OPTIMIZATION OF CHROMIUM, NICKEL AND VANADIUM ANALYSIS IN CRUDE OIL USING GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

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ABSTRACT

Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS) technique had been widely used for the determination of trace metals because of its high sensitivity. However, when this technique is applied for metals in organic samples such as crude oil, inconsistent reading were obtained due to smoke produced during the heating program which in turn interfere light absorption by the analyte. As such, organic components of the crude must first be removed to obtain a more accurate analysis of the metal analyte. This study evaluates the use of different acid combinations such as $H_2SO_4/HNO_3/H_2O_2$, HCl/HNO_3, HNO_3/H_2O_2, H_2SO_4/HNO_3 and $H_2SO_4/HNO_3/HCl$ for the decomposition of crude oil for the determination of nickel, chromium and vanadium. First, the temperature for GF-AAS analysis was optimized. The optimum drying, pyrolysis and atomization temperature for Ni were 110, 1000, and 2600 ^{o}C, while for vanadium were 110, 1100 and 2650 ^{o}C, and for Cr were 110, 1650 and 2500 ^{o}C respectively. The results show that vanadium concentrations in crude oil were 10.60±4.28 µg/g, 32.95±10.00 µg/g and 26.31±10.90 µg/g after being digested using $H_2SO_4/HNO_3/H_2O_2$, $H_2SO_4/HNO_3/HCl$ and H_2SO_4/HNO_3 respectively. The concentration of nickel using the acid combination of $H_2SO_4/HNO_3/HCl$, H_2SO_4/HNO_3 and HNO_3/H_2O_2 are 35.27±2.40 µg/g, 12.35±7.19 µg/g and 37.61±0.85 µg/g respectively. The chromium concentrations are 47.26±3.38 µg/g, 4.46±4.76 µg/g and 6.04±4.73 µg/g for the acid combination of $H_2SO_4/HNO_3/HCl$, H_2SO_4/HNO_3 and HNO_3/H_2O_2, Good recovery was obtained only for vanadium digested with $H_2SO_4/HNO_3/H_2O_2$ with an average of 94.95±13.73 %.

ABSTRAK

Teknik Spektroskopi Serapan Atom Relau Grafit (GF-AAS) telah digunakan secara meluas bagi penentuan logam surih kerana mempunyai sensitiviti yang tinggi. Walau bagaimanapun, apabila teknik ini digunakan untuk penentuan logam dalam sampel organik seperti minyak mentah, bacaan yang tidak konsisten diperolehi disebabkan oleh asap yang dihasilkan semasa program pemanasan mengganggu penyerapan cahaya oleh analit. Oleh itu, komponen organik mesti dikeluarkan terlebih dahulu untuk mendapatkan analisis logam yang lebih tepat. Kajian ini mengkaji penggunaan penggabungan asid yang berbeza seperti $H_2SO_4/HNO_3/H_2O_2$, HCl/HNO_3, HNO_3/H_2O_2, H_2SO_4/HNO_3 dan $H_2SO_4/HNO_3/HCl$ bagi penguraian minyak mentah untuk penentuan nikel, kromium dan vanadium. Terlebih dahulu, suhu untuk analisis GF-AAS dioptimumkan. Suhu optimum bagi pengeringan, pirolisis dan pengatoman untuk Ni, masing-masing adalah 110, 1000, dan 2600 ^{o}C, manakala bagi vanadium adalah 110, 1100 dan 2650 ^{o}C, dan Cr adalah 110, 1650 dan 2500 ^{o}C. Keputusan menunjukkan bahawa kepekatan vanadium dalam minyak mentah adalah 10.60 ± 4.28 µg/g, 32.95 ± 10.00 µg/g and 26.31 ± 10.90 µg/g selepas diuraikan menggunakan $H_2SO_4/HNO_3/H_2O_2$, $H_2SO_4/HNO_3/HCl$ dan H_2SO_4/HNO_3. Kepekatan nikel menggunakan gabungan asid $H_2SO_4/HNO_3/HCl$, H_2SO_4/HNO_3 dan HNO_3/H_2O_2 adalah 35.27 ± 2.40 µg/g, 12.35 ± 7.19 µg/g and 37.61 ± 0.85 µg/g. Kepekatan kromium adalah 47.26 ± 3.38 µg/g, 4.46 ± 4.76 µg/g and 6.04 ± 4.73 µg/g bagi kombinasi asid $H_2SO_4/HNO_3/HCl$, H_2SO_4/HNO_3 dan HNO_3/H_2O_2. Peratus perolehan semula yang baik telah diperolehi hanya untuk vanadium yang diuraikan menggunakan gabungan asid $H_2SO_4/HNO_3/H_2O_2$ dengan purata $94.95\pm13.73\%$.

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LIST OF ABBREVIATION

^{o}C	-	Degree Celcius
Cr	-	Chromium
GFAAS	-	Graphite Furnace Atomic Absorption
HCl	-	Hydrochloric Acid
HClO$_4$	-	Perchloric Acid
HF	-	Hydrogen Fluoride
H$_2$SO$_4$	-	Sulphuric Acid
H$_2$O$_2$	-	Hydrogen Peroxide
ICP	-	Inductive Couple Plasma
MIBK	-	Methyl Isobutyl Ketone
Ni	-	Nickel
RSD	-	Relative Standard Deviation
SO$_4^{2-}$	-	Sulphate Ion
SDS	-	Sodium Dodecyl Sulphate
V	-	Vanadium

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Crude oil is a natural product that exists beneath the earth surface. Crude oil exists in viscous liquid or semi liquid which consists of several types of hydrocarbon. The hydrocarbon can be categorized as paraffinic, naphthenic and asphaltic which varies in type of hydrocarbon composition [1]. Other than hydrocarbon, metals can also be found in the crude oil. Heavy crude oil may contain higher concentration of metals such as potassium, sodium, lithium, calcium, copper, tin, lead, manganese, because of its high density compared to light crude oil [2]. The importance of determination of heavy metals in crude oil has been a greatly increased because of their pernicious effects on petrochemical industry processes [3]. High contamination of metals may deposit on catalysts during the cracking process in petroleum refining will indirectly affect the catalyst activity and selectivity, thus, reducing the cracking yield. It can act as corrosive agents on the gas turbines and may also decrease the production of gasoline and butane-butylenes, and increases the coke and hydrogen gases [4]. Moreover the heavy metal ratio is useful in establishing the genesis of petroleum crudes and consequently in determining the source of seawater pollution [3].

For quantitative measurement of metals in crude oil, numerous analytical methods are used for the determination of the metallic elements present in organic liquids. Among those, atomic absorption spectrophotometry (AAS) is one of the most used techniques for the determination of metal cations due to the crude oil sample contain bulk of volatile organic compound and the analyte metal which can absorp light [5]. Flame excitation is an apparently attractive technique due to the simplicity in the preparation of the sample and speed of measurement. However, it has several limitations, in particular, its relatively low sensitivity and the mechanical difficulties presented by aspiration of highly viscous samples which causes poor reproducibility. Because of this, and because metal elements such as vanadium, which form refractory oxides make it difficult or impossible to volatilize them, the use of the graphite furnace has been introduced as the source of volatilization and excitation [6].

To optimize result of experiment, crude oil sample must undergo a pre-treatment before analysis to reduce its viscosity and to eliminate all hydrocarbon interferences. Most of the analytical procedures are based on wet digestion by using appropriate acid, ashing or dilution of the oil sample with organic solvent in order to give precise result for determination of heavy metals concentration in crude oil. Wet digestion is usually performed by the addition of nitric acid as oxidizing agent or combination of acid mixture to oxidize the metal and hydrocarbon [7]. Direct dilution method uses organic solvents such as ether, MIBK (methyl isobutylketone) or xylene to dilute crude oil and reduce its viscosity. Although heavy metal particles are not uniformly distributed in oils, they are generally determined by using techniques traditionally applicable to the determination of metal in homogeneous solutions. There are some possibilities of unique challenges that may bring limitation of analysis efficiency such as possible loss of certain naturally occurring volatile constituents during unaided ashing or heating, large particles or uneven particle size distribution and sedimentation, and sample non-homogeneity. Hence, to minimize these typical problems and increase reproducible sample surface to the instrument, work on methods used for crude oil analysis need to be further studied and evaluated.

1.2   Problem Statement

Crude oil sample, which contains high amount of hydrocarbon matrix become interferences for determination of heavy metal. High composition of hydrocarbon compounds such as porphyrin, organometallic, asphalt and carbonate may increase the viscosity of crude oil sample. High viscosity liquid sample may stuck in the injector rubber tube and pipe in the nebulization system. Besides that, there is the formation of smoke that occurs during the heating process at the graphite furnace. This lead to an inconsistent result for direct determination of heavy metal in crude oil without sample pre-treatment as the smoke will interfere the absorption of the analyte. Instead of the analyte that will absorp the light, the smoke will be the interference and reduce the intensities of the light. So, a pre-treatment for the crude oil sample is needed to overcome this problem.

It is important to develop and find out a simple method for crude oil analysis. In this study, the testing and the comparison of each method will be used to determine more accurate, fast and suitable method for crude oil analysis. A precise and effective method will be used for diagnostic maintenance to quantify the concentration of desired heavy metals in crude oil. The selections of methods are determined through the results comparison of each method from laboratory test of oil sample.

The suggested method that had been used in this study involved wet digestion method using appropriate couples of acids and direct digest technique using inorganic acids. The analysis conditions such as temperature programmed use, the clarity of solution and amount of dissolved sample that influence the effectiveness of the various applied methods will also be observed.

1.3 Research Objectives

The purposes of this study are:

1. To compare and determine the suitable and effective preparation method for the analysis of crude oil using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS).
2. To determine the amount of chromium, nickel and vanadium in crude oil.
3. To propose the most reliable method for routine analysis of heavy metal in crude oil.

1.4 Significant of Study

This study helps to find out the effective and suitable method for determination of vanadium, chromium and nickel in crude oil and develop a guideline for routine crude oil analysis using GF-AAS. Result from the study will be used to suggest the fix method for sample preparation of crude oil analysis using GF-AAS.

1.5 Scope of Study

The purpose of this study is to determine the concentration of chromium, nickel and vanadium in crude oil analysis by using GF-AAS. In this study light crude oil had been used. This study is focussed to find the most suitable method for sample

preparation of crude oil for metals analysis. Different types of sample preparation were used in order to evaluate the precision and accuracy of analytical results. The method for sample preparation were based on different acid combination from standard method BS ISO 11466 that involved addition of HCl and HNO_3, USEPA Standard Method 3050A that consists of HNO_3 digestion with H_2O_2, Standard Method 3031 of SW846 with the coupling of HCl and H_2SO_4 with HNO_3, Standard Method D-5836 with the combination of H_2SO_4 and HNO_3, and a method that involves the combination of H_2SO_4 and HNO_3 with the addition of H_2O_2.

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