DETERMINATION OF METALS: NICKEL, CHROMIUM, COPPER, ZINC AND CADMIUM (Ni, Cr, Cu, Zn AND Cd) IN CRUDE OIL SAMPLES

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KUALA LUMPUR

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ABSTRACT

Samples of crude oil from two different oil fields, North Lukut and Penara, off shore of Terengganu, Malaysia were analyzed for trace metals: cadmium, chromium, copper, nickel and zinc. There were five crude oil samples from North Lukut oil field and three crude oil samples from Penara. All of the crude oil samples were from different wells and undergo sample preparation *via* wet digestion by using mixture of concentrated acids which were sulphuric acid, nitric acid and hydrochloric acid. The digested crude oil samples were then analyze by atomic absorption spectrometry (AAS) analysis. The results showed that the highest concentration of trace metals was zinc which read 1.562 ppm in North Lukut A-2 sample whereas the lowest concentration of trace metals is copper which was 0.095 ppm in Penara A-5L sample. It was reported that the concentration of the trace metals in the North Lukut and Penara crude oil samples were lower than the average concentration of crude oils as reported by Petroleum High Production Volume Testing Group by the American Petroleum Institute (API). However, despite their low concentration, the trace metals can still be detrimental to refinery operations and the environment and therefore, should be removed before refining.

ABSTRAK

Sampelminyakmentahdaripadaduamedanminyak yang berbezaiaitu North LukutdanPenara, iaitudaripelantarminyakluarpesisir Terengganu dianalisauntuklogamsurih: kadmium, kromium, kuprum, nikel and zink. Terdapatlimasampelminyakmentahdaripadamedanminyak North Lukutdanterdapattigasampeldaripadamedanminyak Penara. Semuasampelminyakmentahdiambildaripadatelaga yang berbezadanmenjalanipenyediaansampelmelaluipencernaanbasahdenganmenggunakancampuran acid pekatiaituasidsulfuric, asidnitrikdanasidhidroklorik. Sampelminyakmentah yang telahmenjalanipencernaanbasahakandianalisismelaluispektroskopipenyerapan atom. Keputusananalisismenunjukkankepekatanlogamsurih paling tinggiadalahzinkdi dalamsampelminyakmentah North Lukut A-2, iaitusebanyak 1.562 ppm manakalakepekatanlogamsurih paling rendahialahlogamkuprum di dalamsampelminyakmentahPenara A-5L iaitu 0.095 ppm. Kepekatanlogamsurih di dalamsampelminyakmentah North LukutdanPenaradilaporkanmempunyaikepekatan yang lebihrendahdaripadapuratakepekatanminyakmentahseperti yang dilaporkandalamlaporan American Petroleum Institute (API) dalamlaporannya, Petroleum High Production Volume Testing Group. Walaubagaimanapun, kepekatanlogamsurih yang rendahmasihbolehmemudaratkanoperasipenapisandanalamsekitar. Olehitu, logamsurihperludiekstrakkeluarsebelumoperasipenapisan.

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LIST OF ABBREVIATIONS

LPG	Liquefied petroleum gas
API	American Petroleum Institute
°API	API gravity
NAA	Neutron activation analysis
LOD	Limit of Detection
EDXRF	Energy dispersive X-ray fluorescence
GFAAS	Graphite furnace atomic absorption spectroscopy
ICP-OES	Induced coupled plasma optical emission spectroscopy
ICP-MS	Induced coupled plasma mass spectroscopy
AAS	Atomic absorption spectrometry
Pb	Lead
Hg	Mercury
PTFE	Polytetrafluoroethylene
W/O	Water-in-oil
O/W	Oil-in-water
Cd	Cadmium
Cr	Chromium
Cu	Copper
Ni	Nickel
Zn	Zinc
PCSB	PetronasCarigaliSdn. Bhd.
BPD	Barrels per day

HPV	High Production Volume
IARC	International Agency for Research on Cancer
OSHA	Occupational Safety and Health Act
H_2SO_4	Sulphuric acid
HNO_3	Nitric acid
HCl	Hydrochloric acid
FLAA	Flame atomic absorption spectrometry
AA	Atomic absorption
ppm	part per million
mL	mililitre
nm	nanometer
R^2	calibration curve correlation coefficient
X	mean
SD	Standard deviation
RSD	Relative standard deviation
abs	absorbance

CHAPTER 1

INTRODUCTION

Crude oil is a complex mixture of hydrocarbons that occur in the earth in liquid form. It is also known as petroleum. Crude oil is a fossil fuel, meaning that it was made naturally from decaying plants and animals, from the anaerobic process, millions of years ago. There are many theories of how crude oil is formed. There are also many factors taken into consideration when it comes to the formation of petroleum. In the formation of petroleum, it was agreed that crude oil has an organic origin and most crude oil are found in sedimentary rocks whereby in sediments has a highly organic content (T.W. Nelsom,1954). With time, the organic matter would then become crude oil at the (1) optimum pressure, (2) optimum temperature and (3) with microbial activity.

The general considerations that were taken in petroleum formationwere the environment, which indicates that most petroleum was formed in a marine type of environment. Temperature is also an important consideration. The temperature range for petroleum formation is from 75˚C until 200˚C. The temperature of petroleum formation starts with the temperature of the ocean water and it increases with the thickness of sediments deposits, meaning that the temperature of the organic matter will increase with the depth of the sediments, making it favourable for petroleum formation (T.W. Nelsom, 1954). Another factor is pressure. It was reported that the pressure that existsin oil-bearing formations today varies from a few hundred to about 7,500 lbs./sq.in.(T.W. Nelsom, 1954). The theory of origin of petroleum by bacteria is deduced due to the existence of methane-producing bacteria in sediments and also due to existence of small amounts of hydrocarbon as part of the bacteria cell substance. (T.W. Nelsom, 1954) There are also evidence of aerobic and anaerobic bacteria in abundance in sediments, however the number decrease with depth. (T.W. Nelsom, 1954).

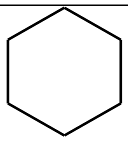
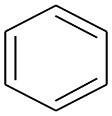
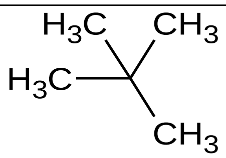
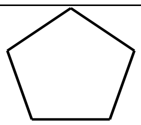
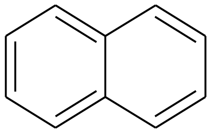
CHAPTER 2

LITERATURE REVIEW

2.1 Constituents of Crude Oil

Crude oils are mostly based on two elements, carbon and hydrogen with trace amounts of sulphur, nitrogen, oxygen and metallic constituents. The hydrocarbon in petroleum ranges from 1 to 50 or more carbon atoms (Rossinil, 1960). Crude oil contains three basic hydrocarbon chemical series, (1) paraffins, (2) naphthalenes or cycloparrafins, and (3) aromatics. The crude oils from different sources may not be completely identical (Evans et al., 1971). Crude oils vary in colour, from clear, yellow, green, brown to tar-black; and in viscosity, from liquid to almost solid.Also, the exact composition of elements in different location sources of crude oil differ accordingly.Table 2.1shows the structures of (1) paraffins, (2) naphthalenes or cycloparrafins, and (3) aromatics hydrocarbons in crude oil.

Table 2.1: The three types of hydrocarbon groups that petroleum are made of.

Paraffin Groups	**Cycloparaffin Groups**	**Aromatic Groups**
		
		

In the early findings of crude oil, it was identified as a substance that could burn and gave out great heat and light (Rossinil, 1960). Therefore, the crude oil has a good reputation as a good fuel.In the present day, crude oil is processed into fuel for domestic and industrial uses such as gasoline for cars, kerosene for aviation jetfuel and diesel oil for heavy machinery. Other thanfuel, the crude oil also provides feedstock for the petrochemical industry that yields products such as plastics, cosmetics and also medical supplies.

2.2 Crude Oil Processing

In the initial stages of crude oil processing technology, it was difficult to obtain hydrocarbon in crude oil in a high state of purity. In later years with the advancement of research, it was discovered that hydrocarbons in crude oil could be purified by the distillation process (Coates, 1906). Crude oil underwent three main unit processes before yielding as consumer products. The three main unit processes were (1) distillation, (2) cracking and (3) reforming and blending. In the distillation unit process, the batch of crude oil entered a distillation column whereby the components of crude oil would be separated according to their boiling point. A more detailed explanation on the crude oil distillation products was illustrated in figure 2.1.

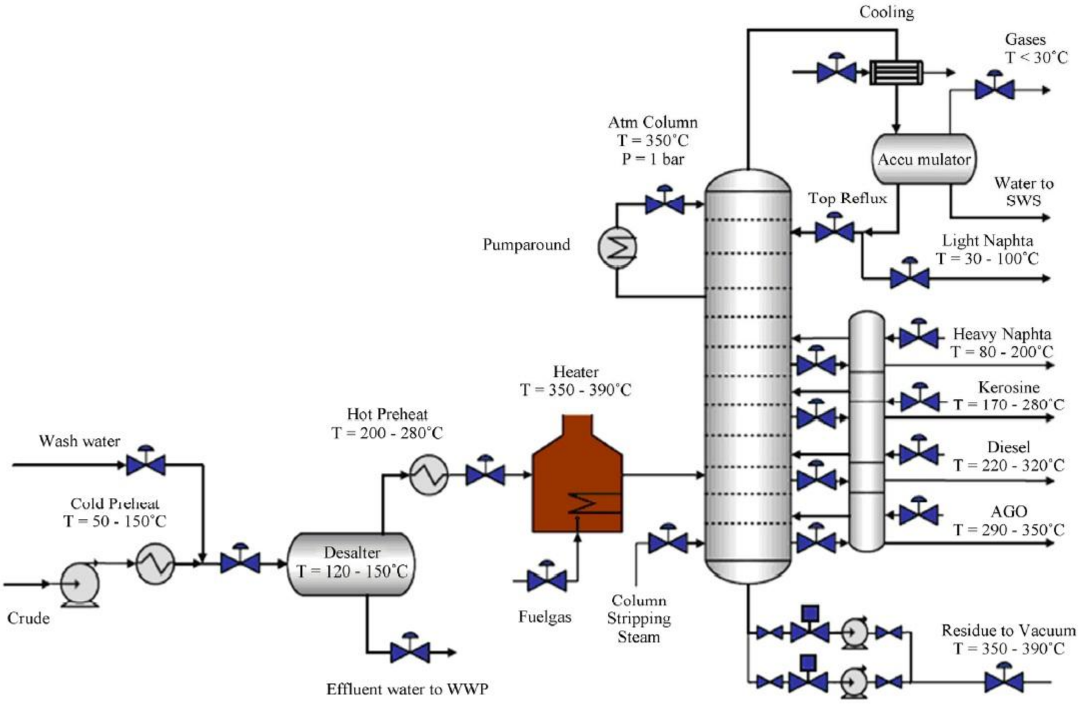


Figure 2.1: Process overview of crude oil distillation column (L. T. Popoola et al., 2012)

Crude oil entered the distillation column through a heater, and the crude oil was separated into fractions based on its boiling point. The fractions which rose high in the distillation column before condensing had a lower boiling point while the fractions which condensed in the lower trays had a higher boiling point. Products that were yielded from the distillation process include liquefied petroleum gas (LPG), naphtha, gasoline, kerosene, diesel, lubricant, heavy gas oil and coke. Among the products, only naphtha and heavy gas oil would continue the journey to the next unit process which was the cracking, reforming and blending. The other fractions need not undergo further processing and were ready to be distributed to consumers.

In the cracking process, the larger hydrocarbons were broken into smaller hydrocarbons. It could be done by thermal cracking which was by using heat or by catalytic cracking in the presence of catalyst. The catalysts used were usually zeolite, aluminiumhydrosilicate, bauxite and silica-alumina. They were used to speed up the cracking process. Due to the nature of the processing unit, the cracking process is very sensitive to the existence of metallic constituents as it might behave as catalyst and caused undesirable results.

Next, reforming and blending process. The reforming process involvedthe combination of the smaller hydrocarbons to form larger hydrocarbons. The blending process is the process of rearranging the hydrocarbons to make desired hydrocarbons. These blending processes include alkylation, isomerization and polymerization and are mainly done to produce high octane fuel which is more desirable to reduce knocking process in the engines. (Swanson *et al.*, 1953)

2.3 Metallic Constituents in Crude Oil

Crude oil contains traces of metallic constituents whichhas the ability to disrupt the cracking process. The information on the metallic constituents and their abundance in crude oil can also provide information on the origin, migration and maturation of the petroleum (Muhammad F. Ali *et al.*, 1983). Studies of the ratio of vanadium and nickel (V/Ni ratio) had been done to establish the correlation of the ratio with the age of host rock (Muhammad F. Ali *et al.*, 1983). Metallic constituents in crude oil should be reduced so that it would not interfere in the cracking process as metallic constituents caused catalytic poisoning. This was also done in order to avoid operational problems and to prevent contamination of products.

According to a study done by R.E. Donaldson*et al*., the nickel and vanadium in crude oil caused a 4.5 times increasement in coke yield and 7.9 times reduction in gasoline yield. The presence of vanadium in fuel led to ash deposits on turbine blades and caused severe corrosion in high temperature power generator (R.E. Donaldson *et. al*., 1961). Therefore, there is a need to detect metals in crude oil and also to remove it.

It was also reported that metals such as vanadium and nickel was undesirable in fuel in boilers and combustion turbines. In boiler fuels, the metals accelerate the common refractory materials and in combustion turbines the metals accelerate corrosion and eventually caused failures of the turbine blades. (Howard V. Hess *et al.*, 1959)

In a patent submitted by Howard V. Hess *et al.*, the invention described a method to remove trace metals from crude oil before it undergoes catalytic cracking. The crude oil was to be in contact with hydrogen under conditions so that at least a portion of the hydrogen is reacted with the component of the oil. This is to produce a crude oil that has an increased API gravity and thus, reduces trace metals content and leaves a solid residue that incorporates trace metals. The treated oil is separated from the solid-residue that contained the trace metals. The solid residue could then be further processed to recover metals that contained therein. (Howard V. Hess *et al.*, 1959)

Another study reported that the removal of asphaltene in crude oil causes a reduction of trace metals. The removal of asphaltene in crude oil also causes a decrease in the density and viscosity of the crude oil and the heavy metal contents of permeate is also reduced. (M. Ashtari*et al*., 2010)

2.4 Methods of determination of Metals in Crude Oil

There are many techniques which can be used in the determination of metals in crude oil. The methods of detection of crude oil can be divided into two; (1) direct analysis of the crude oil and (2) methods that required sample preparation. In the direct analysis of crude oil, neutron activation analysis (NAA) can be used for the determination of trace elements. The advantages of the NAA include the capability for multi element detection with very minimal sample preparation. However, this technique involves production of radioactive residue and in some elements, the limit of detection (LOD) obtained by NAA is not enough to produce necessary results (P.A. Mello *et al.*, 2012)

Another direct analysis technique for the determination of metallic elements in crude oil is energy dispersive X-ray fluorescence (EDXRF) spectrometry. As in all direct analysis techniques, the determination of metals using EDXRF requires minimum sample preparation, therefore making the analysis of oils to be more useful. However, several considerations should be taken when using EDXRF for the detection of metals in crude oil; firstly,the instrument parameters have to be determined. If the instrument parameters are properly set, the EDXRF can detect trace elements in part per million ranges in typical samples. Secondly is to determine the good matrix corrections; multielement analyses are very accurate with good matrix corrections programs. The use of an internal standard might also fit this purpose (H. Kubo & T. R. Wilderman, 1978).

Direct analysis of metals in crude oil could also be done using graphite furnace atomic absorption spectrometry (GFAAS). Among the advantages of the GFAAS technique isthat the sample pretreatment can be minimize or even be excluded in certain cases. The sample pretreatment depends on the nature of the crude oil. Less viscous crude oil can be analyzed directly whereas more viscous crude should be heated before analysis. Also, by using GFAAS, the risk of contamination is low as low amount of reagents are required. However, there are several disadvantages to GFAAS technique, namely time constraint whereby only one element can be determined in one run cycle. Also a hard optimization procedure such as pyrolysis, atomization temperature and the use of chemical modifier should be used (P.A. Mello *et al.*, 2012)

Normally, sample preparation is a critical step in atomic spectroscopy methods such as induced coupled plasma optical emission spectroscopy (ICP-OES), induced coupled plasma mass spectroscopy (ICP-MS) and atomic absorption spectrometry (AAS). The most common sample preparation for atomic spectroscopy methods is wet digestion. Crude oil samples are treated with a mixture of concentrated acids and then the digestion is filtered. If there is any presence of coke, the coke is burned off in a muffle furnace at 550°C prior to wet digestion(Muhammad F. Ali *et al.*, 1983). In open vessel wet digestion, the loss of volatile metallic species such as lead (Pb) and mercury (Hg) can be observed. This was due to the heating of the mixture andcan affect the accuracy of the analysis. Another disadvantage of open vessel wet digestion is the long analysis time, as the acid takes a while to digest all the organic material. To overcome these challenges, the use of a closed vessel such as polytetrafluoroethylene (PTFE), assisted by microwave is preferred (P.A. Mello *et al.*, 2012), A major consideration in using wet digestion methods is that the handling of concentrated acids has to be done with care.

An alternative method in the determination of metals in crude oil is direct introduction of samples into the atomic spectroscopy systems. However, this is often not possible and may prove to be difficult in most samples due to the high viscosity of the crude oil samples. In order to overcome this limitation, a crude oil emulsion or micro-emulsion can be formed. The crude oil emulsion is obtained by mixing and stirring two immiscible liquids until water-in-oil (W/O) emulsion or oil-in-water (O/W) emulsion is formed (P.A. Mello *et al*., 2012).A surfactant is added to the emulsion to stabilize it by reducing the high viscosity of the crude oil and to increase the polarity of the oil phase (Charles J. Lord, 1991).

Sample dilution in organic solvent can also be a consideration for sample preparation. Crude oil samples are diluted in an organic solvent such as xylene in respective ratio and were analysed by using ICP-MS. However, there are a few challenges by using this method such as (1) extinction of the plasma, (2) formation of polyatomic ions with carbon, (3) carbon deposits on interface and lens surface and (4) matrix effects due to introduction of solvent. To minimize the solvent effect, a micronebulizer is combined with desolvation systems.(P.A. Mello *et al.*, 2012)

Atomic absorption spectrometry (AAS) is one of the techniques used to measure the concentration of elements. Electrons of elements will absorb energy before they are promoted to another energy level (from ground state to excited state.) This technique works by measuring the wavelength that is absorbed by the element of interest. Different atoms absorb different characteristics of wavelength of lights. In AAS, there are three important components, a light source, an atomization chamber, and means of measuring the specific light absorbed. To analyse a crude oil sample, the lamp that is used must contain the analyte of interest. For instance, if the analyte of interest is nickel, a lamp called the hollow cathode lamp, containing nickel is used to emit light from excited nickel atoms. This light from excited nickel atoms contains the right range of wavelength that can be absorbed by any nickel atoms from the sample. In AAS, the sample is atomized and a beam of electromagnetic radiation is emitted from the excitation of nickel atoms in the hollow cathode lamp, before it is passed through the vapourized sample. The radiation is absorbed by the nickel atoms in the sample. The greater the number of nickel atoms which is in the vapour, the more the radiation is absorbed. The amount of light absorbed is proportional to the number of nickel atoms. In order to know the concentration of nickel in the oil samples, a standard calibration curve is constructed. A standard calibration curve was constructed by running several standard nickel solutions with known concentration under the same conditions as the unknown sample. The standard nickel solutions that wasrunned must be within the range of the sample whereby the analytes of interest exists. The calibration curve showed the concentration of standard against the absorbance of radiance. The amount of light radiation that the sample absorbs was compared with the calibration curve and this enabled the calculation of concentration of nickel in sample.

2.5 Problem statement of Metals in Crude Oil

There is a need to determine the trace metals in the crude oils quantitatively because of their importance in the geochemical characterization of its source and origin. However, there is a more weighted concern onthe presence of trace metals which exist in crude oil. Trace metals determination are of considerable importance, as they have deleterious effects on refinery operation and performance. They may corrode refinery equipments, poisonfoul catalysts and cause undesirable side reactions in refinery operations (Brandao*et al.*, 2007). Metal ions like vanadium, nickel, copper and iron, behave as catalyst poisons during catalytic cracking process in refining of crude oil. As metal ions are released in the environment during exploration, production and refining of crude oil, it is considered necessary to know the concentration of metals in the oils for meaningful impact assessment.

This study is aimed to determine the concentration on cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) in crude oil samples from the oil fields, North Lukut and Penara that is situated in the east coast of Peninsular Malaysia.

CHAPTER 3

MATERIALSAND METHODS

3.1 Crude Oil Samples

Crude oil samples were obtained from Penara and North Lukut oil fields and were provided by PetronasCarigaliSdnBhd (PCSB). Both of the oil fields were located offshore of Kerteh, Terengganu.

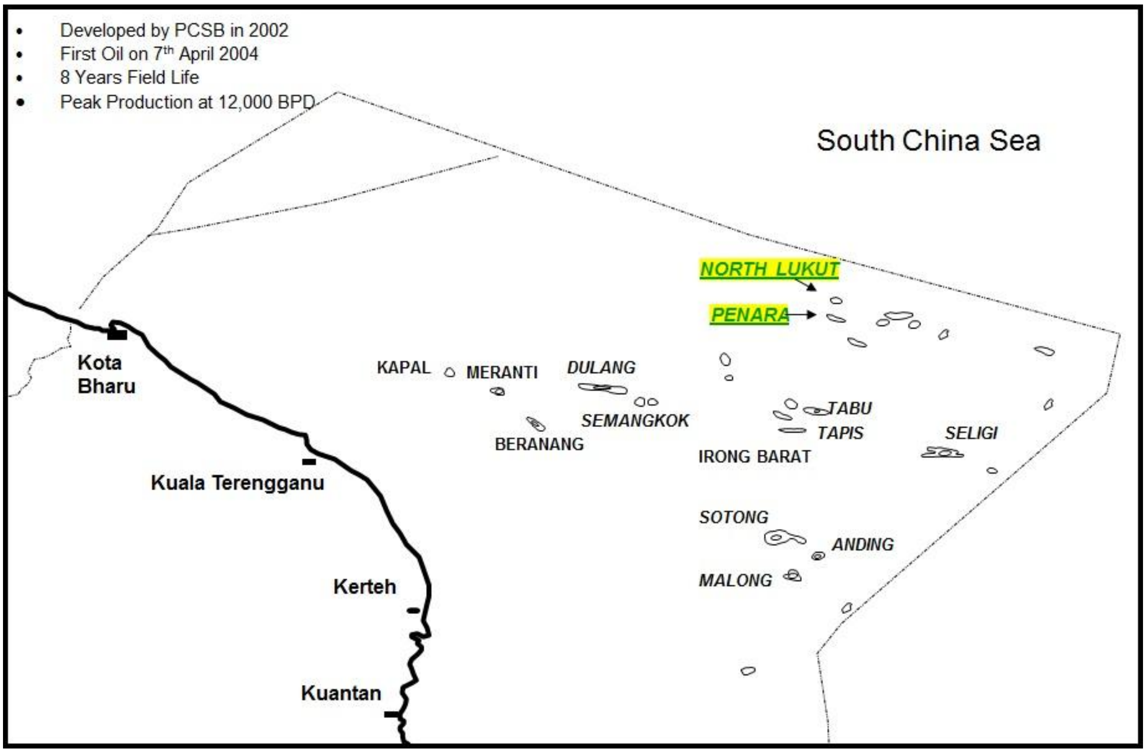


Figure 3.1: Location of the oil fields where the crude oil samples were obtained.

Crude oils are classified according to density, and they are usually designated light orheavy oils. The common measure for crude oil density is denoted by API gravity, which is the American Petroleum Institute and this is a way to express the relative masses of the crude oils. API gravity is a measure of how heavy or light the petroleum liquid is in comparison to water. Samples which have low viscosities, easily move through the formation (API, Petroleum HPV Testing Group, 2011). It is expected to result in good recovery factors and have less concentration of nickel. Table 3.1 exhibits the examples of properties of whole crude oils blends from prominent wells from all over the world. It can be observed that light crudes will have a higher API gravity which is about more than 33˚API; and less than 28˚API for heavy oil(Platt, 2003)

Table 3.1: Properties of whole crude oil (IARC, 1989; Mobil, 1997; OSHA, 1993 & International Crude Oil Market Handbook, 2004)

Crude Source	Parraffins % volume	Naphthenes % volume	Aromatics % volume	Sulfur % weight	API gravity (˚API)
Light Crudes					
Saudi Light	63	18	19	2.0	34
South Louisiana	79	45	19	0.0	35
Beryl	47	34	19	0.4	37
North Sea Brent	50	34	16	0.4	37
Lost Hills Light	50% aliphatics	-	50	0.9	>38
Mid-Range Crudes					
Venezuela Light	52	34	14	1.5	30
Kuwait	63	20	24	2.4	31
USA West Texas Sour	46	32	22	1.9	32
Heavy Crudes					
Prudhoe Bay	27	36	28	0.9	28
Saudi Heavy	60	20	15	2.1	28
Venezuela Heavy	35	53	12	2.3	24
Belridge Heavy	3% aliphatics	3% aliphatics	63	1.1	14

Some observations were made on the crude oil and the summary of the observations are given in the table 3.2:

Table 3.2: Samples of crude oil from North Lukutoil field

Sample	Produced Water	Observation (at normal room temperature)
A-3	< 1%	Liquid and some sediment
A-2	± 60%	Liquid and some emulsion
A-5	± 80%	Liquid and some emulsion
A-6	± 90%	Liquid, less emulsion and crystal clear water
A-1	± 95%	Liquid and less emulsion

Crude oil samples from North Lukut are mainly lighter oil, probably between 30-40°API gravity.

Table 3.3: Samples of crude oil from Penara oil field.

Sample	Produced Water	Observation (at normal room temp.)
A-2	non (evaporated)	Solid black wax
A-5L	non (evaporated)	Solid brownish wax
A-6L	non (evaporated)	Solid black wax

Crude oil samples from Penara Field are classified as medium heavy oil, probably between 20-30°API gravity. Crystallized condition (waxy) is observed at room temperature. The crude oil samples have high viscosity, thus it flows sluggishly through a reservoir. It is usually necessary to reduce the crude's viscosity by injecting steam, in order to attain commercial production rates.

3.2 Sample Preparation

Crude oil is a complex matrix consisting of different varying viscosities and mixed phases (organic, water and particulate matter) and therefore it is not considered an ideal matrix for analysis. The determination of the metals in crude oil requires pretreatment to the sample before it can be analyzed using spectroscopic methods.

3.2.1 Sample decomposition by wet digestion

Sulphuric acid (H_2SO_4), nitric acid (HNO_3) and hydrochloric acid (HCl) were used in the sample digestions. 1g of sample was weighed and then 2cm^3 of concentrated H_2SO_4 was added while the mixture was stirred. A strong exothermic reaction will occur. Then, the mixture was treated with 2cm^3 of concentrated $HNO_{3,}$ followed by 10cm^3 of concentrated HCl and heated until there was no evolution of gas. The mixture was filtered and the residue was washed with hot concentrated HCl. Next, the residual was transferred to a digestion flask, heated with 5cm^3 of concentrated HCl and filtered. The filtrate was heated at temperature below 1500°C to drive off excess HCl, then transferred to a 25cm^3 volumetric flask and made to the mark with distilled water.

The sample was brought to volume andanalyzed using the flame atomic absorption spectrometry (FLAA) for several metals such as cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn).

3.3 Atomic Absorption Instrumentation (AAS)

A Perkin Elmer AAnalyst 400Atomic Absorption Spectrometer (AAS) is used to determine the concentration of elements or trace metals in sample by relatively measuring the absorbance of the light of the elements. Metal atoms interact with radiation that has been pre-set to certain wavelength accordingly to the respective elements.In order to check on the specificityof the instrument, a default condition on primary wavelength check should be done before analyzing the samples. The concentration of the limit of detection (LOD) for each element is prepared accordingly from the AAS standard stock solution. During the setting-up procedure of the instrumentation, the absorption of the samples in AAS is set to 0.2 absorbance. This step is known as the concentration check. Next, the AAS should be programmed to read the concentration of the LOD of each element correctly. If the concentration of the LOD is not the same as the one recorded, some adjustments such as flow rate and size of orifice need to be done before proceeding to the analysis.

Table 3.4: Default condition of primary wavelength

Element	**Wavelength (nm)**	**Concentration check at 0.2 Absorbance**	
		LOD (ppm)	Linear to (ppm)
Cd	228.8	0.5	1.0

Cr	357.9	4.0	5.0
Cu	324.8	1.3	1.6
Ni	232.0	3.0	4.0
Zn	213.9	0.3	0.75

The concentration of the trace metals in crude oil can be determined using the calibration curve method. The values of the concentration of standard solutionsfor the calibration curve depend on the linearity range of each element.

3.4 Preparation of standard solutions

The standard stock solution used was of atomic absorption (AA) grade. The standard stock solution for trace metals is 1000 ppm for all types of metals. A series of working standardsolutions are prepared from the standard stock solution. Therefore, the required concentration for the standard analysis is prepared accordingly from the 1000 ppm standard stock solution.

Below is an example of calculation to prepare the standard solution for Copper at a concentration of 1.0 ppm in a 100 mL volumetric flask, the calculation is as below.

$$M_1V_1 = M_2V_2$$

$$(1000 \text{ ppm})(V_1) = (1.0 \text{ ppm})\ (100 \text{ mL})$$

$$V1 = 100\ \mu\text{L}$$

The concentration of standards wasprepared based on the linearity range and the limit of detection of each element by usingAAS.

Table 3.5: Concentration of standards used for each element.

Elements	**Concentration of Standard (ppm)**			
Cd	0.4	0.5	0.7	1.0
Cr	3.5	4.0	4.5	5.0
Cu	1.0	1.3	1.4	1.6
Ni	2.0	3.0	3.5	4.0
Zn	0.1	0.3	0.5	0.75

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Methods of Quantitative Analysis

There were a few methods which could be used in the quantitative analysis using spectroscopic methods, namely (1) calibration curve method, (2) standard addition method, and (3) internal standard method. The description of the calibration curve method will be discussed in the following sub topic. The standard addition method is usually conducted if there are possible matrix interference and if there is no ideal blank that is available. In standard addition method, one or more increments of a standard solution was added to the sample aliquots of the same size. Then, a plot of analytical signal versus either (1) volume of standard solution added or (2) concentration of analyte added was constructed. The concentration of the unknown sample wasobtained from the extrapolation of the graph to the intercept of the *x*-axis.

The internal standard method was usually done when there were variations in the analytical sample size, position or matrix limit in the precision of a technique. By using the internal standard method, certain types of noise that were produce by the instrument could be corrected. In this method, a calibration curve with the various standard solution concentrationsof the analytewere constructed. Then, a constant amount of an internal standard sample would be added to each of the solutions. The ratio of the signal for the standard solution against the signal of the internal standard versus the concentration of analyteswas constructed. The signal of the internal standard that was chosen should not interfere with the signal of the standard of the analyte. In normal circumstances, the signals of both standard and internal standard were separated by either wavelength or time.

4.2 Calibration Curve of Standard

The calibration curve method is the most common technique for quantitative analysis of metals such as cadmium, chromium, copper, nickel and zinc in AAS. For this analysis, a series of standard solution were prepared and analyzed using AAS spectrometer. Then, a graph of concentration versus absorbance was plotted. The signals from the samples were then used to calculate the concentration of the trace metals in samples.

When using the calibration curve method, a correlation analysis was used to measure the strength of association between two variables, which was the signal and the concentration of analyte. This wasknown as the linear relationship. This was usually done by the calibration curve correlation coefficient (R^2) which was basically the portion of the total variation in the dependant variable, the concentration of analyte, which was explained by the variation in the independent variable, signal of analyte. In the calibration curve method in analytical studies, the acceptable approximate values of

R^2 should be close to one and this indicates a perfect linear relationship between in the dependant variable and the independent variable.

In order to get a linear calibration curve, the correlation coefficient (R^2) for the calibration curve should be 0.99 or more. This indicates a linear graph. For each element in this analysis, the calibration curve coefficient has a R^2 value of more than 0.99. This can be observed infigure 4.1 until figure 4.5. Therefore, all of the calibration curve is considered linear and can be with confidence in the determination of concentration of trace metals in the crude oil samples.

The concentration of trace metals in crude oil is determined by the calibration curve, mainly because it is relative to the absorbance of the samples. There are a few parameters taken into consideration of a reliable analysis, namely (1) mean, (2) standard deviation and also (3) relative standard deviation. The mean is defined as the average values of the data used and is normally used to refer to one measure of the central tendency of either the probability distribution or the random variable. (Feller, 1950) The standard deviation (SD) shows how much variation or dispersion from the average exists (Bland, 1996). A low SD means that the values are distributed near to the mean or average value, thus indicating that it is precise whereas a high SD value means that the data is spread out over a large range of values. The relative standard deviation (RSD) is widely used in analytical chemistry to express the precision and repeatability of an assay.The precision of the data by AAS is being measured by the standard deviation (SD) and relative standard division (RSD). The RSD is a ratio between the standard deviation and the mean (YijieGao *et al*., 2013).

The formulas of both SD and RSD can be observed below:

Mean, $X = \sum \frac{Xi}{N}$ whereby,
X is the mean
N is the number of observation
$\sum X_i$ is the sum of all observation

Standard deviation, SD = $\sqrt{\frac{\sum(Xi - X)^2}{N}}$ whereby,
X_i is the observed value
X is the mean
N is the number of observation

Relative Standard Deviation, $RSD = \frac{SD}{X}\ X\ 100$ whereby,
SD is the standard deviation
X is the mean

An RSD value of less than 10 is considered precise in the measurement.

4.2.1 Determination of Cadmium (Cd) in Crude Oil Samples

For the element cadmium (Cd), the prepared concentration of the standards was 0.4 ppm, 0.5 ppm, 0.7 ppm and 1.0 ppm. As observed in figure 4.1, the correlation coefficient (R^2) is 0.9987 and this indicates a linear calibration graph. Thus, it is reliable to be used for the detection of cadmium in the crude oil samples.

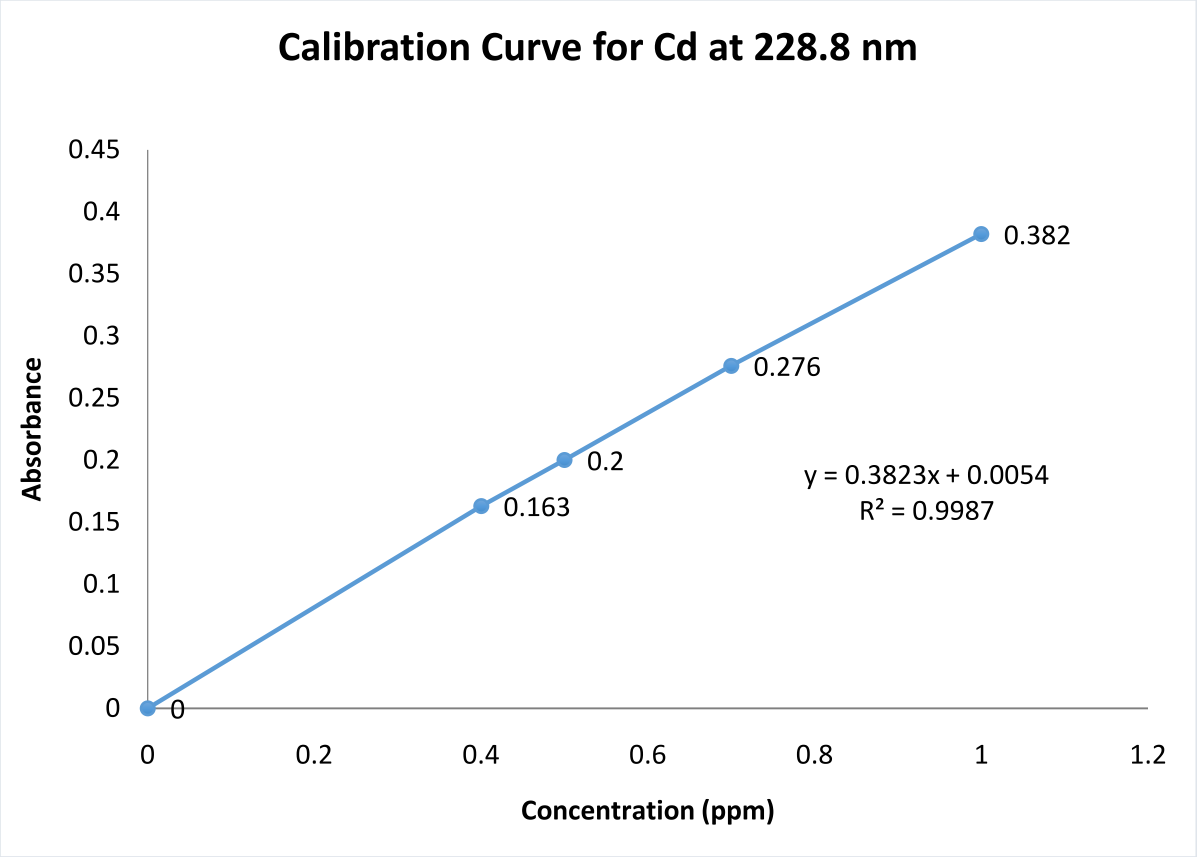


Figure 4.1: Calibration curve for cadmium at wavelength 228.8 nm.

Table 4.1: Concentration of cadmium in crude oil samples

Samples	Absorbance	Concentration (ppm)		
		Mean	SD	RSD
North Lukut A-1	0.057	0.145	0.000	0.197
North Lukut A-2	0.058	0.148	0.001	1.010
North Lukut A-3	0.058	0.149	0.001	0.726
North Lukut A-5	0.061	0.156	0.001	0.818
North Lukut A-6	0.059	0.152	0.002	1.396
Penara A-2	0.047	0.120	0.001	0.834
Penara A-5L	0.050	0.127	0.002	1.523
Penara A-6L	0.048	0.122	0.001	0.523

As observed in Table 4.1, the absorbance of cadmium for the crude oil samples was between 0.047 to 0.059 abs, which basically correlated to the concentration of cadmium in the crude oil samples. By using the calibration curve for cadmium, the concentration of cadmium in the crude oil samples were in a range of 0.12 ppm to 0.156 ppm. The RSD of the analysis was between 0.523 to 1.523, indicating that the results obtained were precise and also repeatable. It could be observed that the concentration of cadmium was lower in crude oils which were in solid form (Penara A-2L, Penara A-5L and Penara A-6L) in comparison to those which were in liquid form (North Lukut A-1, North Lukut A-2, North Lukut A-3, North Lukut A-5, North Lukut A-6). The results from the North Lukut and Penaracrude oil samples were found to have higher content of cadmium in comparison to the average cadmium concentration range for other reported crude oil samples, which were in the range of 0.003 ppm to 0.11 ppm (API, Petroleum HPV Testing Group, 2011).

4.2.2 Determination of chromium (Cr) in crude oil samples

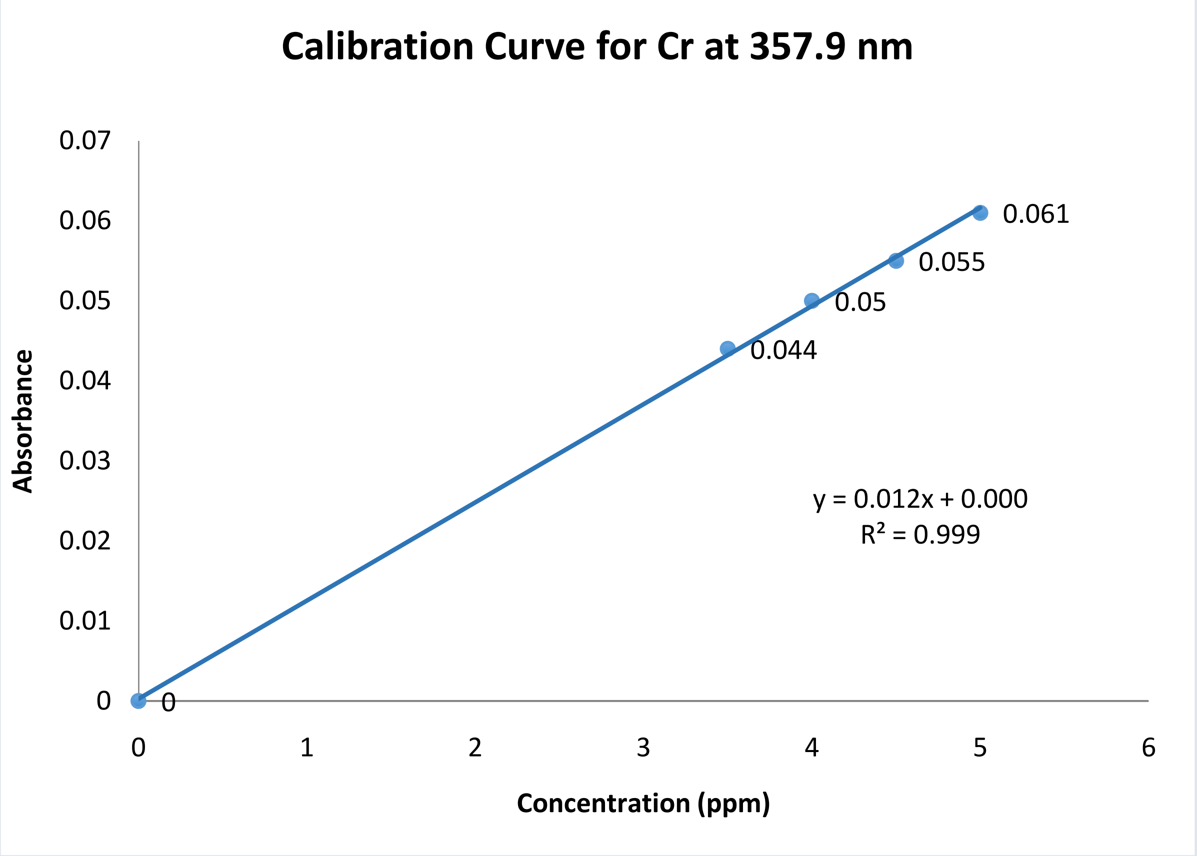


Figure 4.2: Calibration curve for chromium at wavelength 357.9 nm.

The series of standard concentration for chromium (Cr) were3.5 ppm, 4.0 ppm, 4.5 ppm and 5.0 ppm. As observed in figure 4.2, the correlation coefficient (R^2)was 0.9993. Thus, the standard curve was reliable to be used for the detection of chromium in the crude oil samples.

Table 4.2: Concentration of chromium in crude oil samples

Samples	Absorbance	Concentration (ppm)		
		Mean	SD	RSD
North Lukut A-1	0.010	0.799	0.035	4.386
North Lukut A-2	0.008	0.617	0.059	9.547
North Lukut A-3	0.008	0.640	0.011	1.767
North Lukut A-5	0.007	0.539	0.010	1.932
North Lukut A-6	0.008	0.608	0.017	2.871
Penara A-2	0.008	0.632	0.081	12.81
Penara A-5L	0.007	0.542	0.055	10.17
Penara A-6L	0.006	0.497	0.082	16.41

From table 4.2, the absorbance for chromium was between0.007 to 0.010 abs. The corresponding concentrations from the calibration curve of chromium were between in the range of 0.497 to 0.799 ppm. The concentration of chromium in the crude oil samples were in the same range as reported in Petroleum HPV Testing Group, which wass from 0.02 ppm to 1.43 ppm (API, Petroleum HPV Testing Group, 2011) However, the RSD values for the chromium analysis varied from 1.932 to 16.41. There were several samples which had RSD values of more than 10, which wasPenara A-2, Penara A-5L and Penara A-6L. The RSD values for these samples were 12.81, 10.17 and 16.41 respectively. Therefore, the analysis for these samples was considered not precise and could be repeated in order to improve its RSD values. There were a few factors on why the RSD of the analysis was high; (1) the uneven distribution of the analyte in the sample and (2) random errors that existed in the analysis or instrument (M. Valcárcel, 2000). However, the RSD values were not high in other trace metal analysis and this led to the uneven distribution of the analyte in sample as a suggested reason of the high RSD.

4.2.3 Determination of copper (Cu) in crude oil samples

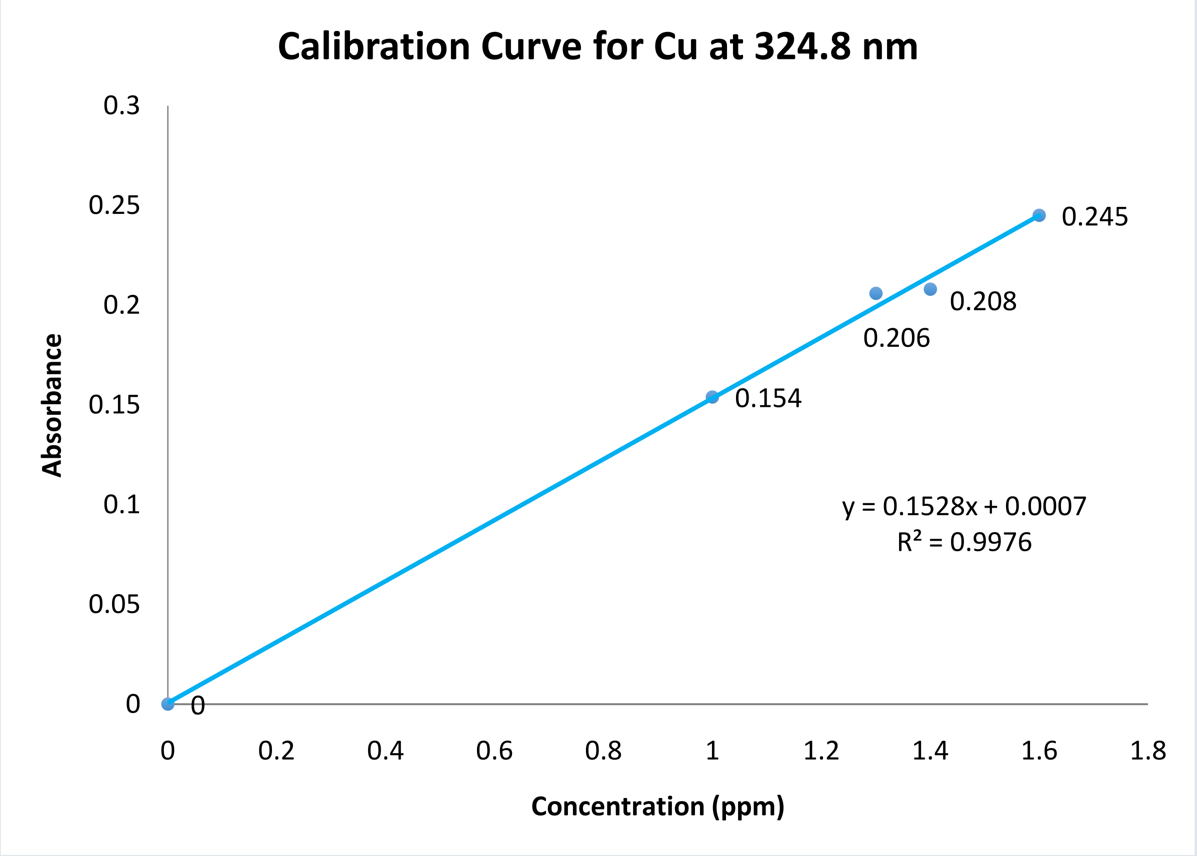


Figure 4.3: Calibration curve for copper at wavelength 324.8 nm.

For the element copper (Cu), the concentration range for the standard solutions were 1.0 ppm, 1.3 ppm, 1.4 ppm and 1.6 ppm. From figure 4.3, the calibration curve correlation coefficient (R^2) was 0.9976 and this indicated a linear calibration graph. Thus, it was reliable to be used for the detection of copper in the crude oil samples.

Table 4.3: Concentration of copper in crude oil samples

Samples	**Absorbance**	**Concentration (ppm)**		
		Mean	**SD**	**RSD**
North Lukut A-1	0.015	0.101	0.001	0.556
North Lukut A-2	0.016	0.107	0.001	0.799
North Lukut A-3	0.016	0.103	0.000	0.183
North Lukut A-5	0.026	0.172	0.001	0.765
North Lukut A-6	0.019	0.122	0.001	0.787
Penara A-2	0.015	0.097	0.000	0.216
Penara A-5L	0.015	0.095	0.000	0.249
Penara A-6L	0.017	0.112	0.000	0.204

From table 4.3,the range of absorbance for copper in crude oil samples was from 0.015 to 0.026 abs. From the analysis, the concentration of copper in crude oil samples ranged from 0.095 to 0.172 ppm. The RSD values for the concentration of copper in crude oil samples were within the range 0.183 to 0.799, indicating that the obtained results were reliable. The average copper concentration in crude oil samples was in the range of 0.01 ppm to 0.23 ppm (API, Petroleum HPV Testing Group, 2011). In this study, the copper concentration of the crude oil samples was within the range reported.

4.2.4 Determination of nickel (Ni) in crude oil samples

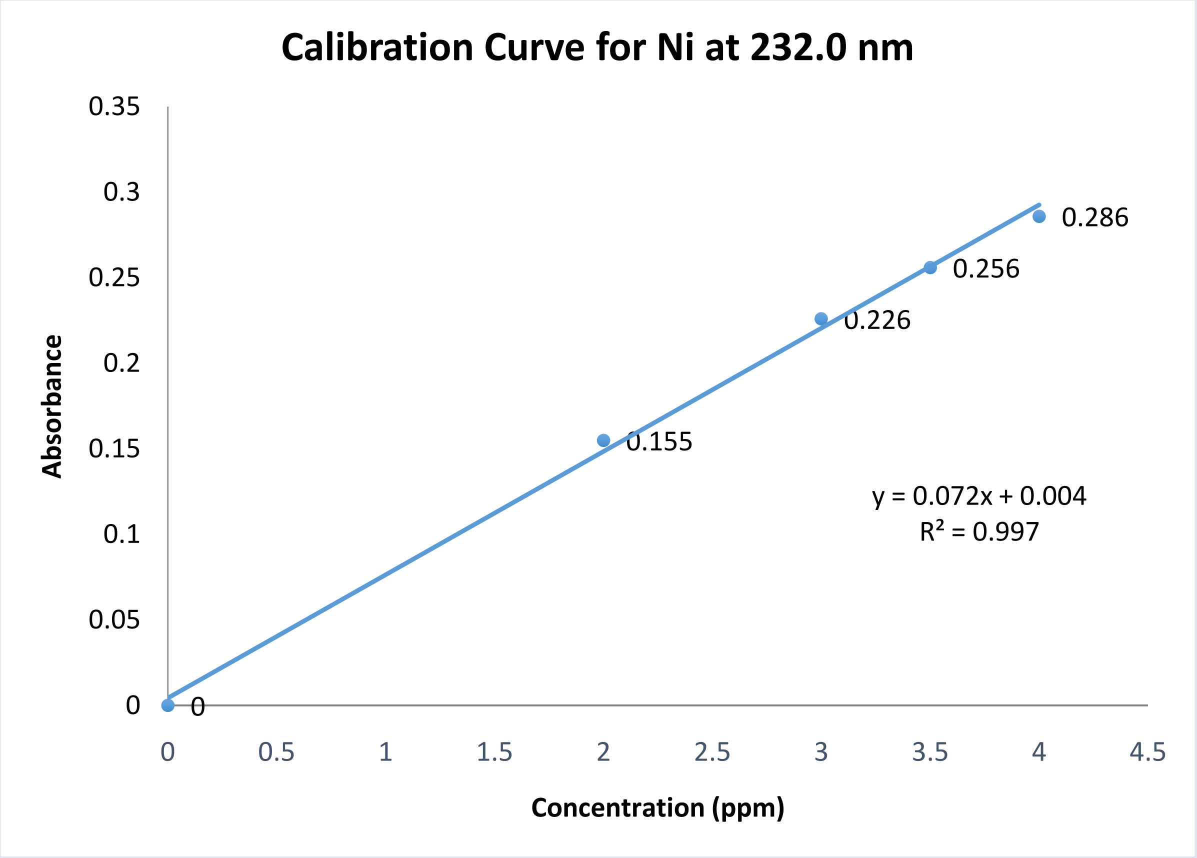


Figure 4.4: Calibration curve for nickel at wavelength 232.0 nm.

The concentration range for the nickel (Ni) standard solutions were 2.0 ppm, 3.0 ppm, 3.5 ppm and 4.0 ppm. The correlation coefficient (R^2) was 0.9974;which indicated a linear calibration graph.

Table 4.4: Concentration of nickel in crude oil samples

Samples	**Absorbance**	**Concentration (ppm)**		
		Mean	**SD**	**RSD**
North Lukut A-1	0.045	0.615	0.004	0.593
North Lukut A-2	0.047	0.642	0.002	0.283
North Lukut A-3	0.046	0.653	0.005	0.801
North Lukut A-5	0.046	0.630	0.006	0.941
North Lukut A-6	0.048	0.653	0.004	0.545
Penara A-2	0.040	0.544	0.003	0.641
Penara A-5L	0.040	0.545	0.004	0.730
Penara A-6L	0.040	0.536	0.009	1.673

As observed in table 4.4, the concentration of nickel in the crude oil samples could be considered as one of the highest amongthe analyzed elements. From the calibration curve, the concentration of nickel in the crude oil samples ranged from 0.536 to 0.653 ppm. Whereas the RSD valuesfor the determination of nickel in crude oil samples rangedfrom 0.283 to 1.673, which were less than 10, indicating that the results were acceptable. From the results, it could be observed that the concentration of nickel in liquid crude oil samples (North Lukut A-1, North Lukut A-2, North Lukut A-3, North Lukut A-5 and North Lukut A-6) were higher than the concentration of nickel in solid crude oil samples (Penara A-2, Penara A-5L, Penara A-6L). The average concentration of nickel in crude oil samples were reported to be in a range between 0.05 ppm to 93.0 ppm (API, Petroleum HPV Testing Group, 2011).From literature, nickel concentration is normally high in crude oilsand it usually used as an indicator for the source rock maturity. The vanadium to nickel ratio often is used as an indicator, whereby the decreasing of the ratio indicates the increasing of the source rock maturity (Mohammad F. Ali *et al.*,, 1983)

4.1.5 Determination of zinc (Zn) in crude oil samples

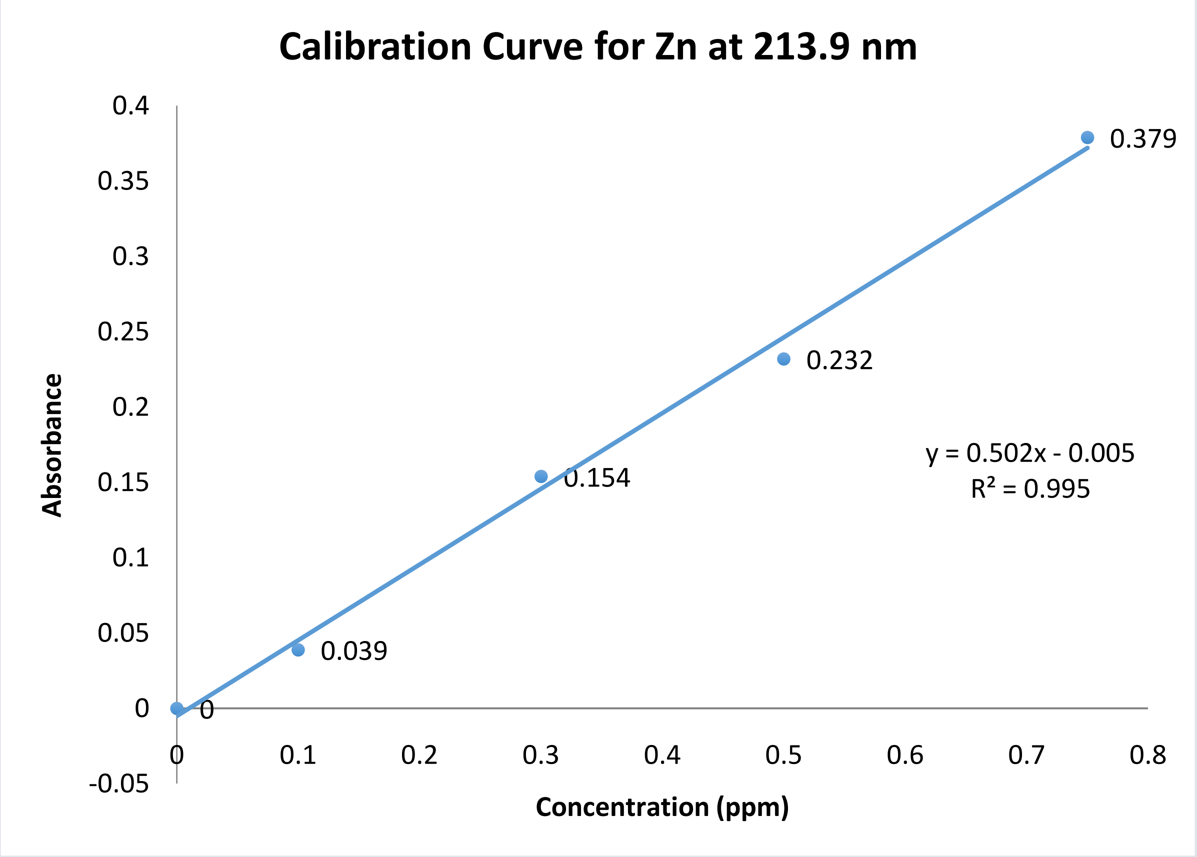


Figure 4.5: Calibration curve for zinc at wavelength 213.9 nm.

For the element zinc (Zn), the concentration of the standard solution were 0.1 ppm, 0.3 ppm, 0.5 ppm and 0.75 ppm. From figure 4.5, the obtainedcorrelation coefficient (R^2) for the calibration curve was 0.9959. Thus, the calibration curve could be usedreliably in the detection of zinc in the crude oil samples.

Table 4.5: Concentration of Zinc in crude oil samples

Samples	**Absorbance**	**Concentration (ppm)**		
		Mean	**SD**	**RSD**
North Lukut A-1	0.213	0.431	0.002	0.258
North Lukut A-2	0.199	0.403	0.001	0.135
North Lukut A-3	0.246	0.497	0.003	0.624
North Lukut A-5	0.773	1.562	0.01	0.657
North Lukut A-6	0.211	0.426	0.002	0.482
Penara A-2	0.217	0.439	0.002	0.479
Penara A-5L	0.144	0.291	0.008	2.756
Penara A-6L	0.339	0.685	0.001	0.189

From table 4.5, the concentration for zinc in crude oil samples ranged from 0.291 to 1.562 ppm,while the RSD value for the determination of zinc in crude oil samples ranged from 0.135 to 2.756, which was less than 10, indicating that the results were precise. The average zinc concentration in crude oil was between 0.58 ppm to 8.52 ppm (API, Petroleum HPV Testing Group, 2011). It can be observed that North Lukut A-5 had the highest zinc concentration. This could be due to the abundance of zinc in the source rock of the crude oil.

4.3 Overall trace metals concentration in crude oil samples

The overall results indicates that the element with the highest concentration in the crude oil samples is zinc which is in the range of 0.291 to 1.562 ppm, followed by nickel which is at a range between 0.536 to 0.653 ppm. This sequence is followed by the concentration of chromium,which is in the range of 0.467 to 0.799 ppm, while the concentration of cadmium is in the range of 0.120to 0.156 ppm. The lowest concentration of elements in the crude oil samples is copper which is in the range of 0.095 to 0.172 ppm.

For all crude oil samples, the trace metals should be removed so that the concentration of trace metals should be at the barest minimum level which is below 0.01 ppm (API, Petroleum HPV Testing Group, 2011). This is important so that the trace metals in crude oil will not cause further catalyst poisoning in some refinery unit process; for example, the cracking process that uses catalysts such as platinum and zeolites. Trace metals such as cadmium, chromium, copper, nickel and zinc can cause (1) toxic pollutants, (2) affect refinery equipment and (3) alter selectivity and activity in cracking actions (Muhammad N Tijjani, 2013). The presence of the metallic constituents in the crude oil maybe due to a few factors; (1) to emulsify sub-surface waters, (2) to a true solution of the minerals in the oil or (3) to form chemical compounds between the metals and the organic constituents of the oil (William B. Shirey, 1931).

The presence of metallic constituents is also connected to the difference in (1) geological activity of the rocks, (2) the source rock type, (3) depositional and sedimentation environment and (4) the maturation or the age of the rock (Akinlua*et al.*, 2007). There is a need to know the metal contents and concentration in the crude oil sample as this is important in designing the metal removing process and evaluate its effectiveness (Muhammad N. Tijjani*et al.*, 2013)

CHAPTER 5

CONCLUSION

The determination of trace metals in crude oil samples from North Lukut and Penara was conducted by using atomic absorption spectrometry (AAS). The trace metals that were determined were cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn). The concentration of the trace metals in the crude oil samples were determined by the calibration curve method, whereby the calibration curve correlation coefficient (R^2) for all elements were more than 0.99 which indicated that the graph was linear and reliable for quantitative analysis.

The concentration of the metallic constituents varied and did not depend on the API of the crude oil samples. The highest concentration of trace metals was zinc which read 1.562 ppm in North Lukut A-2 sample whereas the lowest concentration of trace metals is copper which was 0.095 ppm in Penara A-5L sample. The results obtained showed that both the oil field North Lukut and Penara had low metals contents in comparison to the average trace metal concentration as reported in Petroleum High Production Volume Testing Group by the American Petroleum Institute. However, after the determination of the trace metals in crude oil sample, measures need to be taken for the removal of the trace metals as it hada devastating environmental and processing aftermath.

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APPENDICES

Figure 1:Crude oil samples,North Lukut A-1.Figure 2:Crude oil samples,North Lukut A-2

Figure 3: Crude oil samples, North Lukut A-3. Figure 4: Crude oil samples, North Lukut A-5.

Figure 5: Crude oil samples, North Lukut A-6.Figure 6: Crude oil samples, Penara A-2.

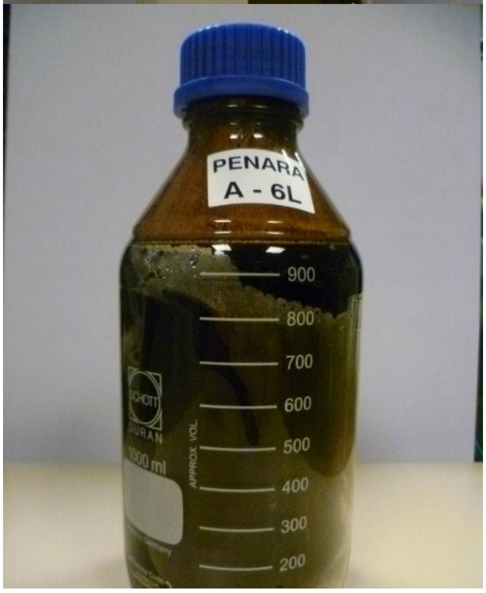
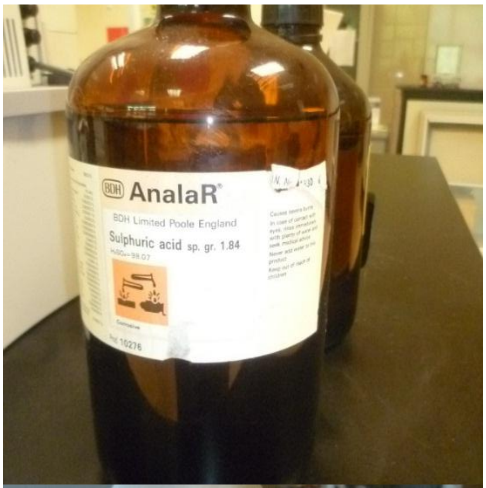


Figure 7: Crude oil samples, Penara A-5L.Figure 8: Crude oil samples, Penara A-6L.



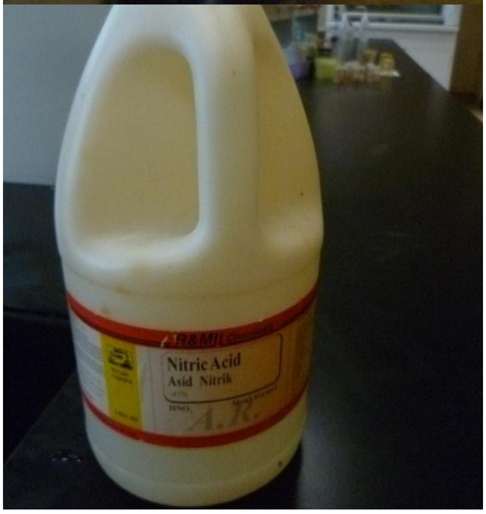


Figure 10: Nitric acid (HNO_3) that was used for wet digestion.

Figure 9: Sulphuric acid (H_2SO_4) that was used for wet digestion.

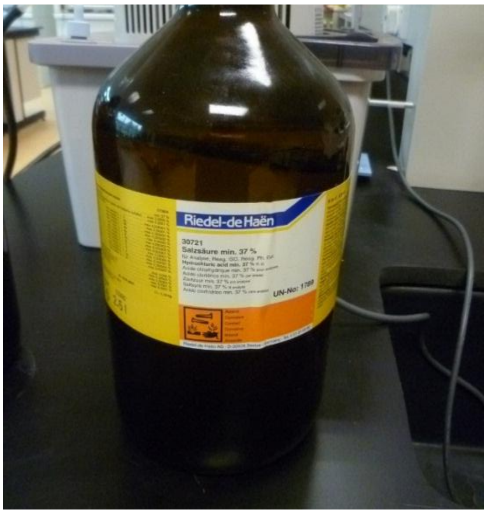


Figure 11: Hydrochloric acid (HCl) that was used for wet digestion.

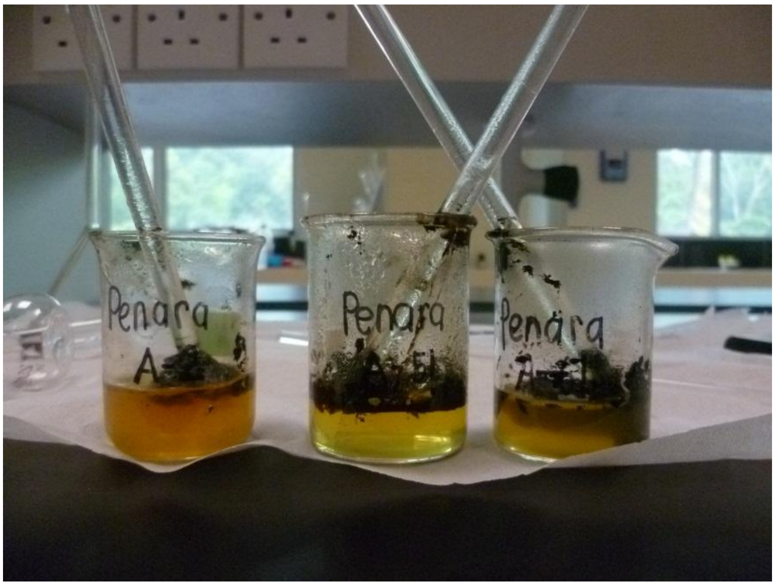


Figure 12: Sample preparation of the crude oil samples.

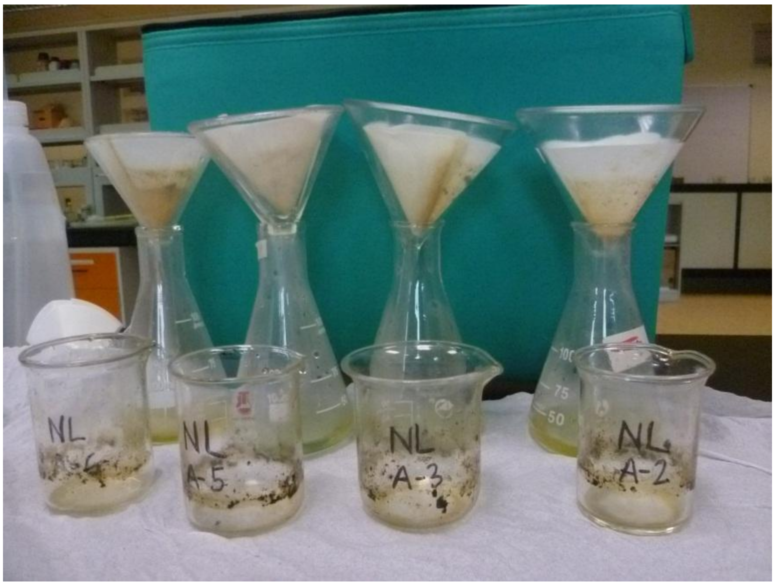


Figure 13: Samples that were being filtered.

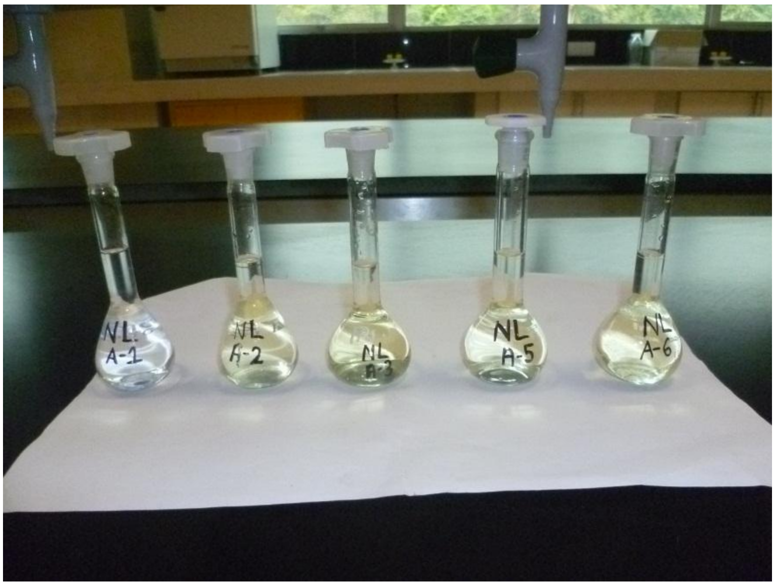


Figure 14: Crude oil samples (from North Lukut oil field) that had already been digested and ready for AAS analysis

Figure 15: Crude oil samples (from Penara oil field) that had already been digested and ready for AAS analysis

Figure 16: A Perkin Elmer AAnalyst 400Atomic Absorption Spectrometer (AAS) that was used for the determination of trace metals in the crude oil samples.

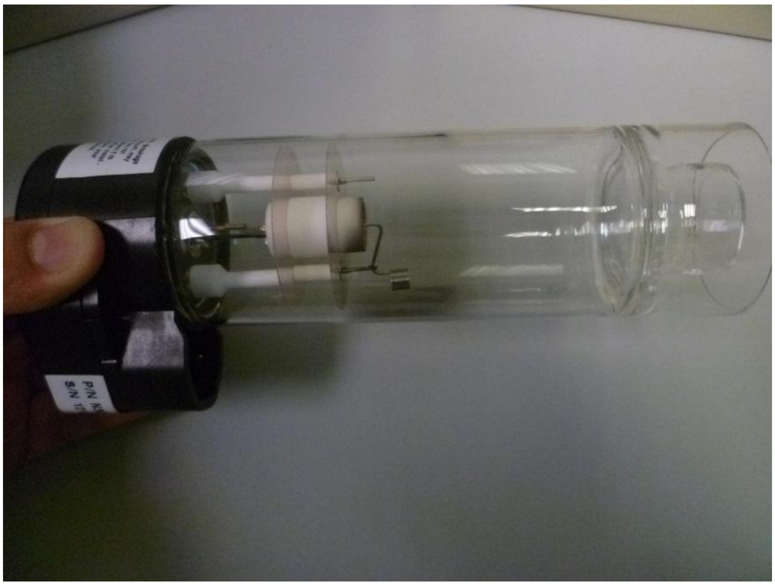


Figure 17: A hollow cathode lamp (HCL)

Figure 18: The copper stock standard (1000 ppm) that was used for making the standard solutions for the calibration curve.

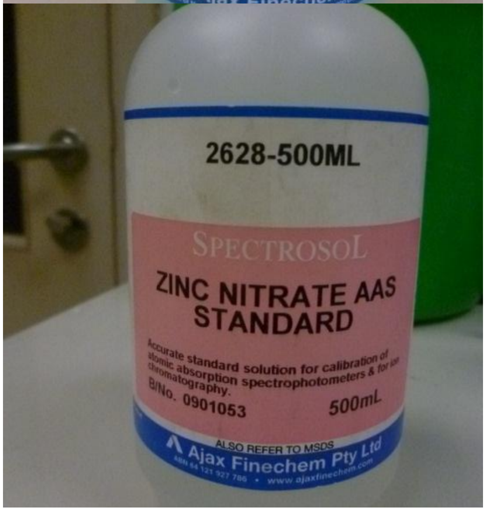
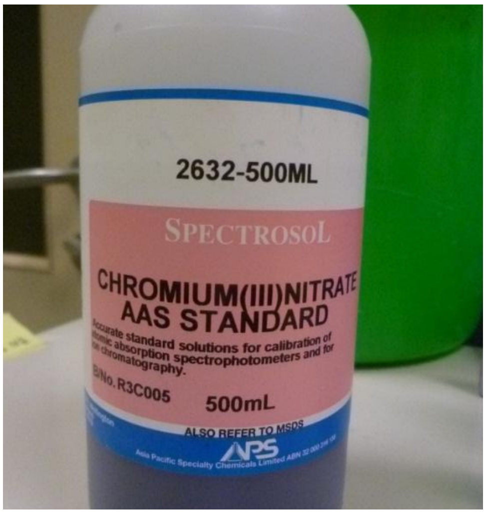


Figure 19: The zinc stock standard (1000 ppm) that was used for making the standard solutions for the calibration curve.

Figure 20: The nickel stock standard (1000 ppm) that was used for making the standard solutions for the calibration

Figure 21: The chromium stock standard (1000 ppm) that was used for making the standard solutions for the calibration curve.



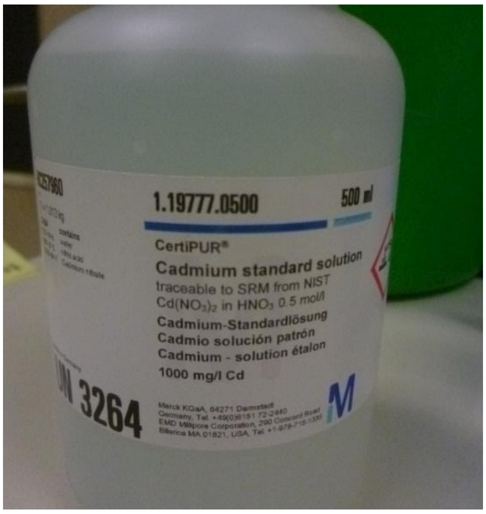


Figure 22: The cadmium stock standard (1000 ppm) that was used for making the standard solutions for the calibration curve.