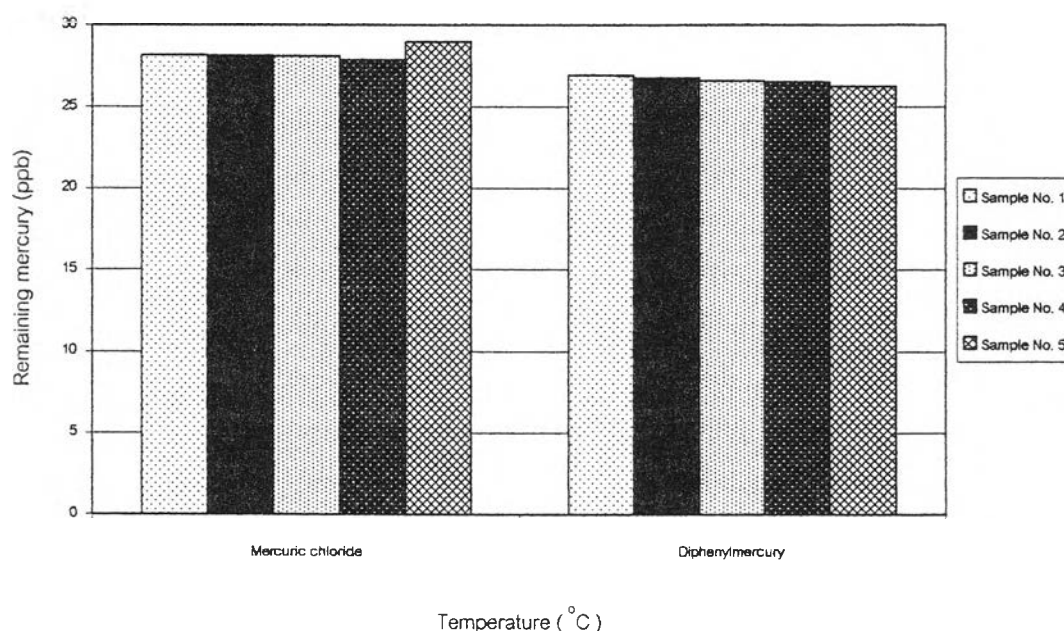

Figure 3.7 Samples concentration in study on Error from Analysis by AAs

Table 3.4 Average Value of Concentration and Percent of Deviation Range of Mercury Compounds in digestion study.

Mercury Type	Sample Conc. (ppb)					Average Value (ppb)	% of Deviation Range
Mercuric Chloride	28.154	28.121	28.096	27.883	28.964	28.044	-0.57 to +0.39
Diphenylmercury	26.930	26.779	26.601	26.544	26.293	26.629	-1.26 to +1.23

From results above, it certain that the value of concentration after repeating analysis for both of mercury compounds seem nearly constant. Table 3.2 shows percent of deviation range that is in range of 1% and 1.5 % deviate from average concentration of mercuric chloride and diphenylmercury, respectively. That can consider to be neglected the error from analysis by AAs for both of mercury compounds.