

Determination of Metal Ions in Crude Oils

M.Y. Khuhawar¹, M. Aslam Mirza² and T.M. Jahangir¹

¹*Institute of Advanced Research Studies in Chemical Sciences,
University of Sindh, Jamshoro,*

²*Mirpur University of Science & Technology (MUST), Mirpur, AJ&K,
Pakistan*

1. Introduction

Crude oil is complex mixture of hydrocarbons that occur in the earth in liquid form. It constitutes an important part of primary fossil fuels. Crude oil was used as a medicine by the ancient Egyptians, presumably as wound dressing, liniment and laxative. Several centuries later, Spanish explorers discovered crude oil in Cuba, Mexico, Boliva and Peru. The industrial revolution brought increasing demand for cheaper and convenient source of energy. Crude oil (liquid petroleum) was easily transportable source of energy, concentrated and flexible from of fuel. At the beginning of the 20th century the industrial revolution had progressed to the extent that the oil industry became the major supplier of the energy, largely because of the advent of automobile. The oil achieved a primary importance as an energy source on which the world economy depends. The growth in the energy production during the 20th century was unprecedented and is the major contributor to the growth. On the time scale within the human history, the utilization of oil as a major source of energy will be affair of a few centres, but it will have profound effect on world industrialization.

The crude oils are mostly based on two elements carbon and hydrogen and almost all crude oil ranges from 82-87% carbon and 12-15% hydrogen. Crude oil contains three basic chemical series: paraffins, naphthenes, and aromatics. The crude oils from different sources may not be completely identical (Evans et al, 1971).

The paraffins are also called methane series, and comprises most common hydrocarbons in crude oil. The paraffins that are liquid at normal temperature boil between 40-200 °C. The naphthenes are saturated closed ring series and are important part of all liquid refinery products. The aromatics are unsaturated closed ring series. Benzene is most common of the series and is present in most of the crude oils, but aromatics constitute a small fraction of all crudes.

The crude oil also contains sulphur, nitrogen and oxygen in small quantities. Sulphur is the third most abundant constituent of crude oil. The total sulphur in crude oil varies from below 0.05% up to 5% or more. Generally greater the specific gravity of the crude oil, higher is its sulphur content. The oxygen contents of the crude oil are usually less than 2%. Nitrogen is present in most of the crude oils, usually in quantities of less than 0.1% (Britannica online).

Preliminary fractionation of crude oil according to chemical class is carried out before identification of individual components. Several such fractionation and isolation schemes

are available (Rudzinski and Aminabhavi, 2000) depending on the type of crude oil under investigation. One of the separation scheme is based on SARA method, which has name from the fractions produced, namely saturates (S), aromatics (A) resins (R) and asphaltenes (A). The sample is adsorbed on the silica (Isitas-Flores et al., 2005), (Andersen et al., 1997); (Goreli et al., 2008) or alumina, followed by the selective elution of the components with increasingly polar solvent (Seidl et al., 2004), (Sharma et al., 1998), (Seidl et al., 2004). Mansfield et al (1999) have reviewed the crude oil separation and identification including SARA method. HPLC and infra red spectroscopy have also been used for SARA characterization (Fan and Buckley, 2002), (Aske et al., 2001).

Asphaltenes consist of polar fraction of the crude oil comprising polyaromatics, heteroaromatics and various metals (Kaminski et al., 2000).

2. Metal ions in crude oil

The metals present in the crude oils are mostly Ni(II) and VO(II) porphyrins and non-porphyrins. Other metal ions reported from crude oils, include copper, lead, iron, magnesium, sodium, molybdenum, zinc, cadmium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver and arsenic. Metalloporphyrins are among the first compounds identified to belong to biological origin. Treibs et al (1936) proposed that plant chlorophylls transformed into the geoporphyrins. Metalloporphyrins in crude oils are of fundamental interest from geochemical context for better understanding geochemical origin of petroleum source. The information could be useful for catagenetic oil formation, maturation of organic matter, correlation, depositional and environmental studies. Vanadium and nickel metalloporphyrins are present in large quantity in heavy crude oils. Their presence cause many problems because such metals have a deleterious effect on the hydrogenation catalysts used in upgrading processes (Pena et al., 1996).

Among the porphyrins encountered in the crude oils, etioporphyrins (etio) and dexophylloerithroetioporphyrin (DPEP), and their homologues are more frequently observed (Baker and Louda, 1988), (Barwise and Roberts, 1984). The complexity of porphyrin mixtures have made the isolation of these pigments difficult, but the improved chromatographic and spectroscopic techniques have made possible the separation and identification of a number of metalloporphyrins (Les Ebdon et al., 1994). The identification of Ni and V porphyrin was quite earlier (Treibs et al., 1936) but the organic forms of other metals in crude oils was achieved only later, with the advent of hyphenated techniques, e.g. HPLC or GC coupled to AAS or ICP-MS for elemental detection. The porphyrins of Co, Cr, Ti and Zn were identified in oil shales by HPLC-ICP-MS (Les Ebdon et al., 1994).

It was earlier observed that V/Ni or V/(V+Ni) ratio was constant in crude oils of common rock source and was dependent on geological age of the rocks (Ball et al., 1960) and this ratio was used for tracing source effects (Shahristani and Al-Alyia, 1972), (Gayer et al., 2002). The studies on the thermal evolution of the major VO complex of DPEP to etio indicated a maturity dependence (Didyk et al., 1975), (Barwise et al., 1987), thus suggesting these compounds as biomarkers (Peters et al., 2004), (Duyck et al., 2007).

The organic forms of metalloporphyrins are described as tetrapyrrolic complexes with structure similar to chlorophyll and heme (Treibs et al., 1936), but the chemical nature of nonporphyrins is not well established. These are polar compounds and largely exist as

cations of organic acids. Nitrogen, oxygen and sulphur can all act as donor atoms in various combinations in nonporphyrins (Amorin et al., 2007). These are predominantly associated with the asphaltenes. Some of the elements in crude oils may be present in associated mineral matter or entrained formation waters. A number of metal complexes may be associated with humic substances that have large capacities for metal complexations (Choudhry et al., 1983) which may be precursors to kerogen.

3. Determination of metals in crude oils

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. Trace metals have been used as a tool to understand the depositional environments and source rock (Alberdi-Genolet and Tocco, 1999). The metal ions and their ratios have been observed as a valuable tool in oil-oil correction and oil-source rock correlation studies (Barwise et al., 1990), (Akinlua et al., 2007). The trace metals are also indicated as biomarkers of the source rocks (Odermatt and Cruriale, 1991). The determination of metal ions in crude oils has environmental and industrial importance. The metal ions like vanadium, nickel, copper and iron, behave as catalyst poisons during catalytic cracking process in refining of crude oil. The metal ions are released in the environment during exploration, production and refining of crude oil. The determination of mercury content in crude oil is also important for petroleum industry, because the metal can deposit in the equipment, which could affect the maintenance and operation (Willhelm et al., 2006). It is therefore considered necessary to know the concentration of metals in the oils for meaningful impact assessment.

Metals and metalloids may be naturally found in the crude oils and these could be added during production, transportation and storage. In general these elements are present in the crude oils as inorganic salts (mainly as chloride and sulphate of K, Mg, Na and Ca), associated with water phase of crude oil emulsions, or as organometallic compounds of Ca, Cu, Cr, Mg, Fe, Ni, Ti, V and Zn adsorbed in water-soil interface acting as emulsion stabilizers (Speight et al., 2001).

Molecular absorption spectrophotometry (Milner et al., 1952), atomic absorption spectrometry (AAS), (Langmyhr and Aadalen, 1980), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Fabbe and Ruschak, 1985), inductively coupled plasma mass spectrometry (ICP-MS) (Lord et al., 1991), high performance liquid chromatography (HPLC) (Khuhawar and Lanjwani, 1996), gas chromatography (GC) (Delli and Patsalide, 1981), capillary electrophoreses, (Mirza et al., 2009) and X-ray fluorescence spectroscopy (XFS) (Vilhunen et al., 1997) methods have been reported for the determination of metals in crude oils.

3.1 Sample preparation

Crude oil is a complex matrix of varying viscosities and mixed phases (organic, water and particulate matter) and therefore not an ideal matrix for analysis. The determination of the metals in crude oil requires pretreatment to the sample before presentation to the instrument. This is the stage where most of the errors occur and is time consuming. The selection of a particular procedure depends upon (1) analytical technique to be employed, (2) nature and the number of the samples to be analyzed, (3) desired degree of precision and

accuracy required, (4) availability of the equipment, materials and reagents and (5) the cost of analysis (Oliveira et al., 2003). It is generally desired that analysis is completed within shortest time with minimum contamination, using smallest quantities of the reagents and the samples and little residues and waste generation (Amorin et al., 2007).

Metal determination in crude oil is carried out by using dry ashing, dilution in organic solvents (Annual Book of ASTM, 2000, 2002) or using micro-emulsions (Souza et al., 2006), (Santella et al., 2008). The use of micro-wave radiation as a potential sample preparation technique has been applied due to high efficiency of heat transfer and sample digestion efficiency (Mello et al., 2009), (Pereira et al., 2010). Literature data concerning metal and metalloid determinations in the crude oil by direct sample introduction is also available (Anselmi et al., 2002), (de Oliveira et al., 2006).

3.1.1 Sample decomposition by ashing

Drug ashing is used for complete elimination of organic matter, before analytical determination and is based on the ignition of the organic matrix in air or in the stream of oxygen, followed by the dissolution of the residue in an acid medium. This is one of the cheapest sample preparation procedure. Larger quantities of the sample could be used and the analyte could be concentrated into small volume of dilute mineral acid (HCl or HNO₃). This also make possible the use of aqueous standards for the calibration of equipment. The main disadvantages of the dry ashing procedure for crude oils are the risks of contamination or loss of the analyte due to the formation of volatile compounds. (Ekanem et al., 1998). The addition of sulphur containing compounds has long been used for avoiding losses of Ni and V by volatilization during ashing (Udoh et al., 1992). The dry ashing takes longer time for sample preparation with low sample preparation frequency.

3.1.2 Sample decomposition by wet digestion

The sample decomposition of organic constituents by wet digestion is achieved by the use of oxidizing agents prior to analyte determination. Normally concentrated acids are applied under heating, and the important aspects for consideration are the strength of the acids, their oxidizing and complexing power, their boiling points, the solubility of the resulting salts, safely in manipulation and purity (Amorim et al., 2007). The acids and oxidizing agents used for oil samples include mixtures of nitric, hydrochloric and sulphuric acids and hydrogen peroxide. This is also one way to overcome the difference in response caused by the presence of different analyte compounds in the fuel by their conversion in water soluble salts. The procedure is generally performed with larger volume of oxidizing acids (e.g. 10 ml of acid per 0.5 g of sample) and time for complete decomposition is long (up to several days). The use of sulphuric acid in wet digestion procedure for trace metal determination in oils, suggested in literature has been reappraised as standard methods for the determination of Ni, V and Fe in crude oils and residual fuels (Standard test methods, 2005).

3.1.3 Wet digestion assisted by microwave radiation

Wet digestions assisted by microwave radiation have been observed as safer and efficient. The procedures minimize contamination and amount of reagents for sample preparations (Ozcan and Akman, 2005), (Trindade et al., 2006). Microwave heating enhances the

efficiency of acid digestion. US-EPA method 3051 (1994) reported microwave assisted acid digestion procedure for 0.5 g of oil and other samples with 10 ml of nitric acid with 10 min. of heating. Alvarado et al (1990) optimized a procedure for the microwave digestion of crude oil samples using different proportions of HNO_3 and H_2SO_4 for the analysis of Cr, Cu, Fe, Mn, Ni, Na and Zn. Bettinelli et al (1995) examined microwave digestion of fuel oils in a high pressure closed vessel and observed a decrease in sample decomposition time due to higher temperature achieved. Using the conditions, difficult samples were also decomposed completely. Munoz et al (2007) evaluated the use of different microwave ovens for the decomposition of crude oils and diesel fuel to determine the contents of Cu, Pb, Hg and Zn in the digestates. A focused-microwave (FM) oven using $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}_2$ operated at atmospheric pressure, and a closed vessel microwave (CVM) oven using $\text{HNO}_3/\text{H}_2\text{O}_2$, operated under pressure in a vessel, were evaluated. Better detection limits were reported for FM digested solutions with 0.8 - 1.0 g of sample, in contrast low quantities (0.10 - 0.28 g) were used when pressurized vessels were used. However the loss of Hg was verified when samples were decomposed in the FM oven. Sant' Ana et al (2007) reported focused microwave assisted procedure for the wet acid dissolution of diesel oil for the determination of metals in samples. The dissolution process was monitored by measuring residual carbon content (RCC) after application of digestion program. The dissolution program comprised three steps: (1) carbonization with H_2SO_4 , (2) oxidation with HNO_3 and (3) final oxidation with H_2O_2 . It was reported that the first step was important on the dissolution process. At optimized conditions it was possible to digest 2.5 g diesel oil with a 40 min. heating program. At these conditions, residual carbon content was lower than 5%. Optimized methodology was used in the determination of Al, Cu, Fe, Ni and Zn in three diesel oil samples. Pereira et al (2010) described a method for light and heavy crude oil digestion by microwave induced combustion in the closed vessel for the determination of Ag, As, Ba, Bi, Ca, Cd, Cr, Fe, K, Mg, Li, Mn, Mo, Ni, Pb, Rb, Se, Sr, Tl, V and Zn. Conventional microwave assisted digestion in pressurized vessels were also used for results comparison. Accuracy of microwave-induced combustion method was evaluated for As, Ba, Ni, Se, V and Zn using certified reference material with similar matrix. Recovery tests were better than 97% using 2 mol/L nitric acid as absorbing solution. Both sample preparation techniques were suitable for crude oil digestion, but microwave induced combustion was preferable in the view of possibility of using diluted nitric acid as absorbing solution. Mello et al (2009) applied microwave induced combustion for the determination of Ni, V, S from crude oil distillation residues. The results obtained agreed with certified values for Ni, V and S within 99 to 101% using 2 mol/L HNO_3 as absorbing solution.

3.1.4 Dilution with organic solvents

The dilution of crude oils and derivatives with organic solvents is an attractive sample preparation method, because it is simple and rapid and could be used for the determination of the metals by spectro-analytical techniques. The solvents commonly used are xylene, kerosene, methyl isobutyl ketone (MIBK), n-hexane, dimethylbenzene, 1-propanol and mixture of these solvents. The procedure is widely used in industry (Batho et al., 1993), (Botto and Zhu, 1996). Direct dilution of crude oils and residual fuels with an organic solvent for the determination of Ni, V, Fe and Na is proposed in ASTM standard test method (Standard test methods ASTM D 5863-00 a (2005). Ni and V in crudes and heavy crude fractions were determined after dilution in xylene (Fabec and Ruschak, 1985). The

solubilisation of crudes and its burning residues was carried out with MIBK for the determination of V as well as Cd and Ni (Guidr and Sneddon, 2002), (Hammond et al., 1998). Bethinelli and Tillarelli (1994) validated a procedure for the determination of Ni and V in fuel oils based on the 1 + 9 dilution with xylene and calibration was with constant organometallic standards, using base oil for matching the viscosity on fuel oil with known metal contents. The procedure was compared with a series of independent methods in the analysis of six samples with different metal contents. The results very close to the consensus values were reported.

Dilution with organic solvents, in spite of simplicity has number of limitations (1) Analyte concentration may change due to the evaporation of the solvent or due to the adsorption on the walls of container (Campos et al., 2002), (2) The problems of plasma destabilization or extinction in case of ICP technique and the contamination of the instrument with carbon residues persist, as the organic load is not reduced with dilution, (3) The toxicity of many organic solvents requires care to avoid and health hazard for laboratory personnel, (4) different metal – organic compounds often exhibit different sensitivity and require use of expensive organic standards for calibration (Vale et al., 2004). The standards may also show a sensitivity difference from that of the metal organic compounds present in the fuel (Teserovsky and Arpadjan, 1991).

3.1.5 Preparation of emulsion

A fuel sample may be modified by formation of emulsions or micro-emulsion (Three component system). When two immiscible liquids are stirred, a macro emulsion is obtained either oil in water (o/w, droplets of oil in water) or water in oil (w/o, droplets of water in oil), depending on the dispersed phase. In emulsion and micro-emulsion the fuel is dispersed in the aqueous phase as micro drops stabilized by micelles or vesicles generated by the addition of a detergent. The emulsion that is formed is mainly related to the formulation and to the lesser degree to the o/w ratio. In the case of micro-emulsion without detergent a co-solvent allows the formation of a homogenous and long term stable three component solution containing the aqueous and organic phase (das Gracias Andrade Koen et al., 2007), (Pelizzeti and Pramauro, 1985). The procedure enables to use aqueous standards for calibration without the need of sample mineralization. A surfactant with a suitable hydrophilic-lyophilic balance is used in the preparation of emulsion, which permits relatively high solubility between the immiscible phases. In the case of detergentless microemulsions, an alcohol of low molecular weight is added as co-solvent (Cardarelli et al., 1986). Emulsions and micro-emulsions have been successfully applied for the preparation of oil samples, due to homogenous dispersion and stabilization of the oil micro-droplets in aqueous phase, which reduces oil viscosity and the organic load of the system.

Kumat and Gangadharen (1999) applied Triton X-100 emulsions to the determination of V, Co, Ni, As, Hg and Pb in naphtha. Murillo and Chirinos (1994) examined non-ionic emulsifier, polyoxyethylene nonylphenylether for heavy crude oils because of its slightly higher hydrophile-lipophile balance, which enabled higher solubility in water through hydrogen bonding. Souza and da Silveira (2006) reported detergentless emulsions for the determination of elements in crude oils by using acidified water for element stabilization and propan-1-ol as a co-solvent. Meeravali and Kumar (2001) determined Ni and V in naphtha and fuel oils after emulsion formation. The oil samples were diluted in toluene, and

this solution was emulsified by stirring with 3% Triton X-100 in water. Calibrations were prepared with organometallic standards following the same procedure. The emulsions were stable from 20 to 50 min. Good agreement between found and certified results was reported. Vale et al (2004) optimized the emulsification of petroleum for the determination of the nickel. They stabilized samples and analytic solutions as an o/w emulsion consisting of xylene, Triton X-100 and water. Ultrasonic bath was used in the emulsification process and the mixture was further homogenized just before the measurement by manually flushing them with a micropipette. Aucetio et al (2004) determined V in the asphaltene petroleum fraction. The analytic solution was stabilized by mixing with propan-1-ol and 6 mol/L HNO₃ forming a detergentless micro-emulsion. The micro-emulsion was immediately formed and was reported to be stable upto 80 h. Calibration was performed by spiking in organic V in the same micro-emulsion medium. A comparison with established methods (acid digestion or dilution in organic solvent) shows that emulsion or micro-emulsion methodology presents advantages in terms of simplicity of sample preparation, total analysis time, long term sample stability and the use of inorganic standards for calibration instead of expensive metal organic standards (Anorim et al., 2007).

3.1.6 Direct analysis of crude oil

Direct analysis using little or no sample preparation has the advantage of time saving and minimum risk of analytic loss. This technique has been applied for highly viscous liquids and has been examined for the determination of Ni (Brandao et al., 2006), Ni and V (Silva et al., 2007) and Cu, Fe and V (Brandao et al., 2007) in oil samples. However there are some general problems such as volatility, flammability and immiscibility with water. In addition to the problems related to the complexity of the matrix, organic standards, which are indispensable in case of direct sample introduction, are unstable and there are no certified reference materials available for these samples. It is therefore necessary to compare the accuracy of the developed method with results obtained with independent technique, particularly with respect to the sample preparation.

3.1.7 Analyte extraction

Extraction for the analyte from the fuel can be used for sample preparation, which combines the advantages of separating the analyte from the matrix, transferring it to an aqueous phase and may also result in preconcentration. Liquid-liquid extraction procedures present as main advantage for their simplicity. Akinlua and Smith (2010) reported the extraction of trace metals from petroleum source rock by superheated water and the conditions for maximum yield were determined. The optimum temperature for superheated water extraction of the metals from petroleum source rocks was 250°C. The extraction time was 30 min. The leaching of Cd, Cr, Mn and Ni had better yield with superheated water, while V had better yield with acid digestion.

Solid phase extraction is a useful separation and preconcentration procedure for the determination of trace metals in fuels. It is based on the partition between a liquid (sample) and a solid phase (sorbent), which can be unloaded, load on chemically modified with organofunctional groups (Koen et al., 2006). After pre-concentration the analyte is recovered by elution with an appropriate solvent or directly determined in the solid phase.

3.2 Atomic absorption spectrometry

3.2.1 Flame Atomic Absorption Spectrometry (FAAS)

FAAS indicates inherently low sensitivity for metal determinations and a few reports are available in the literature involving the direct analysis of crude oils by FAAS. A sufficiently large sample mass may compensate for lower FAAS sensitivity with longer analysis time. Platteau and Carriillo (1995) determined Fe, Na and Ni in crude oils by FAAS. Ni, V and Fe in crude oils and residual fuels have been determined by FAAS after ashing with H₂SO₄ (standard test methods ASTM 2005). Fabec and Ruschak (1985) determined Ni and V in crudes and heavy crude fraction by FAAS after dilution in xylene. Guidr and Sneddon (2002) determined V by nitrous oxide : acetylene flame AAS and (Hammond et al., 1998) analyzed Cd, Pb and Ni by FAAS in crudes and its burning residues after solubilization in MIBK. Osibanjo et al (1984) determined Ni, Cu, Zn, Na, Pb, Cd and Fe by FAAS in petroleum crudes after dilution with toluene - acetic acid mixture. Calibration was performed with inorganic salts and by analyte addition. Sebor et al (1982) discussed FAAS analysis of crude oils using dilution methods with different solvents or solvent mixtures. Different organic compounds of the same element present different responses in the flame, no matter if an air or a nitrous oxide acetylene flame was used. This led to calibration difficulties as well different responses depending on the organometallic composition of the sample. De la Guardia and Lizondo (1993) determined Ni in fuel oil by FAAS using 4% v/v oil-in-water emulsion.

3.2.2 Electrothermal Atomic Absorption Spectrometry (ET-AAS)

ET-AAS with a graphite furnace is a useful analytical technique for metal analysis from crude oils, because of its high sensitivity and capability to deal with organic loads. In addition ET-AAS requires only small amount of sample. ET-AAS make possible direct analysis of crude oils, because it allows complete elimination of organic matrix, if an appropriate heating program and suitable chemical modifiers are used (das Graces Andrade Koren, 2007).

Turunen et al (1995) determined As, Cd, Cr, Cu, Mn, Ni, Pd and V in heavy oils by ET-AAS after acid digestion with HNO₃-H₂SO₄ mixture. Alvarado et al (1990) analyzed Cr, Cu, Fe, Mn, Ni and V by ET-AAS after micro-wave digestion of various crude oil samples. Bruhn and Cabalin (1983) proposed determination of Ni in gas oil after dilution with xylene by ET-AAS, analyte addition was used for quantitation. Gonzalez et al (1987) determined V, Ni, Fe and Pb in crude and fuel oils following dilution with xylene and MIBK. The quantitation was by analyte addition calibration curves. Bermejo-Barrera (1991) determined V in petroleum samples by ET-AAS after dissolution in xylene. They proposed that the crude oil is diluted to the extent that matrix interference is eliminated. Thomainidis and Piperaki (1996) examined the behavior of a series of chemical modifiers for the determination of V in a water and oil matrix. In the determination of V in a multi-element standard diluted with MIBK, the addition of Pt as modifier enhanced the pyrolysis temperature from 1000 to 1400 °C with improvement in the sensitivity. Stigter et al (2000) determined Cd, Cr and Cu in crude oils by ET-AAS using Zeeman-effect background correction as well as oxygen ashing during the pyrolysis step. Finally they used mixture of toluene and acetic acid 4:1 v/v as a solvent for dissolution of the samples. Nakamoto et al (2004) determined V in heavy fuel oils

using tungsten coated graphite furnace. The effect of sulphur interference on the determination was examined. The sulphur content less than 1% can be tolerated. An agreement between proposed and comparative procedures was reported. Meeravali and Kumar (2001) analyzed Ni and V in naphtha and fuel oils after emulsion formation by ET-AAS using W-Ir as permanent modifier. The oil samples diluted in toluene was emulsified with 3% Triton X-100 in water. Calibration was performed with organometallic standards prepared in same manner. Burguera et al (2003) analyzed Cr in heavy crude oil and in bitumen in water emulsion by ET-AAS after sample emulsification. Vale et al (2004) optimized the determination of Ni in petroleum using both line source and high resolution continuum source ET-AAS. They stabilized sample and analyte solutions as an emulsion consisting of xylene, Triton X-100 and water. The authors observed a significant Ni loss at pyrolysis temperature of 500 °C, most probably due to the presence of volatile Ni species. However better results were reported at pyrolysis temperature of 400 °C. Aucelio et al (2004) determined V in the asphaltene petroleum fraction by ET-AAS. The solution of the sample was stabilized by mixing with 1-propanol and HNO₃, forming detergentless micro-emulsion. Calibration was performed by spiking inorganic V in the same micro-emulsion medium. Damini et al (2005) determined Ni and V in oil samples by line source ET-AAS, Pd (20 µg) was used as chemical modifier. Good agreement was reported between found and expected values. Quadros et al (2010) determined Ni and V simultaneously as their total and nonvolatile fractions in crude oil samples using high resolution continuum source graphite atomic absorption spectrometry. Determination was carried out at 305.432 nm and 305.633 nm for Ni and V respectively using linear charge - coupled device array detection. Oil-in-water emulsions were used for crude oil sample preparation. Nitric acid was added to emulsion for the determination of total Ni and V concentration. In the absence of acid volatile fraction was lost in the pyrolysis and thermally stable fractions were determined. The concentration of the volatile fraction was obtained by difference. Vale et al (2006) used ET-AAS to differentiate between volatile and nonvolatile Ni and V compounds in crude oil. Two crude oil samples were separated in two steps: firstly the asphaltenes were precipitated with n-heptane. Another portion was loaded on a silica column and eluted with solvents of increasing polarity. Four fractions 1, 2, 3 and 4 were separated. Oil in water emulsions were prepared for determination of Ni and V by ET-AAS. The analysis was carried out without chemical modifier (stable compounds) and with 20 µg Pd (Total Ni and V) and the volatile fraction was calculated by difference (Fig.1). Brandeo et al (2007) proposed a procedure for direct determination of Cu, Fe and V in petroleum samples by ET-AAS using a solid sampling accessory without any sample pretreatment or dilution. A Pd + Triton X-100 solution was used as chemical modifier. The limits of detection at the optimized conditions were 10, 200 and 800 pg for Cu, Fe and V respectively for sample masses ranging 0.10-3.0 mg. Aqueous calibrations were used for quantitation. Luz and Oliveira (2011) determined Cr, Fe, Ni and V in crude oil using emulsion sampling by ET-AAS. The emulsion was prepared in a mixture of n-hexane + Triton X-100, Mg(NO₃)₂ was used as chemical modifier. The reliability of the proposed method was checked by fuel oil standard reference material analysis. Dittert et al (2010) simultaneously determined Co and V in crude oils by high resolution continuum source ET-AAS, V and Co were determined at 240.674 nm and 240.725 nm. The samples were analyzed directly without dilution; Pd and Triton X-100 were added as chemical modifiers. Aqueous solutions were used for calibration. Two certified oil reference materials were analyzed and results were in agreement with certified and reported values.

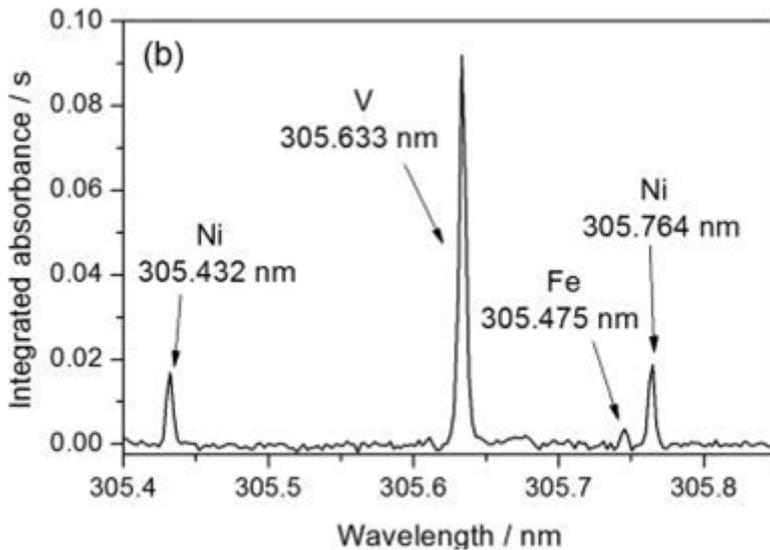


Fig. 1. Absorbance spectrum for the OB-2 crude oil sample emulsion in the vicinity of the vanadium secondary line at 305.633nm, with a pyrolysis temperature of 1000 °C, Wavelength resolved integrated absorbance spectrum (Quadros et al. 2010) with permission.

3.2.3 Chemical vapour generation AAS

The elements Hg, As and Sb are present in the fuels at low concentrations and chemical vapour generation (CVG) technique can be applied to provide required sensitivity. However CVG when applied to crude oils is susceptible to spectral interference from aromatic organic compounds in the gas stream. Cold vapour (CV) technique for mercury and hydride generation (HG) technique for As & Sb requires the analyte to be present in inorganic form in a defined oxidation state. Therefore the applications of CVG to the analysis of fuels generally requires complete mineralization of the metal-organic compounds and separation from organic phase (das Gracias Andrade Korn, 2007). Campbell and Karmel (1992) determined As, Sb and Se in oil waters by hydride generation AAS, after complete oxidation of the organic matrix using microwave-assisted digestion in the closed system. Puri and Irgolic (1989) determined As in crude oils after extraction of As in boiling aqueous nitric acid, followed by mineralization of the extract with concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$ and reduction of arsenate to arsine in hydride generator. Wilhelm and Bloom (2000) have reviewed mercury in petroleum and have described the use of cold vapour AAS for sensitive detection of mercury.

3.3 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES has the advantage of multi-elemental detection capability and offers a wide linear dynamic range. However, the introduction of organic solvents, such as fuels cause plasma destabilization or even plasma extinction and the use of ICP accessories may be necessary, such as direct injection nebulizer, ultrasonic nebulizer with micro-porous membrane

dessolvator, a thermostated condenser between the spray chamber and the plasma torch or a chilled spray chamber. Alternatively the sample is digested to obtain aqueous solutions (Das Gragas Andrade Korn (2007).

Botto (1993) and Botto and Zhu (1996) determined metal by ICP-OES in petroleum oils after dilution with organic solvents. Souza et al (2006) determined Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in crude oil by ICP-OES using detergentless emulsions comprising of acidified water for element solubilization and propan-1-ol as a cosolvent with the addition of oxygen to the nebulizer gas flow. Fabec and Ruschak (1985) determined Ni and V in crudes and heavy crude fractions by ICP-OES after dilution in xylene. Mello et al (2009) determined Ni, V and S in crude oils distillation residues by ICP-OES after digestion of sample by microwave induced combustion. De Souza et al (2006) determined Mo, Cr, V and Ti in diesel and in used fuel oil by ICP-OES. Detergent and detergentless emulsion sample preparation procedures were evaluated and better results were obtained for detergent emulsions with recoveries ranging from 90.1-106.5%. Borszeki et al (1992) determined Al, Cr, Cu, Fe, Mg, Ni and Pb in oil and petroleum products by ICP-OES using a minitorch. The samples were prepared as aqueous emulsions. Quantitation was with aqueous standards and the results were in good agreement with those obtained using oil standard solutions. Brenner et al (1996) determined lead in gasoline by ICP-OES using argon and argon-oxygen as plasma gas.

3.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is highly sensitive multielement technique, but the introduction of organic solvents and the compounds in plasma requires special care similar to ICP-OES, because the organic load may destabilize or extinguish the plasma. ICP-MS encounters additional problems of formation of carbon deposit on the sampler and skimmer cone and in the ion lens of the mass spectrometer and spectral interferences owing to carbon based species (Lord et al., 1991), (Brenner et al., 1997). In ICP-MS spectral interferences may also occur as crude oil contains a number of elements at low concentrations (ng/g) levels (Tan and Horlick, 1986). The effect of polyatomic interferences may be minimized by the choice of alternate isotopes or the use of desolvation system to reduce the solvent load (Jakubowski et al., 1992). The problem of the deposition of carbon on the sampler and skimmer cone in ICP-MS was decreased by the addition of O₂ to the argon (Magyar (1986).

Duyck et al (2002) determined Ag, Al, Ba, Cd, Co, Cu, Fe, La, Mg, Mo and Mn in residual fuel oil and crude oils by ICP-MS after dilution of the samples in toluene, using ultrasonic nebulization. Good accuracy was reported for the determinations of the metals. Wondimu et al (2000) analysed residual fuel oil for Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe and Hg by ICP-MS after micro-wave acid decomposition. H₂O₂ was used after acid decomposition for better carbon removal. Lord (1991) determined Li, Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Sr, Mo, Ag, Cd, Sn, Sb, Ba and Pb in crude oils by ICP-MS with micro-emulsion sample introduction. Kowalewska et al (2005) determined Cu in crude oils and crude oil distillation products by ICP-MS after ashing and micro-wave assisted decomposition of analyte and transferred to aqueous solution. Good recovery of Cu was reported. Kelly et al (2003) determined Hg in crude oils and refined products by cold Vapor ICP-MS after decomposition of the sample by closed system combustion. Botto (2002) analysed crude oil, petroleum naphthas and tars for Na, P, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Y, Mo, Cd, Sn, Sb,

Hg, Pb and Bi by ICP-MS using direct injection technique after the dilution of the samples in xylene. Al-Swaidan (1996) determined Pb, Ni and V in crude oil by coupling sequential injection with ICP-MS. A microemulsion crude oil sampling procedure was used. The quantitation was by standard addition technique using oil soluble organometallic elements. Pecira et al (2010) analyzed light and heavy crude oil for the determination of Ag, As, Ba, Bi, Ca, Cd, Cr, Fe, K, Mg, Li, Mn, Mo, Ni, Pb, Rb, Se, Sr, Ti, V and Zn by ICP-MS after microwave induced combustion in closed vessel. Akinlua et al (2008) determined rare earth elements of crude oil from the offshore-shallow water and onshore fields in the Niger delta by ICP-MS. The samples were prepared by acid digestion into colourless aqueous solutions. The concentrations of the detected elements La, Ce, Pr, Nb, Sm, Eu, Gd, Dy, Er and Yb ranged from 0.01-1.58 µg/L with an average of 0.98 µg/L (% RSD < 5).

3.5 Chromatographic techniques

Chromatography is a separation technique and has been used for the determination of metal ions in crude oils. The methods are based on determination of total metal ions, after complete mineralization of the crude oil or as metalloporphyrins using hyphenated techniques..

Quimby et al (1991) described selective detection of volatile Ni, V and Fe metalloporphyrins in crude oil samples. Gas chromatography connected with an atomic emission detector (AED) was used for the simultaneous detection of Ni 301.2 nm, V 292.4 nm and Fe 302.1 nm. Detection limit for these metals ranged from 0.05-5 pg/sec. The presence of volatile forms of these metals in several crude oil samples was confirmed.

Les Ebdon et al (1994) examined high temperature gas chromatography (HTGC) and high performance liquid chromatography (HPLC) coupled to ICP-MS for the determination of geoporphyryns from crude oil. HTGC-ICP-MS was used for rapid identification of Co, Cr, Fe, Ni, Ti, V and Zn metalloporphyrins. Quantitative data was obtained by HPLC-ICP-MS and HPLC with UV absorption detector. Levels of Ni geoporphyryns were in the range 15-20 µg/g. Khuhawar et al (1996) determined V in crude petroleum oils from lower Indus basin oil fields by GC after wet acid digestion. Tetradentate ligand bis(trifluoroacetylaceton)dl-stilbenediimine was used as chelating reagent for elution from GC column BP-1. Khuhawar and Arain (2006) reported liquid chromatographic method for the determination of V in the petroleum oils using 2-acetylpyridine-4-phenyl-3-thiosemicarbazone as derivatizing reagent from Kromasil 100 C-18 column. The vanadium contents were reported 0.32-2.3 µg/g with RSD 1.5-4.5%. Khuhawar et al reported normal phase HPLC procedure for the determination of V from crude petroleum oils using bis(salicylaldehyde) tetramethylethylenediimine as complexing reagent. The V contents in petroleum oils were reported 0.47-0.54 µg/g. Amoil et al (2006) analyzed V, Ni, Fe and Cu by HPLC using 10 cm reversed phase HPLC column. The metals were extracted with 8-hydroxyquinoline from acidic medium. The recoveries of metal ions were reported within 85-99% with HPLC separation time less than 4 min. Khuhawar and Lanjwani (1996) described simultaneous HPLC determination of Cu, Fe, Ni and V in crude petroleum oils based on pre-column complexation of analytes by bis(acetylpyridylmethane)ethylenediimine, followed by solvent extraction and HPLC separation on a reversed phase C-18 column with UV detection at 260 nm. The crude petroleum oils collected from the Indus south basin oil

fields were analyzed for metal contents. Caumette et al (2010) coupled size exclusion chromatography (SEC) and normal phase (NP) HPLC with ICP-MS and investigated molecular distribution of Ni and V in crude oils. The metal species in SEC fractions were reported to be sufficiently stable to be collected and preconcentrated to allow the development of a bidimensional chromatography SEC-NP-HPLC -ICP-MS for the probing of the metal distribution in crude oils in terms of molecular weight and polarity. Ellis et al (2011) coupled GC with ICP-MS for the determination of Ni and V in crude oils and its fractions. The method required a transfer line and ICP injector heated at 350 °C for rapid transfer of separated species from GC to the ICP-MS in heated argon gas. Ni and V determination was carried out in different crude oils. Mirza et al (2009) reported the determination of Fe, Co, Ni and V from crude petroleum oil samples after chelation with bis(salicylaldehyde) tetramethylethylenediimine by micellar electrokinetic chromatography (MEKC). Uncoated fused silica capillary was used with an applied voltage of 30 kV with photodiode array detection at 228 nm. SDS was added as micellar medium at pH 8.2 with sodium tetraborate buffer (0.1M). The determinations of Fe, Cu, Co, Ni and V in crude petroleum oils were reported with RSD within 1.1-4.1% (n=3) (Fig.2). Zeng and Uden (1994) used high temperature GC coupled with micro-wave induced plasma atomic emission for the determination of V, Ni and Fe porphyrins in crude oils.

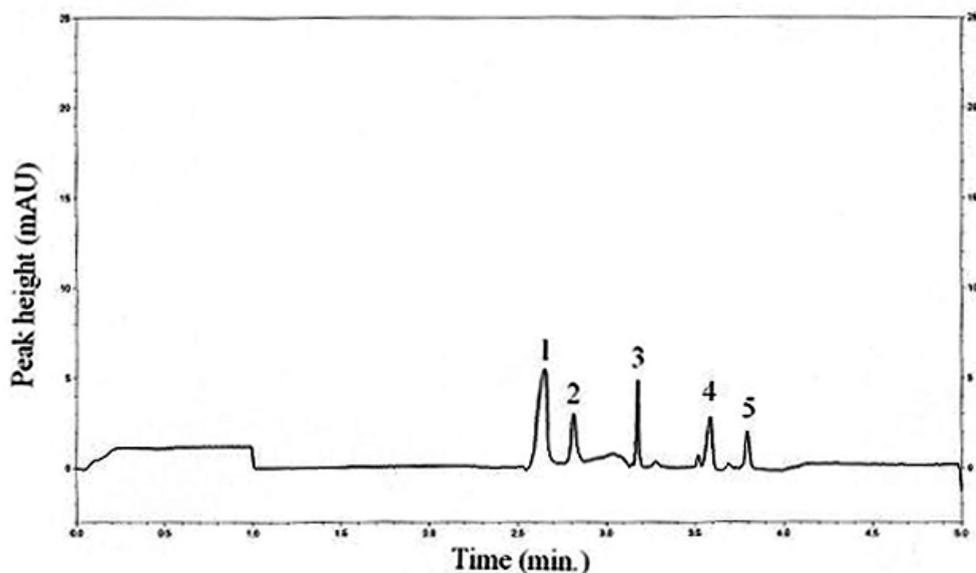


Fig. 2. Analysis of crude oil sample (1) H_2SA_2Ten , (2) $Co(II)$, (3) $V(IV)$, (4) $Fe(II)$, and (5) $Ni(II)$, as chelates of H_2SA_2Ten ., on uncoated silica capillary with total length 50 cm and effective length 38.8 cm with 75 μm id at 25°C. Run buffer tetraborate (0.1 M), SDS (0.04 M) 3:1 v/v, voltage 30 kV, pH 8.2, and photodiode array detection at 228 nm (Mirza et al 2009) with permission.

3.6 Other techniques

Other techniques can be used, but they are not widely reported. Gondal et al (2006) examined laser induced breakdown spectroscopy (LIBS) for the analysis of Ca, Fe, Mg, Cu, Zn, Na, Ni, K and Mo from Arabian crude oil residue samples. The dependence of time delay and laser beam energy on the elemental spectra was investigated. Quantitation was carried out by calibration of LIBS system with standard samples containing these trace elements. Mumoz et al (2007) examined electroanalytical stripping techniques for determination of Cu, Pb, Hg and Zn from crude oil and petroleum based fuels. The samples were decomposed by different microwave ovens before determinations. Square-wave stripping voltametry (SWSW) and stripping chromopotentiometry (SCP) at gold film electrodes were applied for Cu, Pb and Hg. Potentiometric stripping analysis (PSA) at mercury film electrodes was applied for Cu, Pb and Zn. SCP presented higher sensitivity for Cu and Hg at gold electrodes. PSA at mercury electrodes was preferred for Pb and Zn determinations. Xu et al (2005) extracted Ni and V petroporphyrins from Chinese heavy crude oils and then purified by silica gel chromatography. The extraction and purification were monitored using ultraviolet visible spectroscopy and the total petroporphyrins were analyzed using laser desorption ionization coupled with time of flight mass spectrometry. Yang et al (2003) determined Fe, Cu, Zn and Pb of engine oil by mild acid digestion and energy dispersive X-ray fluorescence spectrometry. A small aliquot (0.5 ml) of the acid digested sample was spotted onto a C-18 solid phase and then analyzed directly by X-ray fluorescence spectrometry.

3.7 Speciation of metal ions

Speciation studies are also directed towards isolation and identification of elements in different forms in crude oils. More is reported on V and Ni species. In majority of these studies focus has been the organometallic forms. The information may be of help in development of metal removal methods and in understanding the molecular environment associated in crude oils. The hyphenated HPLC and GC with ICP-MS, ICP-OES, and AAS have been examined (Les Ebdon et al., 1994), (Kumar et al., 1994), (Fish and Komlenic, 1984), (Fish et al., 1984), (Tao et al., 1998) for speciation studies of V, Ni and Hg in heavy crude petroleum, asphaltenes and natural gas condensates. Margueza et al (1999) used FAAS in comparison of three analytical methods to isolate and characterize V and Ni porphyrin from heavy crude oils. Lepri et al (2006) have carried out speciation analysis of volatile and nonvolatile vanadium compounds using high resolution continuum source atomic absorption spectrometry with a graphite furnace, taking advantage of higher volatility of the vanedyl porphyrin complexes, compared to nonporphyrins. Ackley et al (2005) examined capillary electrophoresis for the separation of metalloporphyrins, however the separation was limited to ionizable metalloporphyrins (with COOH functional group).

4. Conclusion

A significant improvement in the analytical instrumentation has been observed during last decade which has enabled to improve the sensitivity and selectivity of the determinations. The choice of the methodology for the determination of elements should be based on the matrix, the elements to be determined and the equipment available. Sample decomposition by wet digestion, preferably with microwave assisted heating is more robust and accurate

than direct sample introduction after dilution. Sample dilution is attractive because of its simplicity, but complete solubilization may be difficult due to the complex nature of the crude oil. The concentration of the diluted solution may change rapidly due to the adsorption on the walls of the container. Alternatively dilution with the three component system (emulsions and micro emulsions) are reported to provide better precision and accuracy of results. The use of aqueous standards for calibration is an added advantage. Electrothermal AAS with graphite furnace atomizer and ICP-MS appear to be more sensitive techniques. In case of ET-AAS stabilization of volatile compounds during pyrolysis step must be considered. The use of appropriate modifier, even for the element known as a nonvolatile may be necessary. ICP-MS requires periodic cleaning of lens, sampler and skimmer due to carbon build up. Polyatomic interferences in quadruple ICP-MS must also be considered. Metal speciation using hyphenated techniques has important place in oil analysis for less explored crude oils and resins.

5. References

- Ackley, K.L., Day, J.A., Caruso, J.A., (2005), Separation of metalloporphyrins by capillary electrophoresis with UV detection and inductively coupled plasma mass spectrometric detection, *J. Chromatogr. A.*, 888, 293-298.
- Akinlu, A, Smith, M.S. (2010), Supercritical water extraction of trace metals from petroleum source rock, *Talanta*, 81, 1346-1349.
- Akinlua, A., Ajayi, T.R., Adeleke, B.B., (2007), Organic and inorganic geochemistry of Northwestern Niger delta oils, *Geochem. J.* , 41, 271-281.
- Akinlua, H., Torto, N., Ajayi, T.R., (2008), Determination of rare earth elements in Nigar delta crude oil by inductively coupled plasma-mass spectrometry, *Fuel*,87, 1469-1477.
- Alberdi-Genolet, M., Tocco, R., (1999), Trace metals and organic geochemistry of the Machiques Member (Aptian-Albian) and La Luna Formation (Cenomanian-Campanian), Venezuela, *Chem. Geol.* 160, 19-38.
- Al-Shahristani, H., Al-Atya, M.J., (1972), Vertical migration of oil in Iraqi oil fields: Evidence based on vanadium and nickel concentrations, *Geochim. Cosmochina Acta*, 36, 929-938.
- Al-Swaidan, H.M. (1996), The determination of lead, nickel and vanadium in Saudi Arabian crude oil by sequential injection analysis inductively coupled plasma mass spectrometry, *Talanta*, 43, 1313-1319.
- Alvarado, J., Picon, A.R., de Vecchi, C.M., (1990), Microwave wet acid digestion in the preparation of crude oil samples for AAS determination of their chromium, copper, iron manganese, sodium, nickel, vanadium and zinc contents, *Acta Chim. Ven.* 41, 306-319.
- Amoli, H.S., Porgam, A., Sadr, Z.B., Mohanazadeh, F., (2006), Analysis of metal ions in crude oils by reversed phase high performance liquid chromatography using short column, *J. Chromatogr. A.*, 1118, 82-84.
- Amorin, F.A.C., Welz, B., Costa, A.C.S., Lepri, F.G., Vale, S.L.C., Ferreira, M.G.R., (2007), Determination of vanadium in petroleum and petroleum products using atomic spectroscopic techniques, *Talanta*, 72, 349-359.
- Andersen, S.I., Keul, A., Stenby .E., (1997), Variation in composition of sub fractions of petroleum asphaltene, *Pet. Sci. Technol.* 15, 611-645.

- Annual Book of ASTM Standard*, ASTM-D5863 (2000), Standard test method for determination of nickel, vanadium, iron and sodium in crude oils and residual fuels by flame atomic absorption spectrometry, American Society for Testing and Materials, West Conshohockm, PA.
- Annual Book of ASTM Standard*, ASTM-D5708 (2002), Standard test method for determination of nickel, vanadium and iron in crude oils and residual fuels by inductively coupled plasma (ICP) atomic emission spectrometry, American Society for Testing and Materials, West Conshohockm, PA.
- Annual Book of ASTM Standard*, ASTM-D5863-00A (2005), Method for determination nickel, vanadium, iron and sodium in crude oils and residual fuels by flame atomic absorption spectrometry, American Society for Testing and Materials, West Conshohockm, PA.
- Anselmi, A., Tittarelli, P., Katskov, D.A., (2002), Determination of trace elements in automotive fuels by filter furnace atomic absorption spectrometry *Spectrochim. Acta Part B*, 57, 403-411.
- Aske, N., Hallevik, H., Sjoblom, J., (2001), Determination of Saturate, Aromatic, Resin, and Asphaltenic (SARA) components in crude oils by means of infrared and Near-Infrared Spectroscopy, *Energy Fuels*, 15, 1304-1312.
- Aucelio, R.Q., Doyle, A., Pizzorano, B.S., Tristao, M.L.B., Campos, R.C., (2004), Electrothermal atomic absorption spectrometric method for the determination of vanadium in diesel and asphaltene prepared as detergentless micro-emulsions, *Microchem. J.* 78, 21-26.
- Baker, E.W., Louda, J.W., (1986), Porphyrin geochemistry of Atlantic Jurassic-Cretaceous black shales, *Adv. Organic Geochem.* 10, 905-914.
- Ball, J.S., Wenger, W.J., Hyden, H.J., Horr, C.A., Myers, A.T., (1960), Metal content of twenty-four petroleum, *J. Chem. Eng. Data* 5, 553-557.
- Barwise, A.J.G., (1987), Mechanisms involved in altering Deoxophylloerythroetioporphyrin-Etioporphyrin ratios in sediments and oils, *J. Am. Chem. Soc. Spec. Pub.* 344, 100-109.
- Barwise, A.J.G., (1990), Role of nickel and vanadium in petroleum classification, *Energy Fuel*, 4, 647-652.
- Barwise, A.J.G., Roberts, I., (1984), Diagenetic and catagenetic pathways for porphyrins in sediments, *Organic Geochem.* 6, 167-176.
- Bermejo-Barrera, P., Pita-Calvo, C., Bermejo-Marinez, F., (1991), Simple preparation procedures for vanadium determination in petroleum by atomic absorption spectrometry with electrothermal atomization, *Anal. Lett.*, 24, 447-458.
- Bethinetti, M., Spezia, S., Baroni, U., Bizzarri, G. (1995), Determination of trace elements in fuel oils by inductively coupled plasma mass spectrometry after acid mineralization of sample in microwave oven, *J. Anal. At. Spectrom.*, 10, 555-560.
- Bettinelli, M., Tittarelli, P., (1994), Evaluation and validation of Instrumental procedures for the determination of nickel and vanadium in fuel oils, *J. Anal. At. Spectrom.* 9, 805-812.
- Borszeki, J., Knapp, G., Halmos, P., Bartha, L., (1992), Sample preparation procedure for the determination of sulphur and trace metals in oil products by the ICP with a minitorch using emulsions, *Microchim. Acta*, 108, 157-161.
- Botto, R.I., (2002), Trace element analysis of petroleum naphthas and tars using direct injection ICP-MS, *Can. J. Anal. Sci. Spectrosc.* 47, 1-13.

- Botto, R.I., (1993), Applications of ultrasonic nebulization in the analysis of petroleum petrochemical by inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 8, 51-57.
- Botto, R.I., Zhu, J., (1996), Universal calibration for analysis of organic solution by inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 11, 675-681.
- Brandao, G.P., Camps, R.C., de Castro, E.V.R., de Jesus, H.C., (2006), Direct determination of nickel in petroleum by solid sampling-graphite furnace atomic absorption spectrometry, *Anal. Bioanal. Chem.* 386, 2249-2253.
- Brandas, G.P., de Campos, R.C., de Castro, E.V.R., de Jesus H.C. (2007), Direct determination of copper, iron and vanadium in petroleum by solid sampling graphite furnace atomic absorption spectrometry, *Spectrochim. Acta, Part B*, 62, 962-969.
- Brener, I.B., Zander, A., Kim, S. Shkolnik, J., (1996), Direct determination of lead in gasoline using emulsification and argon and argon-oxygen inductively coupled plasma atomic emission spectrometry, *J. Anal. Atom. Spectrom.* 11, 91-97.
- Brenner, I.B., Zander, A., Plantz, M., Zhu, J., (1997), Characterization of an ultrasonic nebulizer - member separation interface with inductively coupled plasma mass spectrometry for the determination of trace elements by solvent extraction, *J. Anal. At. Spectrom.* 12, 273-279.
- Bruhn, C.F., Cabalin, V.G., (1983), Direct determination of nickel in gas oil by atomic absorption spectrometry with electrothermal atomization, *Anal. Chim. Acta*, 143, 193-203.
- Burguera, J.L., Avila-Gomez, R.M., Burgera, M., de Salaguer, R.A., Salaguer, J.L., Bracho, C.L., Burguera-Pascu, M., Burguera-Pascu, C., Brunetto, R., Gallignani, M., de Pena, Y.P., (2003), Optimum phase-behavior formulation of surfactant oil/water system for the determination of chromium in heavy crude oil and in bitumen in water emulsion, *Talanta*, 61, 353-361.
- Cardarelli, E., Cifani, M., Mecozzi, M., Sechi, G., (1986), Analytical application of emulsions: Determination of lead in gasoline by atomic-absorption spectrophotometry, *Talanta*, 33, 279-280.
- Caumette, G., Lienemann, C.P. Merdrignae, I., Bouyssiere, B., Lobinski, R., (2010), Fractionation and speciation of nickel and vanadium in crude oils by size exclusion chromatography ICP-MS and normal phase HPLC-ICP-MS, *J. Anal. At. Spectrom.* 25, 1123-1129.
- Choudhry, G.G., (1983), Humic substances: Sorptive interactions with environmental chemicals, *Toxicol. Envir. Chem.* 6, 127-171.
- Damin, I.C.F., Vale, M.G.R., Silva, M.M., Welz, B., Lepri, F.G., Santos, W.N.I., Ferricira, M., (2005), Palladium as chemical modifier for the stabilization of volatile nickel and vanadium compounds in crude oil using graphite furnace atomic absorption spectrometry. *J. Anal. At. Spectrom.* 20, 1332-1336.
- das Gracias Andrade Korn, M., Sodre dos Santos, D.S., Welz, B., Rodrigues Vale, M.G., Teixeira, A.P., de Castrolima, D., Ferreira, S.L.C., (2007), Atomic spectrometric methods for the determination of metals and metalloids in automotive fuels. A review, *Talanta*, 73, 1-11.

- de Campos, R.C., dos Santos, H.R., Grinberg, P., (2002), Determination of copper, iron, lead and nickel in gasoline by electrothermal atomic absorption spectrometry using three-component solutions, *Spectrochim. Acta, Part B* 57, 15-28.
- de la Guardia, M., Lizondo, M.J., (1993), Direct determination of nickel in fuel oil by atomic absorption spectrometry using emulsion, *At. Spectr.*, 6, 208-211.
- de Oliveira, A.P., Gomes Neto, J.A., Ferreira, M.M.C., (2006), Use of exploratory data analysis in the evaluation of chemical modifier for direct determination and simultaneous metals in fuel ethanol by GFAAS, *Eclét. Quim.* 31,7-12.
- de Souza, R.M., da Silverira, C.L.P., (2006), Determination of Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in crude oil using inductively coupled plasma optical emission spectrometry and sample introduction as detergentless micro-emulsions, *Microchem. J.*, 82, 137-141.
- de, B.M Souza, R.M., Mathias., Searminio, I.S, de Silveira, C.L.P Aucelio, R.Q., (2006), Comparison between two sample emulsification procedures for the determination of Mo, Cr, V and Ti in diesel and fuel oil by ICP OES along with factorial design, *Microchim. Acta*, 153, 219-225.
- Dilli, S., Patsalides, E., (1981), Determination of vanadium in petroleum crudes and fuel oils by gas chromatography, *Anal. Chem. Acta*, 128, 109-119.
- Dittert, I.M., Silva, J.S.A., Araujo, R.G.O., Curtius, A.J., Welz, B., Becker-Ross, H., (2010), Simultaneous determination of cobalt and vanadium in undiluted crude oil using high resolution continuum source graphite furnace atomic absorption spectrometry. *J. Anal. At. Spectrom.* 25, 590-595.
- Duyck, C., Miekeley, N., Porto da Silveria, C.L., Aucelio, R.Q., Campos, R.C., Grinberg, P., Brandao, G. P., (2007), The determination of trace elements in crude oil and its heavy fractions by atomic spectrometry, *Spectrochim. Acta, Part B, At. Spectrom.* 62, 939-951.
- Duyck, C.; Miekley, N. Silveira, C.L.P. Szatmari, P., (2002), Trace element determination in crude oil and its fractions by inductively coupled plasma mass spectrometry using ultrasonic nebulization of toluene solutions, *Spectrochim. Acta*, 57B, 1979-1990.
- Ebdon, E.L., Evans, H., Pretorius, W. G., Rowland, S.J., (1994), Analysis of geoporphyryns by high-temperature gas chromatography ion chromatography with inductively coupled plasma mass spectrometry., *J. Anal. At. Spectrom.* 9, 939-943.
- Ekanem, E.J., Lori, J.A., Thomas, S.A., (1998), Ashing procedure for the determination of metals in petroleum fuels, *Bull. Chem. Soc. Ethiop.* 2, 9-16.
- El-Gayar, M., Mostafa, M.S., Abdelfallah, A.E., Barakat, A.O., (2002), Application of geochemical parameters for classification of crude oils from Egypt into source-related types , *Fuel Process. Technol.* 79, 13-28.
- Ellis, J., Rechsteiner, C., Moir, M., Wilbur, S. (2011), Determination of volatile nickel and vanadium species in crude oil and crude oil fractions by gas chromatography coupled to inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, 26, 1674-1678.
- Encyclopedia Britannica*, Available at <http://www.britannica.com>., Accessed October 16,2011.
- Evans, C.R., Rogers, M.A., Baily N.J.I., (1971), Evolution and alteration of petroleum in western Canada ,*Chem. Geol.* 8,147-170.

- Fabec, J.L., Ruschak, M.L., (1985), Determination of nickel, vanadium and sulphur in crude and heavy crude fractions by inductively coupled argon plasma atomic emission spectrometry and flame atomic absorption spectrometry, *Anal. Chem.* 57, 1853-1863.
- Fan, T.G., Buckley, J.S., (2002), Rapid and accurate SARA analysis of medium gravity crude oils, *Energy Fuels*, 16, 1571-1575.
- Fish, R.H., Komlenic, J.J., (1984), Molecular characterization and profile identification of vanadyl compounds in heavy crude petroleum by liquid chromatography/graphite furnace atomic absorption spectrometry, *Anal. Chem.* 56, 510-517.
- Fish, R.H., Komlenic, J.J., Wines, B.K. (1984) Characterization and comparison of vanadyl and nickel compounds in heavy crude petroleum and asphaltene by reverse phase and size-exclusion liquid chromatography/graphite furnace atomic absorption spectrometry, *Anal. Chem.* 56, 2452-2460.
- Gondal, M.A., Hussain, Y., Baig, M.A., (2006), Detection of heavy metal in Arabian crude oils residue using laser induced breakdown spectroscopy, *Talanta*, 69, 1072-1078.
- Gonzalez, M.C., Rodriguez, A.R., Gonzalez, V., (1987), Determination of vanadium, nickel, iron, copper, and lead in petroleum fraction by atomic absorption spectrophotometry with a graphite furnace, *Mirochem. J.* 57, 94-106.
- Goreli, M., Vale, V., Silva, M.M., Damin, I.C.F., Filho, P.J. S., Welz, B., (2008), Determination of volatile and non-volatile nickel and vanadium compounds in crude oil using electrothermal atomic absorption spectrometry after oil fractionation into saturates, aromatics, resins and asphaltene, *Talanta*, 74, 1385-1391.
- Guidr, J.M., Snaddon, J., (2002), Fate of vanadium determined by nitrous oxide-acetylene flame atomic absorption spectrometry in unburned and burned Venezuelan crude oil, *Microchem. J.*, 73, 363-366.
- Hammond, J.L., Lee, Y., Noble, C.O., Beck, J.N., Proffitt, C.E., Snaddon, J., (1998), Determination of cadmium, lead and nickel by simultaneous multi element flame atomic absorption spectrometry in burned and unburned Venezuelan crude oils, *Talanta*, 47, 261-66.
- Istas - Flores, C.A., Buenrostro-Gonzalez, E., Lira-Galeana, C., (2005), Comparisons between open column chromatography and HPLC. SARA fractionations in petroleum, *Energy Fuels*, 19, 2080-2088.
- Jakubowski, N., Feldmann, J. Stuewere, D., (1992), Analytical improvement of pneumatic nebulization in ICP-MS by desolvation, *Spectrochim. Acta*, 47B, 107-118.
- Kaminski, T.J., Fogler, H.S., Wolf, N., Wattana, P., Mairal, A., (2000), Classification of asphaltene via fractionation and the effect of heteroatom content on dissolution kinetics, *Energy Fuels*, 14, 25-30.
- Kelly, R.W., Long, S.E., Mann, J.L., (2003), Determination of mercury in SRM crude oils and refined products by isotope dilution cold vapour ICP-MS using closed system combustion, *Anal. Bioanal. Chem.*, 376, 753-758.
- Khuhawar, M.Y., Arain, G.M., (2006), Liquid chromatographic determination of vanadium in petroleum oils and mineral ore samples using 2-acetylpyridine-4-phenyl-3-thiosemicarbazone as derivatizing reagent, *Talanta*, 68, 535-541.
- Khuhawar, M.Y., Lanjwani, S.N., (1996), Simultaneous high performance liquid chromatographic determination of vanadium, nickel, iron and copper in crude

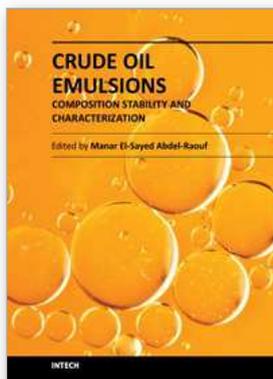
- petroleum oils using bis(acetylaldehyde)ethylenediimine as complexing reagent, *Talanta*, 43, 767-770.
- Khuhawar, M.Y., Lanjwani, S.N., Khaskhely, G.Q., (1995), High performance liquid chromatographic determination of vanadium in crude petroleum oils using bis(salicylaldehyde)tetramethylethylenediimine, *J. Chromatogr. A*, 689, 39-43.
- Khuhawar, M.Y., Memon, A.A., Bhangar, M.I., (1997), Capillary gas chromatographic determination of vanadium in crude petroleum oil using fluorinated ketoamines as derivatizing reagents, *J. Chromatogr. A*, 766, 159-164.
- Korn, M.G.A., Andrade, J.B., de Jesus, D.S., Valfrado, A., Lemos, M.L.S.F., Bandeira, W.N.L., dos Santos, M.A., Bezerra, F.A.C., Amorim, A.S., Ferreira, S.L.C., (2006), Separation and preconcentration procedures for the determination of lead using spectrometric techniques: A review, *Talanta*, 69, 16-24.
- Kowalewask Z., Ruszezynska, E., (2005), Cu determination in crude oil distillation, products by atomic absorption and inductively coupled plasma mass spectrometry after analyte transfer to aqueous solution, *Spectrochim. Acta*, 60B, 351-359.
- Kumar, U., Dorzey, J.G., Caruzo, J.A., (1994), Metalloporphyrins speciation by liquid chromatography and inductively coupled plasma mass spectrometry, *J. Chromatogr. Sci.*, 32, 282-285.
- Kumat, S.J., Gangadharan, S., (1999), Determination of trace elements in naphtha by inductively coupled plasma mass spectrometry using water-in-oil emulsion, *J. Anal. At. Spectrom.*, 14, 967-971.
- Langmyhr, F.J., Adalen, U., (1980), Direct atomic absorption spectrometric determination of copper, nickel and vanadium in coal and petroleum coke, *Anal. Chim. Acta*, 115, 365-368.
- Las Ebdon, E.H.V., Warren, G.R., Stephen, J.R., (1994), Analysis of geoporphyrins by high temperature inductively coupled plasma mass spectrometry and high performance liquid chromatography inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 9, 939-943.
- Lepri, F.G., Welz, B., Borges, D.L.G., Silva, A.F., Vale, M.G.R., Heitmann, U., (2006), Speciation analysis of volatile and nonvolatile vanadium compounds in Brazilian crude oils using high resolution continuum source graphite furnace atomic absorption spectrometry, *Anal. Chim. Acta*, 558, 195-200.
- Lord, C.J., (1991), Determination of trace metals in crude oil by inductively coupled plasma mass spectrometry with micro-emulsion sample introduction, *Anal. Chem.*, 63, 1594-1599.
- Luz, M.S., Oliveira, P.V., (2011), Simultaneous determination of Cr, Fe, Ni and V in crude oil by emulsion sampling graphite furnace atomic absorption spectrometry, *Anal. Methods*, 3, 1280-1283.
- Magyar, B., Lieneman, P., Vonmont, H., (1986), Some effects of aerosol drying and oxygen feeding on the analytical performance of an inductively coupled nitrogen-argon plasma, *Spectrochim. Acta*, 41B, 27-38.
- Mansfield, C.T., Berman, B.N., Thomas, J.V., Mehrotra, A.K., McCann, J.M., (1995), Lubricants : Petroleum and coal, *Anal. Chem.*, 67, 333R-337R.
- Marqueza, N., Ysambertta, F., De La Cruz, C. (1999), Three analytical methods to isolate and characterize vanadium and nickel porphyrins from heavy crude oils, *Anal. Chim. Acta*, 395, 343-349.

- Meeravali, N.N., Kumar, S.J., (2001), The utility of a W-Ir permanent chemical modifier for the determination of Ni and V in emulsified fuel oils and naphtha by transverse heated electrothermal atomic absorption spectrometer, *J. Anal. At. Spectrom.*, 6, 527-532.
- Mello, P.A., Pereira, J.S.F., Moraes, D.P., Dressler, V.L., Flores, E.M.M., Knapp, G., (2009), Nickel, vanadium and sulphur determination by inductively coupled plasma optical emission spectrometry in crude oil distillation residues after microwave, induced combustion, *J. Anal. At. Spectrom.* 24, 911-916.
- Microwave assisted acid digestion of sediments, sludges, soils and oils, (1994), US-EPA, A 3051, <http://www.epa.gov/osw/hazard/testmethods>.
- Milner, O.J., Glass, J.R., Kirchner, J.P., Yurick, A.N., (1952), Determination of trace metals in crudes and other petroleum oils, *Anal. Chem.*, 24, 1728-1732.
- Mirza, M.A., Kandhro, A.J., Khuhawar, M.Y., Arain, R., (2009), MEKC determination of vanadium from mineral ore and crude petroleum oil samples using precapillary chelation with bis(salicylaldehyde)tetra-methylethylenediimine, *J. Sep. Sci.*, 32, 3169-3177.
- Munoz, P.A.A., Correia, P.R.M., Nascimento, A.N., Silva, C.S., Oliveira P.V., Angnes, L., (2007), Electroanalysis of crude oil and petroleum based fuel for trace metals: Evaluation of different micro-wave assisted sample decompositions and stripping techniques. *Energy and Fuel*, 21, 295-302.
- Munoz, R.A.A., Correia, P.R.M., Nascimento, A.N., Silva, C.S., Oliveira, P.V., Angnes, L., (2007), Electroanalysis of crude oil and petroleum based fuels for trace metals, Evaluation of different microwave-assisted sample decomposition and stripping techniques, *Energy and Fuel*, 21, 295-302.
- Murillo, M., Chirinos, J., (1994), Use of emulsion systems for the determination of sulphur, nickel and vanadium in heavy crude oils samples by inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 9, 237-240.
- Nakamoto, Y., Ishimaru, T., Endo, N., Matsusaki, K., (2004), Determination of vanadium in heavy oils by atomic absorption spectrometry using graphite furnace coated with tungsten, *Anal. Sci.* 20, 739-741.
- Odermatt, J., Curiale, J., (1991), Organically bound metals and biomarkers in the Monterey formation of the Santa Maria basin, California, *Chem. Geol.* 91, 99-113.
- Oliveira, E., (2003), Sample preparation for atomic spectroscopy: evolution and future trends *J. Braz. Chem. Soc.*, 14, 1-17.
- Osibanjo, O., Kakulu, S.E., Ajayi, S.Q., (1984), Analytical application of inorganic salt standards and mixed-solvent systems to trace-metal determination in petroleum crudes by atomic absorption spectrophotometry, *Analyst*, 109, 109-127.
- Ozcan, M., Akman, S., (2005), Determination of Cu, Co and Pb in gasoline by electrothermal atomic absorption spectrometry using aqueous standard addition in gasoline-ethanol-water three-component system, *Spectrochim Acta*, Part B 60, 399-402.
- Pelizzetti, E., Pramauro, E., (1985), Analytical applications of organized molecular assemblies, *Anal. Chim. Acta*, 169, 1-29.
- Pena, M.E., Manjarrez, A., Campero, A., (1996), Distribution of vanadyl porphyrins in a Mexican offshore heavy crude oil, *Fuel processing Technol.*, 46, 171-182.
- Periria, J.S.F., Moraes, D.P., Antes, F.G., Dieht, L.D., Santos, F.P., Guimaraes, R.C.L., Fonseca, T.C.O., Dressler, V.L., Flores, E.M.M., (2010), Determination of metals and

- metalloids in light and heavy crude oil by ICP-MS after digestion by microwave-induced combustion, *Microchem. J.*, 96, 4-11.
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2nd ed., *The biomarker guide, Volume 2: Biomarkers and isotopes in the petroleum exploration and earth history*, Cambridge University Press, New York, 2004.
- Platteau, O., Carrillo, M., (1995), Determination of metallic elements in crude oil-water emulsion by flame AAS, *Fuel*, 74, 74-76.
- Quadros, D.P.C., Chaves, E.S., Lepri, F.G., Borges, D.L.G., Welz, B., Becker-Ross, H., Curtius, A.J., (2010), Evaluation of Brazilian and Venezuelan, Crude oil samples by means of the simultaneous determination of Ni and V as their total and non-volatile fractions using high resolution continuum source graphite furnace atomic absorption spectrometry, *Energy Fuels*, 24, 5907-5911.
- Quimby, B.D, Dryden, P.C. Sullivan, J.J. (1991), A selective detection of volatile nickel, vanadium and iron porphyrins in crude oils by gas chromatography atomic emission spectroscopy, *J. High Res. Chromatogr.*, 14, 110-116.
- Ridyk, B.M., Alturki, Y.I.A., Pillinger, C.T., Eglinton, G., (1975), Petroporphyrins as indicators of geothermal maturation, *Nature* 256, 563-565.
- Rudzinski, W.E., Aminabhavi, T.M., (2000), A review on extraction and identification of crude oil and related products using supercritical fluid technology, *Energy Fuels*, 14, 464.
- Sant Ana, F.W., Santelli, R.E., Cassella, A.R., Cassella, R.J., (2007), Optimization of an open focused microwave oven digestion procedure for determination of metal in diesel oil by inductively coupled plasma optical emission spectrometry, *J. Hazardous Materials*, 149, 67-74.
- Santella, R.E., Bezerra, M.A., Freire, A.S., Oliveira, E.P., de Carvalho, M.F.B., (2008), Non-volatile vanadium determination in petroleum condensate, diesel and gasoline prepared as detergent emulsion using GFAAS, *Fuel*, 87, 1617-1622.
- Sebor, G., Long, I., Kolihoval, D., Wasser, O., (1982) Effect of the type of organometallic iron and copper compounds on the determination of both metals in petroleum samples by flame atomic absorption spectroscopy, *Analyst*, 107, 1350-1355.
- Seidl, P.R., Chrisman, E.C.A.N., Carvalin, C.C.V., Leal, K.Z., de Menezes, S.M.C., (2004), NMR analysis of asphaltenes separated from vacuum residues by selected solvents, *J. Dispersion Sci. Technol.* 25, 349-353.
- Seidl, P.R., Chrisman, E.C.A.N., Siwa, R.C., de Menezes, S.M.C., Teixeira, M.A.G., (2004), Critical variables for the characterization of asphaltenes extracted from vacuum residues, *Pet. Sci. Technol.*, 22, 961-971.
- Sharma, B.K., Sarowha, S.L.S. Bhagat, S.D., Tiwari, R.K., Gupta, S.K., Venkataramani, O.S., (1998), Hydrocarbon group type analysis of petroleum heavy fractions using the TLC-FID technique, *J. Anal. Chem.*, 360, 539-544.
- Silva, M.M., Damin, I.C.F.; Vale, M.G.R., Welz, B., (2007), Feasibility of using solid sampling graphite furnace atomic absorption spectrometry for speciation analysis of volatile and non-volatile compounds of nickel and vanadium in crude oil. *Talanta*, 71, 349-359.
- Speight, J.G., (2001), *Handbook of Petroleum Analysis*, John Wiley and Sons Inc. New Jersey, 519.

- Stiger, H.P.M., de Haan, R., Guicherit, C.P.A., Dekkers, M.L., (2000), Determination of cadmium, zinc, copper, chromium and arsenic in crude oil cargoes, *Environ. Pollut.* 107, 451-464.
- Tan, S.H., Horlick, H., (1986), Background spectral features in inductively coupled plasma/mass spectrometry, *Appl. Spectrosc.* 40, 445-460.
- Tao, H., Murakami, T., Tominaga, M., Miyazaki, A., (1998), Mercury speciation in neutral gas condensate by gas chromatography - inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 13, 1085-1093.
- Teserovsky, E., Arpadjan, E., (1991), Behaviour of various organic solvents and analytes in electrothermal atomic absorption spectrometry, *Anal. Atom. Spectrom.* 6, 487-491.
- Thomaidis, N.S., Piperaki, E.A., (1996), Comparison of chemical modifiers for the determination of vanadium in water and oil samples by electrothermal atomization atomic absorption spectrometry, *Analyst.* 121, 111-117.
- Treibs, A., (1936), Chlorophyll and minerals in organic Häminderivate, *Angew Chemie*, 49, 682-686.
- Trindade, J.M., Marques, A.L., Lopes, G.S., Margues, E.P., Zhang, J., (2006), Arsenic determination in gasoline by hydride generation atomic absorption spectroscopy combined with a factorial experimental design approach, *Fuel*, 85, 2155-2161.
- Turunen, M., Peraniemi, S., Ahlgren, M., Westerholm, H., (1995), Determination of trace elements in heavy oil samples by graphite furnace and cold vapour atomic absorption spectrometry after acid digestion, *Anal. Chim. Acta*, 311, 85-91.
- Udoh, A.P., Thomas, S.A., Ekanem., (1992), Application of P-xylenesulphonic acid as ashing reagent in the determination of trace metals in crude oils, *Talanta*, 39, 1591-1595.
- Vale, M.G.R., Damin, I.C.F., Klassen, A., Silva, M.M., Welz, B., Silva, A.F., Lepri, F.G., Borges, D.L.G., Heitmann., (2004), Method development for the determination of nickel in petroleum using line-source and high resolution continuum-source graphite furnace atomic absorption spectrometry, *Microchem. J.*, 77, 131-140.
- Vale, M.G.R., Silva, M.M., Damin, I.C.F., Sanches Filho, P.J., Welz, B., (2008), Determination of volatile and non-volatile nickel and vanadium compounds in crude oil using electrothermal atomic absorption spectrometry after oil fraction into saturates, aromatics, resins and asphaltenes, *Talanta*, 74, 1385-1391.
- Vilhunen, J.K., Bohlen, A., Schmeling, M., Klockenkamper, R., Klockow, D., (1997), Total reflection X-ray fluorescence analyses of samples from oil refining and chemical industries, *Spectrochim Acta*, B, 52, 953-959.
- Wilhelm, S.M., Bloom, N., (2000), Mercury in petroleum (Review), *Fuel processing Technology*, 63, 1-27.
- Wilhelm, S.M., Liang, L., Kirchgesser, D., (2006), Identification and properties of mercury species in crude oil, *Energy Fuels* 20, 180-186.
- Wondimu, W., Goessler, W., Irgolie, K.J., (2000), Microwave digestion of residual fuel oil for the determination of trace elements by inductively coupled plasma mass spectrometry. *Fresenius J. Anal. Chem.*, 367, 35-42.
- Xu, H., Que, G., Yu, D., Lu, J.R., (2005), Characterization of petroporphyrins using ultraviolet-visible spectroscopy and laser desorption ionization time of flight mass spectrometry, *Energy and Fuel*, 19, 517-524.

- Yan, Z., Hou, X., Jones, B. T., (2003), Determination of wear metals in engine oil by mild acid digestion and energy dispersive X-ray fluorescence spectrometry using solid phase extraction disks, *Talanta*, 59, 673-680.
- Zang, Y.D. Uden, P.C., (1994), High temperature gas chromatography - atomic emission detection of metalloporphyrins in crude oils, *J. High Resolut. Chromatogr.*, 17, 217-222.



Crude Oil Emulsions- Composition Stability and Characterization

Edited by Prof. Manar El-Sayed Abdul-Raouf

ISBN 978-953-51-0220-5

Hard cover, 230 pages

Publisher InTech

Published online 02, March, 2012

Published in print edition March, 2012

Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

M.Y. Khuawar, M. Aslam Mirza and T.M. Jahangir (2012). Determination of Metal Ions in Crude Oils, Crude Oil Emulsions- Composition Stability and Characterization, Prof. Manar El-Sayed Abdul-Raouf (Ed.), ISBN: 978-953-51-0220-5, InTech, Available from: <http://www.intechopen.com/books/crude-oil-emulsions-composition-stability-and-characterization/determination-of-metal-ions-in-crude-oils>

INTECH

open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.