DEVELOPMENT OF GREENER SAMPLE PREPARATION METHODS FOR EXTRACTION AND SPECTROMETRIC DETERMINATION OF METALS IN SELECTED FUEL SAMPLES

By

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DECLARATION

I hereby declare that this dissertation, which I herewith submit for the research qualification "Masters in Chemistry" to the University of South Africa, Department of Chemistry, is my work and it has not previously been submitted by me to any other institution to obtain any degree.

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DEDICATION

This dissertation is dedicated to my parents (Sibongile and Mphesheya Mdluli), my siblings (Sifiso and Siyabonga), my fiancé (Nomfundo Sandra Mthembu) and my kids, Wandile and Mandisa for their support and understanding during the period of my study.

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PUBLICATIONS

This thesis consists of four manuscripts, these includes published manuscripts, submitted manuscripts and manuscripts in preparation.

1. Njabulo S. Mdluli, Philiswa N. Nomngongo & Nomvano Mketo. A critical review on application of extraction methods prior to spectrometric determination of trace-metals in oily matrices, *Critical Reviews in Analytical Chemistry.* DOI: 10.1080/10408347.2020.1781591 (PUBLISHED).
2. Njabulo S. Mdluli. Philiswa N. Nomngongo & Nomvano Mketo. Multivariate optimization of a greener microwave-assisted hydrogen peroxide digestion method followed by inductively coupled optical emission spectroscopic analysis for the determination of metal ions in selected fuel oils (SUBMITTED).
3. Njabulo S. Mdluli. Philiswa N. Nomngongo & Nomvano Mketo. Ionic liquid assisted extraction induced by emulsion breaking procedure prior to ICP-OES analysis for metal determination in crude oil, diesel, kerosene and gasoline samples (IN PREPARATION).
4. Njabulo S. Mdluli. Philiswa N. Nomngongo & Nomvano Mketo. Magnetic solid phase extraction based on $Fe_3O_4@Al_2O_3$ adsorbent for simultaneous preconcentration of selected metal ions from crude oil, diesel, kerosene and gasoline samples followed by ICP-OES determination (IN PREPARATION).

CONFERENCE PRESENTATIONS

1. University of South Africa Florida campus, CAES-CSET Innovation week (19 November 2021). Poster presentation, Njabulo S. Mdluli. Philiswa N. Nomngongo & Nomvano Mketo, "*Ionic liquid assisted extraction induced by emulsion breaking procedure prior to ICP-OES analysis for metal determination in crude oil, diesel, kerosene and gasoline samples*"

ABSTRACT

Crude oil is an unrefined petroleum which forms because of dead organisms buried under mud over a long period of time (million years). The mud is then converted to sedimentary rocks, which create intense heat and pressure, resulting in the formation of crude oil reservoir. However, crude oil contains trace elements which cannot be controlled as they occur naturally during crude oil formation. Some of these elements are unfavourable. For example, Cr, Fe and Ni can cause severe corrosion on refinery equipment. Additionally, Cd, Hg, Pb and As are associated with air pollution, while Ni, V, Pb, Pt and As are known to be catalyst poisoners during refinery process. The crude oil is then refined to form crude oil derivatives like gasoline, diesel, kerosene, just to name the few. Therefore, the challenges associated with metal ions in crude oil and crude oil derivatives have ignited an interest for many researchers to conduct investigations on the development of analytical methods for quantitative determination of metal ions in various fuel oils. However, most of the literature reported methods showed several limitations which include the use of toxic and costly reagents, long extraction time, high temperatures, etc.

Therefore, this study aimed at developing greener and cost-effective sample preparation methods, followed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) for the determination of metals and metalloids in crude oil and crude oil derivatives (gasoline, diesel and kerosene). The developed sample preparation methods were; a) microwave assisted-hydrogen peroxide digestion (MA-HPD), b) ionic liquid assisted-extraction induced by emulsion breaking (ILA-EIEB) and magnetic-solid phase extraction (m-SPE). For all the above mentioned sample preparation methods, multivariate optimization was used for the determination of the most influential parameters. During multivariate optimisation of MA-HPD it was observed that 245 ℃ microwave temperature, 25 minutes digestion time, 0.1 g sample mass and 5 M H_2O_2 were the optimum digestion conditions with accepted accuracy (104.8-117.7%) and precision (≤ 4.1%). The proposed MA-HPD method resulted in MDL of 0.046, 0.030, 0.408 and 0.057 µg/g for Ba, Na, Ni and V, respectively. The concentration levels of the selected metals (Al, Ba, Cd, Co, Cr, Cu, Mg, Na, Ni, Pb, Sb, Ti and V) ranged between 1.21-58.86 µg/g, 0.55-36.37 µg/g, 0.56-47.0 µg/g and 0.6-35.1 µg/g for crude-oil, diesel, kerosene and gasoline, respectively. The sensitivity, accuracy and precision of the MA-HPD method made it qualify to be an alternative digestion method for mineralization of fuel oils.

Additionally, ILA-EIEB and the m-SPE were evaluated for the preconcentration of the selected elements (As, Ba, Cd, Cr, Cu, Mn, Mo, Ti, V, Pb, Sb, Sn, Tb, Te and Zn) that were in trace levels. The optimum conditions for ILA-EIEB were found to be 0.035 % for 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl), 18% for nitric acid, 15% for Triton X-100 and 0.1 g for sample mass. The emulsions were broken by heating at a controlled water bath at 80 ±2 °C for 30 ±4 minutes and a further centrifugation step was performed for 15 minutes at 3 500 rpm. The optimum conditions were able to give good accuracy (80.1-101%) and precision (1.9-4.7 %). This method was also able to report very low MDL for Ba, Na, Ni and V which were 0.107, 0.013, 3.494 and 0.560 µg/g, respectively. The concentrations of As (0.084- 0.46 µg/g) reported in this study ware in line with other literature reports. Alternatively, m-SPE was also used for the preconcentration of selected metals in fuel oils. The $Fe_3O_4@Al_2O_3$ nanoparticles were used as adsorbents and their formation was confirmed by various characterization techniques (FT-IR, SEM-EDX, TEM, XRD and UV-Vis). The two level fractional factorial design (FrFD) and the central composite design (CCD) resulted in optimum conditions of 40 mg adsorbent mass, 35 minutes sonication time, 6.5 pH, 20 µg/L spike concentration and 1M of HNO_3 eluent concentration. The optimised m-SPE was able to give good accuracy (74-96%), precision (0.9-4.8%) and MDL (0.114-0.62 µg/g). The optimised and validated m-SPE method was then applied in real fuel oil samples. All the investigated metal ions below 10 µg/g.

The ILA-EIEB was compare with m-SPE, in terms of their sensitivity, accuracy and precision. The ILA-EIEB was more sensitive (0.013-3.494 µg/g), accurate (80.1-101.1%) and precise (1.9-4.7%) than m-SPE (0.114-0.62 µg/g, 74-96% and 0.9-4.8%, respectively). Therefore it can be concluded that the three sample preparation methods (MA-HPD, ILA-EIEB and m-SPE) were greener. This is because, dilute H_2O_2 coverts to water during MA-HPD, ionic liquids are environmentally friendly as compared to organic solvent when performing EIEB and $Fe_3O_4@Al_2O_3$ used as adsorbent in m-SPE is also environmental friendly and accelerates the separation process by the use of an external magnet.

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LIST OF ABBREVIATIONS

AAS-Atomic Absorbtion Spectrometry ... 7
CRM- Certified Reference Material ... 55
E.T-Extraction time ... 43
ED-XFS-Energy Dispersive -X-ray Fluorescence Spectrometry ... 19
EIEB-Extraction induced by emulsion breaking ... 10
ETV-ICP-MS-Electrothermal Vaporisation-Inductively Coupled Plasma-Mass Spectrometry ... 19
FT- Fischer Tropsch ... 4
GF-AAS-Graphite Furnance Atomic Absorption Spectrometry ... 19
ICP-MS- Inductively coupled plasma mass spectrometry ... 7
ICP-OES -Inductively Coupled Plasma Optical Emission Spectrometry ... 8
LA-ICP-TOFMS- Laser Ablation- Inductively Coupled Plasma- Time - of - Flight Mass Spectrometry ... 19
LLME-Liquid-liquid microextraction ... 39
LOD- Limit of detection ... 21
LPG-Liquified Petrolium Gases ... 4
MAAD-Microwave Assisted Acid Digestion ... 29
MAE-Microwave-assisted extraction ... 63
MA-HPD-Microwave assisted hydrogen peroxide digestion ... 10
MIC-Microwave induced combustion ... 29, 39, 43
MP-AES- Microwave Plasma- Atomic Emission Spectrometry ... 19
MSPE-Magnetic solid phase extraction ... 10
MW-AHPD- Microwave Assisted Hydrogen Peroxide Digestion ... 29
NAA-Neutron Activation Analysis ... 7
RP-DLLME- Reversed -Phase Dispersive Liquid Liquid Micro-extraction ... 41
SD-LLME ... 39
XRF-X-ray fluorescence spectrometry ... 7

CHAPTER 1 (INTRODUCTION)

Preamble

This chapter provides the background information about crude oil formation, composition, crude oil types, oil conversion and general negative effects of metal ions. This chapter also includes the problem statement, hypothesis and justifications for conducting the current research project. Finally, the ultimate goal and specific objectives addressed by the study are listed, followed by the scope of the entire dissertation.

1.1 Background information

Since the beginning of industrial revolution, there has been an increase in the use of fossil fuels for energy production. For example, coal has been widely used for the production of electricity in many countries such as South Africa, United State of America, China, India and Russia, just to mention the few [1]. Coal has also been used during Fischer-Tropsch catalytic system at SASOL, for the production of synthetic fuels (synfuels) like gasoline, diesel, kerosene, lubricating oil, etc. [2]. On the other hand, fuel oils can also be obtained from refining process of crude oil. The latter is a non-renewable energy resource, which is commonly refined in a fractional distillation column, where its derivatives are separated based on their boiling point differences to produce: (i) hydrocarbon gases (methane, ethane, propane etc.); (ii) fuel oils like (gasoline, kerosene, jet fuel and diesel); (iii) lubricating oils (grease), etc. [3]. Therefore, the above facts show that humans overreliance on fossil fuels for their daily survival. The following sections address fossil fuels like crude oil and selected crude oil derivatives which include diesel, kerosene and gasoline.

1.1.1 Crude oil formation

Crude oil is a fossil fuel that occurs in the earth's crust and it is mainly composed of hydrocarbons with a proportion of carbon (82-87%) and hydrogen (12-15%) [4]. Crude oil forms as a result of large quantities of plants and animals that die and get sandwiched between the muds. Over million years of time, the mud forms sedimentary rock that creates very high pressure and temperature, and the organic material from the plant and animal remains get to be converted to hydrocarbons [5]. At a later stage, the sedimentary rock becomes porous and non-porous. [6]. These rock structures become folded due to plate tectonic movement resulting in the formation of spaces between the porous and non-porous rocks. Then, the hydrocarbons move up the porous rock into the spaces forming a reservoir below non-porous rock (**Fig.1.1**). In the reservoir, the hydrocarbon gases form the first layer on top as they are less dense, followed by the crude oil and fossil water at the bottom [5]. It is worth noting that a young crude oil reservoir (65-145 million years) generally has heavy crude oil (>20 American Petroleum Institute [API] [7]. In contrast, light crude oil is normally observed in oil reservoirs that are older than 145 million years [8]. Additionally, the levels of sulfur are influenced by the specific gravity of the crude oil, the higher the specific gravity, the lesser the sulfur content. Therefore, levels of sulfur affects the quality of the oil, as crude oil with less sulfur content has high market value in comparison to the one with the higher sulfur content [9]. Sulphur normally ranges from 0.05-5% in crude oil and is not the only problematic element [10].

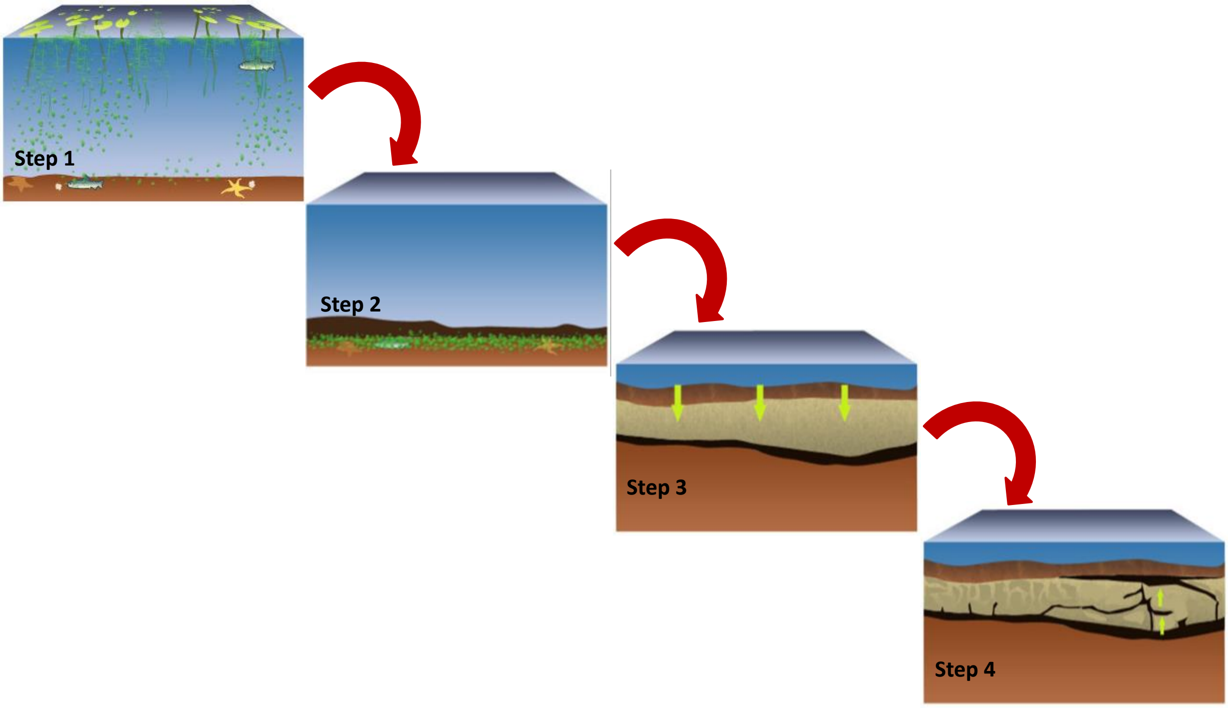

Figure 1.1. Crude oil formation

1.1.2 Crude oil composition and types

The presence of metals in crude oil cannot be prevented or controlled, as these metals occur naturally during crude oil genesis. Metals like Ni and V are naturally found in crude oil as salts or/and as organometallic compounds (**Fig 1.2**) [11, 12]. However, some of the metals (Co and Fe) are added during the refinery process, storage and some during transportation of crude oil derivatives [13]. Additionally, crude oil consists of pure hydrocarbons (branched or straight chains) and heteroatom hydrocarbons [14]. Heteroatoms are the atoms that replaces hydrogen in hydrocarbons, thereby changing the physical and chemical properties of the overall compound [15]. These heteroatoms include O, S, N, Cl, P, etc. and can also combine to form different functional groups which may include the carboxyl, hydroxyl, ketone, aldehyde, amine, amide groups, etc. On the other hand, pure hydrocarbons are compounds that contain only hydrogen and carbon and are either saturated or unsaturated. Saturated hydrocarbons contain single bonds with all the hydrogen bonded to all the carbon present while in unsaturated hydrocarbons, double or triple bonds are observed [16]. Crude oil can also contain the inorganic compounds which include the organometallic compounds (Ni, V, Fe and Cu) and inorganic salts (Na, Ca and Mg) [17].

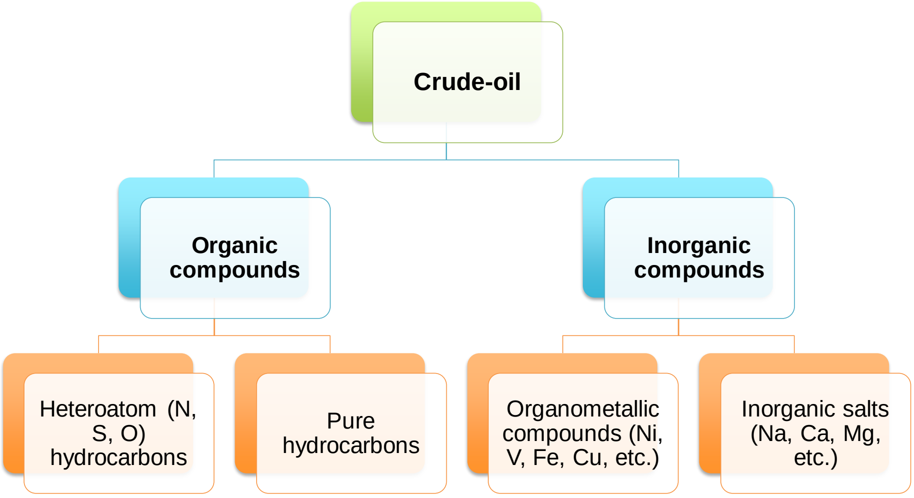

Figure 1.2: Crude oil composition

Crude oil comes in different forms which are heavy crude oil (extra heavy crude oil) and light crude oil (**Fig. 1.3**). Heavy crude oil is characterised by high viscosity and has a high specific gravity than that of light crude oil [11]. Crude oil becomes heavy as a result of biodegradation in which lighter ends are consumed by bacterial activities in the reservoir, leaving heavier hydrocarbons behind. These oils are normally found in shallow reservoirs on which the rocks are younger than 25 million years [11]. Additionally, crude oil can either be termed as sweet or sour based on the levels of hydrogen sulfide and carbon dioxide present. Therefore, sweet crude oil has less of the two compounds and it has less challenges associated with different types of corrosion, hence highly favoured over sour crude oil [18]. Crude oil can be refined to form diesel, gasoline, heating oil, jet fuel, kerosene and a variety of other chemicals called petrochemicals [12]. However, kerosene, gasoline and diesel can be produced from crude oil refinery process or/and from coal Fischer-Tropsch (FT) catalytic technology owned by SASOL [3]. Additionally, FT synthetic crude shows some advantages over crude oil as it does not contain S and N while crude oil has 0.1-5% and 0-2% for S and N, respectively [19]. The presence of S and N are not favourable as they are associated with corrosion of refinery equipment during the oil refinery processes. In contrast, the main disadvantage of FT is that, several steps are involved as the synthetic crude produced from coal if further refined in a distillation column to get transport fuels like kerosene, gasoline, jet fuel and diesel fuels (**Fig. 1.4**) [20]. It is worth in noting that the transport fuels produced by FT do not differ in energy production from those derived from crude oil [21].

Figure 1.3: Different types of crude oil that are observed all over the world [22].

1.1.3 Crude oil extraction, conversion and its derivatives

Firstly, in fractional distillation, the crude oil derivatives are separated based on their boiling point differences, compounds with the lowest boiling point are very light, have short carbon-carbon chains and will be the first ones to come out of the fractional distillation column [18]. In fractional distillation, the first hydrocarbons to come out are the gases (methane, ethane, propane and butane). Then, the less viscous and less dense hydrocarbon liquid will come out secondly. It must be noted that, the number of carbon-carbon chain (C-C) influence the boiling point of the crude oil derivative, the longer the C-C chain, the higher the boiling point [23]. For example, during the refinery process, liquefied petroleum gases (LPG) are the first ones to come out due their low boiling point. LPG have three to four carbon-carbon chain (C_3-C_4) with a boiling point of (-1 ℃), gasoline has C_5-C_{12} (216 ℃), kerosene/jet fuel has C_{10}-C_{16} (258 ℃) and diesel fuel oil has C_{14}-C_{20} (421 ℃) [24] (**Table 1**). Gasoline is composed of hydrocarbon that may range from 5 to 12 carbons and diesel is having carbon chains ranging from 14 to 20, making diesel to come at the bottom of the fractional distillation column (**Fig. 1.4**) in comparison to gasoline [25].

Table 1.1: Crude oil derivatives and their daily uses and applications

Number of carbon	**Name of compound**	**Daily uses**
C_1 to C_4	LPG domestic gas petrochemicals e.g. propane	Heating appliances and cooking equipment
C_1 to C_9	Naphta e.g. spirit	Cleaning solvents
C_5 to C_{12}	Gasoline	Energy production to move a car
C_{10} to C_{16}	Kerosene and Jet fuel	For lighting and heating
C_{14} to C_{20}	Diesel fuel	Generate energy to move a motor vehicle
C_{20} to C_{50}	Lubricants e.g. polish and waxes	Waxes are used in making of plastics and candles
C_{20} to C_{70}	Heavy fuels	Boiler district heating
C_{70} and above	Bitumen asphalt	For road and roofing

LPG: Liquefied petroleum gas

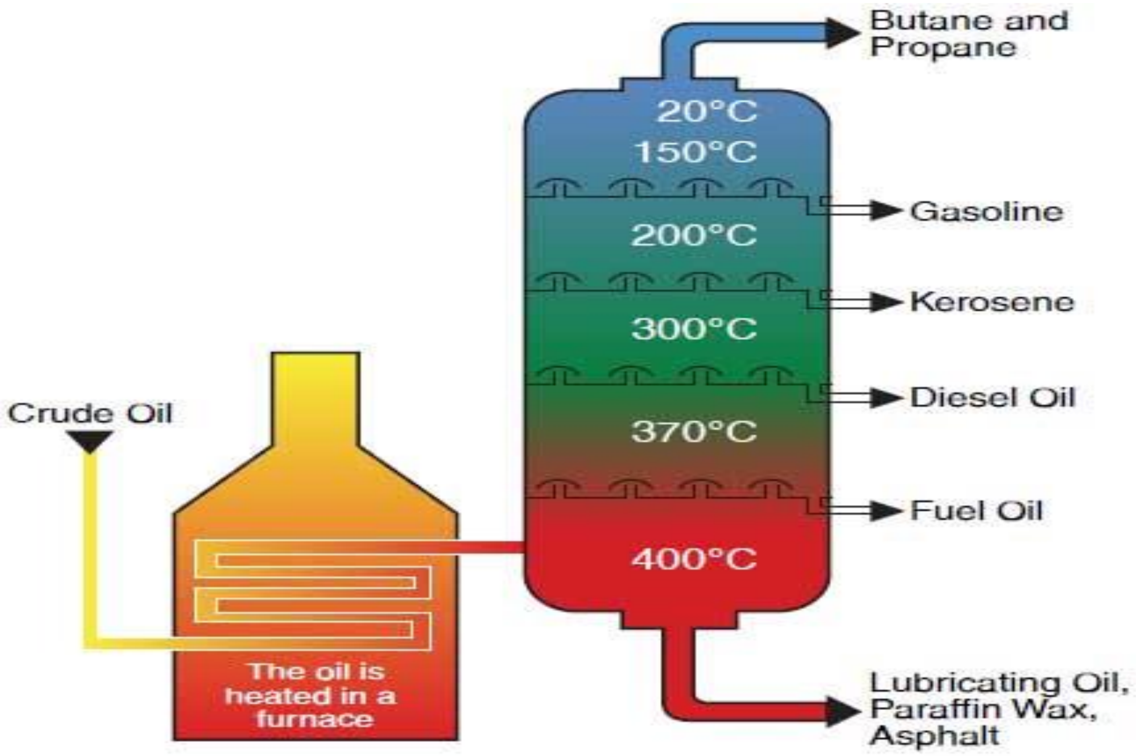

Figure 1.4: Fractional distillation showing the crude oil derivatives and their boiling points [26]

1.1.4 General toxic effects of metal ions in human health

Some metals such as Fe, Ca and Na are known to play a very important role in human lives, Ca is largely known for the formation of strong bones and teeth, while Fe helps in the formation of the red pigment of the blood, haemoglobin [27]. However, most metals are of no good use in human and plant health. Metals do accumulate in human bodies and cause diseases such as, cancer, bone disease, kidney infection, fertility problems in females, brain damage and the malfunctioning of the central nervous system [28]. In the environment, metals can cause the soil to be acidic [27]. Additionally, in plants, high concentration of metals can inhibit growth, cause oxidative stress, cause chlorosis and reduce the rate of photosynthesis [29]. The different metals and their negative impact in both plant and animals is discussed in **Table 1.2.**

Table 1.2: Adverse effects of some toxic metals in plants and animal life

Metal or metalloid	**Negative effects on plants**	**Negative effects on animals**	**Refs**
Al	Inhibit roots growth and cellular modifications in leaves	Bone disease, inhibit enzymes such as hexokinase and phosphokinase	[29]
As	Causes malfunctioning of cells, respiration and mitosis	Visceral cancer and skin manifestations	[27, 30]
Cd	Oxidative stress and induces nutritional deficiencies in plants	Carcinogenic, bone mineralization, and causes nephrotoxicity in the kidney	[29]
Co	Inhibit nutrient uptake	Neurotoxic and retarded growth	[29]
Cr	Chlorosis and necrosis	Mutagenic and carcinogenic	[27]
Cu	Inhibits plant growth	Insomnia, liver and kidney damage	[27]
Fe	Inhibit growth	Damages cell organelles (mitochondria and lysosome)	[29, 30]
Hg	Induced phytotoxicity	Brain necrosis, malfunctioning of nerves, kidney and muscles	[27, 30]
Ni	Inhibit growth	Carcinogenic, chronic asthma and nausea	[29]
Pb	Damages chlorophyll (slows rate of photosynthesis),	Damages the central nervous system,	[29]

	inhibit plant growth, instability in ion uptake and oxidative stress	gastrointestinal tract and carcinogenic	
Sb		Female infertility	[27]
Zn	Chlorosis	Depression and damages central nervous system	[29, 30]

1.2 Problem statement

Crude oil is a natural energy resource that is mainly composed of hydrocarbons. Crude oil can contain nitrogen, oxygen, sulfur and trace amounts of metals such as Fe, Ni, Cu and V together with other element [31, 32]. The presence of metals in crude oil and its derivatives has several negative impacts on human life, plant life, environment, car body parts and on oil refinery machinery [33]. Some of these trace elements (Cr, Fe and Al) can cause significance corrosion of refining equipment [11, 12]. Corrosion makes the refinery machine less effective, thus reducing its lifespan. Additionally, the maintenance and repairing of the refinery machines may be very costly. The huge expense on oil refinery maintenance in turn negatively influence the market price of the petroleum products [13]. Therefore, it is important to determine the content of such trace metals in crude oil, so that a decision can be made on whether these metals need to be removed prior to refining processing [36-38].

During direct analysis of metal ions, several analytical instruments have been used which include XRF spectrometry, ICP-MS, AAS and NAA [9, 40, 41]. Direct analysis is a quick way to elemental determination and reduce chances of contamination [42-44]. However, this direct analysis is most associated with carbon overlord in the plasma which affects sensitivity and thereby causes matrix effects and poly atomic interferences during ICP analysis [45]. On the other hand, the NAA showed very good detection limits and the multielement capabilities made it to be very good for direct analysi**s** [46]. However, this technique is very expensive, known for generating radioactive waste which is very dangerous and requires the nuclear reactor that is not easy to find in most laboratories [11]. Therefore**,** several sample preparation methods were introduced which included, ashing, digestion, liquid-liquid extraction, emulsification, and solid phase extraction. The problem with ashing is the time spent on ashing and the loss of volatile analytes [47]. With digestion, the use of potential explosive and corrosive concentrated acids like HNO_3, $HClO_4$ and HCl, makes this sample preparation method to be environmentally unfriendly [48]. With liquid-liquid extraction, the use of carcinogenic organic solvents has been a major problem [49]. Under the solid phase extraction, the major problems are the number of extraction steps which can increase chances of contamination, large volumes of concentrated acids for elution and separation of the adsorbent from the aqueous medium [50]. After looking at the risks associated with some sample preparation methods, a need to develop greener sample preparation methods for extraction of metal ions prior to spectrometric determination becomes vital.

1.3 Aims and objectives

1.3.1 Main aim

The essential focal point of this research project was to develop greener sample preparation methods for extraction of metal ions in fuel samples prior to ICP-OES determination.

1.3.2 Specific objectives

The specific objectives of the proposed research project were to:

(i) Develop greener microwave assisted hydrogen peroxide digestion method for extraction of heavy metal ions and metalloids in crude-oil, diesel, kerosene and gasoline samples, followed by ICP-OES analysis.

- Parameters such as sample amount, microwave temperature, digestion time and hydrogen peroxide concentration will be optimized by using multivariate mathematical tool.
- Analytical features such as method detection limits, accuracy and precision will be investigated by using certified reference materials.
- The optimum parameters will be applied in real fuel oil samples.

(ii) Investigate the possibility of using ionic liquid assisted emulsion breaking extraction methods for pre-concentration of trace metals and metalloids in crude oil, diesel, kerosene and gasoline samples prior to spectrometric detection.

- Alternative surfactants will be investigated during emulsion breaking technique.
- Multivariate optimization of the most significant parameters will be carried out.
- Validation of the emulsion breaking extraction methods using certified reference materials and standard methods will be conducted.
- The application of the optimum parameters in real fuel samples will be carried out.

(iii) Study magnetic solid phase extraction (m-SPE) procedure for pre-concentration of metal ions in fuel samples, followed by ICP-OES analysis.

- The exploration of various parameters (adsorbent mass, eluent concentration, eluent volume and extraction time) that affect the extraction efficiency of the proposed m-SPE will be performed by using multivariate optimization methods.
- The application of the proposed pre-concentration system (m-SPE) will be tested for the pre-concentration / extraction of metal ions in real fuel oil samples.

1.4 Justification

Several methods have been reported on metal determination in food [51], fossil fuels [18] and water matrices [52] to mention a few, and this is due to the negative impact that metals have in plants, animals and the environment. Metals have been determined from the different matrices using direct analysis (without sample preparation) and other different sample preparation methods were reported. Microwave digestion [53], liquid-liquid extraction (LLE) [54] and solid phase extraction (SPE) [55] were among the most preferred sample preparation methods for metal extraction. The use of concentrated acids like HCl, $HClO_4$ and HNO_3 in wet digestion have helped in attaining complete digestion thus getting high percentage recoveries for the analyte of interest. However, the use of concentrated acids was associated with corrosion and possible explosion. It must be noted that Mketo *et al.*,[56] reported for the first time the use of diluted HNO_3 and H_2O_2 for digestion of coal matrix to determine trace elements. There was no generation of hazardous waste with this sample preparation method and high percentage recoveries (89-101 %) were obtained. This greener sample preparation method had not been reported in other samples, therefore there is a need to use it in other samples. In LLE, the extraction induced by emulsion breaking (EIEB) was the mostly favoured method. This sample preparation method proved to be greener than most LLE methods, but the use of high volumes of the carcinogenic organic solvents (toluene, hexane and xylene) in crude oil to reduce its viscosity and sometimes the use of concentrated acids for EIEB were a major drawback. This study proposes the use of small volume of xylene (µL) for diluting the crude oil and ionic liquid for enhancing extraction, making this method much greener. The other sample preparation mostly favoured was SPE and magnetic solid phase extraction was chosen as this sample preparation method reported high enrichment which favours detection of elements in trace levels. To the best of our knowledge, m-SPE have never been reported in crude oil, diesel, kerosene and gasoline samples. Additionally, for the analysis, the ICP-OES was chosen as this technique had very low detection limits and showed multi-elemental capabilities which favoured detection of trace elements.

1.5 Hypothesis

Determination of metals and metalloids in crude oil and its derivatives can be achieved through the three different sample preparation methods which are microwave assisted hydrogen peroxide digestion (MA-HPD), ionic liquid assisted-extraction induced by emulsion breaking (ILA-EIEB) and magnetic solid phase extraction (m-SPE) followed by spectrometric analysis.

1.6 Dissertation outline

This dissertation is divided into 7 chapters and each and every chapter is discussed in each subsection as follows:

Chapter one gives a background of crude oil, crude oil genesis, uses of crude oil, the different types of crude oil and the elements that make up the crude oil. This chapter also highlights the different crude oil derivatives and the challenges associated with metals being present in crude oil and its derivatives. These problems are viewed based on their negative impact in living and non-living organisms. The problem statement, hypothesis, justification, aim and objectives are all highlighted in this chapter.

Chapter two critically reviews the studies that have been reported for the determination of metals in crude oil and the main focus is on the use of different sample preparation methods for metal determination. This chapter also evaluates different ways of oil sample preparation methods, which included, zero sample preparation/direct analysis, dilution with organic solvent and extensive sample preparation. Under extensive sample preparation, several different sample preparation methods were reported which were microwave assisted digestion, liquid-liquid extraction, cloud point extraction and solid phase extraction. This chapter also gives a clear picture of all the different parameters that were examined in achieving the intended objectives of every reported sample preparation procedure.

Chapter three is an overview of how the three objectives were achieved; it gives a scope of the three different sample preparation methods prior to ICP-OES spectrometric determination. These sample preparation methods discussed under this chapter were microwave assisted digestion, extraction induced by emulsion breaking and magnetic solid phase extraction. This chapter also highlights the parameters that were optimised for the three different sample preparation methods.

Chapter four shows the results obtained from microwave assisted digestion using diluted hydrogen peroxide. This chapter also discusses the multivariate optimization step for the four influential parameters (sample mass, concentration of nitric acid, concentration of hydrogen peroxide and digestion temperature). Additionally, this chapter reported in greater depth the instrument operating condition for digestion (microwave parameters) and for analysis (ICP-OES parameters).

Chapter five presents the results obtained from ionic liquid assisted-extraction induced by emulsion breaking (ILA-EIEB). Discussion on the multivariate optimization of parameters that affect the proposed ILA-EIEB is presented under this section. These parameters that were optimized were acid type, surfactant concentration and acid concentration. This chapter also report and discuss the results obtained from the best parameters used after the multivariate optimization step. Additionally, this chapter also highlights the analysis of target analytes using ICP-OES and the comparison of results with other literature reports.

Chapter six describes the results that were obtained from magnetic solid phase extraction (m-SPE). The parameters that affected the extraction such as sorbent amount, pH, eluent volume and extraction time were multivariate optimised. This chapter also discusses in greater details the synthesis and the functionalization of the magnetic nano-sorbent ($Fe_3O_4@Al_2O_3$) and the latter was applied as an adsorbent for trace-metal ions. The characterisation of the synthesized Fe_3O_4 and $Fe_3O_4@Al_2O_3$ using different characterization techniques are reported. Results obtained from the m-SPE were presented and compared with other literature reports.

Chapter seven gives the entire findings of the proposed research project and compare the results obtained from the three sample preparation methods. Lastly, this chapter discusses conclusion remarks of the overall project and gives future recommendations. It is worth noting that for every chapter, references were sited at the end of that chapter.

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CHAPTER 2 (LITERATURE REVIEW)

Preamble

This chapter surveys the literature for various sample preparation methods that have been reported for elemental extraction in oil matrices prior to their spectrometric determination. The merits and drawbacks associated with each sample preparation are highlighted. This chapter also looks in greater depth on the spectrometric techniques that have been used in elemental detection, advantages and disadvantages reported for each technique. Lastly, literature concludes on the sample preparation methods that were reported to be the best analytical technique and/or elements.

2.1 Background information

In the past 20 years, most researchers have shown interest in determination of multi-elementals in various oily matrices. This is because of the negative impacts that are associated with high levels of these elements when accumulated into animal, human and plant tissues. These oils can be edible oils or fuel oils like biodiesel, crude oil, and crude oil derivatives. Edible oils play a vital role in humans as they provide the body needs such as energy. The latter is used in the formation of phospholipid bilayer in cell membranes and other structural body components [1, 2]. The levels of trace elements in oily samples determine the quality of the oil, as high levels of these elements make the oil to be of low quality [1]. The presence of metals in edible oils can be due to different factors which may include, metals being added during food processing or/ and absorbed by plants as mineral ions through a process of active transport. The addition of elements in biodiesel is much similar to that of edible oil, as the metals are naturally found in the plants and are uncontrollable [3, 4]. Additionally, in fuel oils, metals can be added during crude oil refinery process, transportation and storage of crude the oil derivatives [5]. Lastly, in crude oil, trace elements are naturally found due to the nature of crude oil occurrence [6]. The presence of metals in fuels has several negative impact in the environment, human life, refinery equipment and motor vehicles [7]. Therefore, their determination and monitoring is very important.

2.2 Metal determination in oily matrices

Several analytical techniques have been used for the determination of metal ions in oily samples. These techniques include, atomic absorption spectrometry (AAS) [3, 8], X-ray fluorescence spectrometry (XRF) [9, 10], neutron activation analysis (NAA) [11], inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). However, it is worthy to indicate that, some of these analytical techniques (AAS, ICP-OES/MS) required sample preparation and others (NAA, GF-AAS and XRF) can manage matrix effects, thereby allow direct analysis without the sample preparation steps, as illustrated in **Fig. 2.1**.

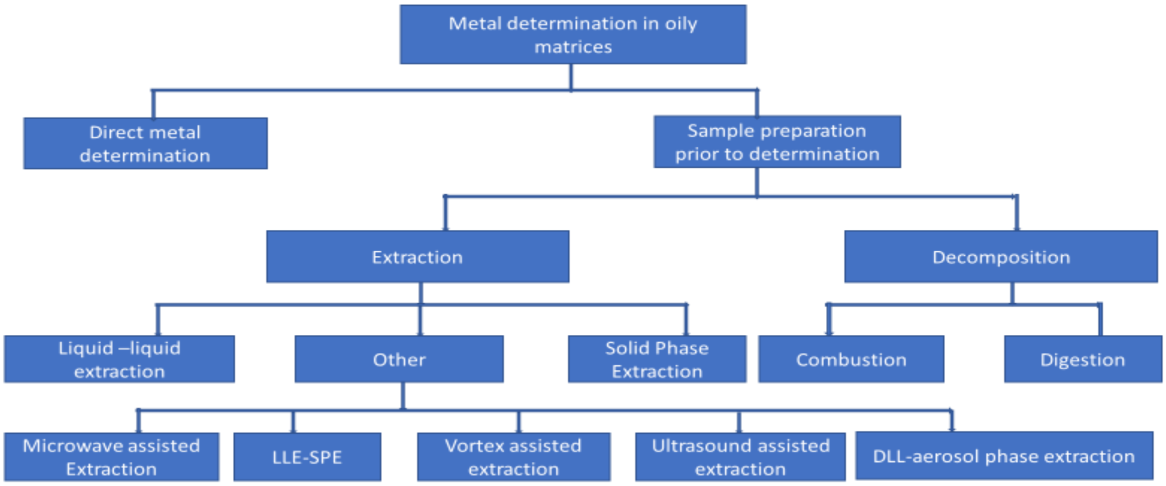

Figure 2.1: Metal determination strategies applied in oily matrices

2.2.1 Direct metal determination in oily samples

Direct analysis methods are regarded as the fastest and easiest methods of elemental determination as they eliminate or minimise the time-consuming sample preparation step. In zero sample preparation, the sample is directly subjected into the proposed analytical technique as it is (**Fig. 2.2**). It has to be noted that, analytical techniques that have been widely reported in direct elemental analysis include, neutron activation analysis (NAA) [12, 13], electrothermal vaporisation-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) [14, 15], X-ray fluorescence spectrometry (XRF) [16-18], microwave plasma-atomic emission spectrometry (MP-AES) [19], laser ablation-inductively coupled plasma-time-of-flight mass spectrometry (LA-ICP-TOFMS) [20], ultrasonic nebulizer-inductively coupled plasma-mass spectrometry (USN-ICP-MS) [11], energy dispersive-X-ray fluorescence spectrometry (ED-XFS) [21], graphite furnace-atomic absorption spectrometry (GF-AAS) [22] and laser induced breakdown spectroscopy (LIBS) [23]. However, some samples like crude oil have high viscosity, therefore, they might require a simple dilution step with an organic solvent prior to their direct elemental analysis [24]. The mostly reported organic diluent solvents were xylene, hexane and isopropanol [10, 25]. The uses of direct dilution with an organic solvent have been commonly applied during ICP-MS elemental determination. These minimal sample preparation methods have shown several advantages, which include minimisation of sample losses and contaminations, time reduction needed for elemental determination and cost-effectiveness (since less reagents will be required for dilution) [26].

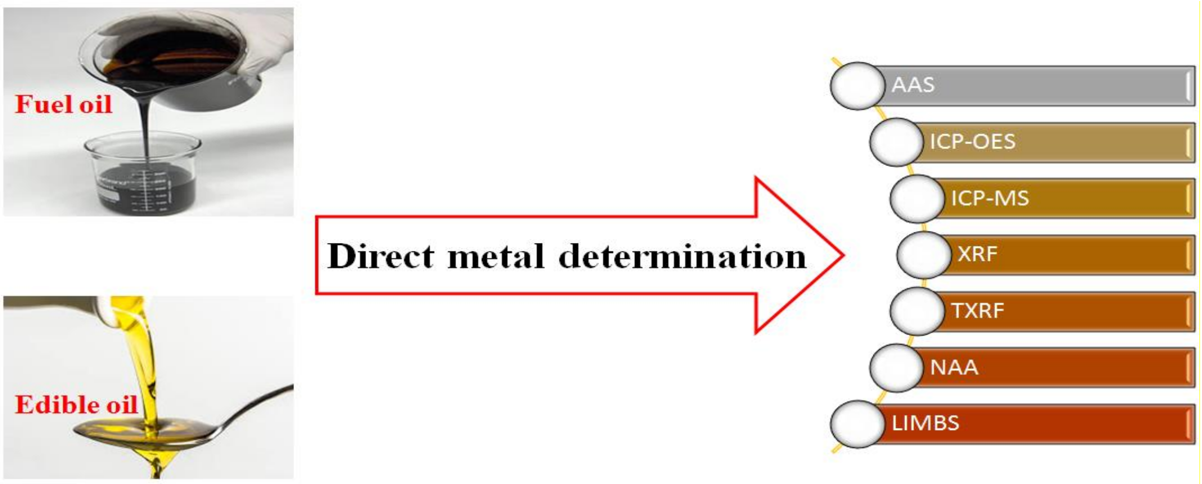

Figure 2.2: Direct metal determination in various oily matrices using different analytical methods

The reported literature on direct metal analysis in oily matrices is illustrated in **Table 2.1**. From this table, it can be observed that edible and crude oils were the most studied oily matrices for direct metal analysis while biodiesel was the least reported matrix. Direct analysis in oily matrices focused mainly on metals and as a result, Cl and S were the only non-metals reported. **Table 2.1** also shows that AAS was the mostly favoured detection technique. Canario et al. [27] reported the direct determination of Cd and Pb in edible oils using AAS with transverse heated filter atomizer. This study reported very poor accuracy (61-100%) for Pb. On the other hand, the accuracy for Cd showed some improvement (70-100%). The precision reported for both Pb and Cd was ≤6%. The major challenges with direct analysis of edible oils using AAS with transverse heated atomizer were the remains of matrix and storage of carbonaceous residue over the collector [27]. This method was therefore, proved not to be good for the detection of Pb and Cd based on the obtained accuracy. Then, Matos Reyes et al. [28], also reported the use of AAS coupled with graphite furnace for direct analysis of Cu and Ni in vegetable oils. The study reported low detection limits of 0.001 µg/g and 0.002 µg/g for Cu and Ni, respectively [28]. Despite, the low LODs reported, accuracy was not good (50-144%)

making this analytical technique less favourable for Cu and Ni analysis. However, GF-AAS was also used for Cr and Ni in 300 mg of lubricating oils. Detection limits of these two metal ions ranged from 0.82 to 0.86 mg/L, with precision of less than 13% and accuracy of greater than 95% [29]. The direct analysis using GF-AAS reported several limitations. The high organic content in the oil that was inserted into the graphite tube gave very high background signal during atomization. The accumulation of carbonaceous residue on platform surface due to partial oxidation of organic, negatively affected the repeatability of the absorbance signals [29]. In addition, the difference in viscosity and surface tension between the sample and aqueous calibration standards resulted in molecular spectral and matrix interferences in some elements [30].

Therefore, Nelson et al. [31] reported the direct determination of chloride in crude oil by using a triple quadrupole ICP-MS. The LOD for chlorine was reported to be 0.01 ng/g and acceptable accuracy of ^{35}Cl ranged from 82 to 108%. Vorapalawut et al. [32], used LA-ICP-MS for direct analysis of Ba, B, Co, Fe, Li, Na, Rh, Sc, U, Y and K in petroleum samples. The use of LA-ICP-MS with doubly focusing sector field mass analyser prevented the carbon related polyatomic interferences and LODs for Ba, Co, Fe, Li, Na, Sc, U, Y and K were reported to be 1.2, 4.6, 3.1,11, 6.0,2.1, 1.8, 10 and 10 ng/g, respectively [32]. The precision of the method was ≤5% and the accuracy ranged from 96 to 100%. The use of LA-ICP-MS reported good results as the method was validated using the two certified reference materials (NIST 1084a and 1085b). Additionally, Poirier et al. [33] reported the determination of Ni, V, Fe and Ca in crude oil after dilution with xylene prior to analysis by ICP-MS/OES. This study reported accuracy of 93 to 112 % with reproducibility of 0.54 to 2.25% when using ICP-OES. Alternatively, accuracy for ICP-MS analysis ranged from 94 to 111% with precision of 0.65 to 3.52% [33]. These results showed no differences in terms of recoveries and precision between the ICP-MS and ICP-OES metal determinations. However, the obtained LODs showed noticeable differences, thus, ICP-MS analysis resulted in very low LOD 0.22 to 2.16 ng/g in comparison to ICP-OES analysis with around 20 ng/g for all the metals analysed.

Another analytical technique that has been reported in direct analysis of metals in oily matrices is XRF. Stas et al.[34] used the total X-ray florescence (TXRF) spectroscopy in direct determination of uranium in kerosene. This direct determination technique reported the precision of 5.1 to 8.1%, accuracy of 88 to 106% and detection limits of 1.5 µg/L. Doyle and co-workers reported direct analysis of S, Ca, Fe, Ni and V in crude oil samples using energy dispersive X-ray fluorescence (ED-XRF) spectroscopy. It must be noted that, crude oil samples were firstly diluted with toluene prior to elemental analysis. The dilution step was conducted in order to reduce oil viscosity [10].The use of direct analysis using ED-XRF gave reliable results which were quite comparable with the values obtained from the certified reference material. It is worthy in noting that, XRF analysis cannot be used for the determination of elements lighter than Na and Mg. Therefore, this is one of the major drawbacks for this analytical technique [35]. Another analytical technique that is considered reliable with direct elemental analysis is the NAA. The latter is advantageous as it has multi-elemental capabilities [6]. However, NAA showed some limitation with the determination of other trace-elements like rare earth elements (REEs) and nuclear interferences of major elements are easily observed with this analytical technique [36, 37]. The use of NAA also comes with very high cost, making it very difficult to own it. This is because, NAA generates hazardous radioactive waste and requires a nuclear reactor which is commonly not found in most laboratories [38]. It has to be noted that, most of the organic solvents used during dilution step are carcinogenic. Therefore, limitations showed by direct analysis or dilution have called for a need to develop extensive sample preparation methods such as extraction and decomposition.

Table 2. 1: Application of direct elemental analysis in different oily matrices

Oily matrix	**Sample mass (mg)**	**Dilution solvent**	**Analyte**	**Detection technique**	**LODs (µg/g)**	**Precision (%)**	**Accuracy (%)**	**Ref.**
Biodiesel	N/A	Kerosene	Na, Mg, K, and S	ICP-MS	2.6, 2.4, 5.9 and 3.1	<6.4	87.1-122	[39]
Biodiesel	500	HCl, HNO_3 and $HClO_4$	Cu (II)	Screen printed electrodes	0.0017	5	99.3-107.6	[40]
Crude oil	8 and 10	o-xylene	Ni, V, Fe, Ca and Na	MP-AES	0.0049,0.028, 0.0021,0.067 and 0.0035	<20	89-109	[41]
Crude oil	100	N/A	Cd and As	DS-GF-AAS	5.1	<7	99-102	[42]
Crude oil	8 and 10	o-xylene	Cl	ICP-MS/MS	14.03	<20	88-109	[31]
Crude oil	1000	o-xylene	Ni, V, Fe and Ca	ICP-MS and ICP-OES	0.007-0.01	<3.54	91-111 and 93-119	[33]
Crude oil	N/A	N/A	S, V, Fe and Ni	TXRF	20, 0.6,0.1 and 0.4	4	N/A	[9]
Crude oil	176	Toluene	S, Ca, Fe, Ni and V	ED-XRF	17.0, 2.1, 2.2 , 1.7 and 1.9	<5	99-104	[10]
Edible oil	N/A	N/A	Cd and Pb	AAS	0.06 and 0.7 mg/L	6	61-100	[27]

Edible oils	250	N/A	Cu and Fe	Flow injection FAAS	0.0004, 0.0002	<12	95-106	[26]
Edible oil	N/A	N/A	Fe, Cu, Cr, Al, Ca, Mg and Mn	ICP-AES	0.463, 0.055, 0.029 0.066, 0.641, 0.125 and 0.044	N/A	85-106	[43]
Engine oil	N/A	N/A	Zn, Mo, Fe, Cu, Pb, Cr, Mn and Ni	ED-XRF	N/A	N/A	14.3 - 161.6	[44]
Kerosene	N/A	N/A	U, Fe, Ni, Cu and Zn	TXRF	0.15 µg/L	5.1-8.1	1.0-2.5	[34]
Liquid petroleum	N/A	N/A	Al, Ba, Ca, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Si, Ti, V and Zn	WD-XRF			N/A	[30]
Lubricating oil	400	N/A	Na, Mg, Al, Tl, Cr, Fe, Ni, Co, Cu, Ag and Pb	LA-ICP-TOFMS	0.0005-0.028	6	73-100	[20]
Lubricating oil	N/A	N/A	Fe, Cr and Ni	LIBS	1.65, 3.78 and 1.56	<26	95-120	[23]

Lubricating oil	300	Triton X-100, HNO_3 and H_2O_2	Cr and Ni	GF-AAS	0.86 and 0.82	<13	95-99	[29]
Lubricating oil	N/A	N/A	Ni, Mo, Sn and Pb	ICP-ID-MS	12.02, 16.3, 31.1 and 6.01	<3	98-102	[45]
Oil samples (edible and fuel)	N/A	Xylene/butanol	Cr and Ni	ICP-MS	0.051 and 0.045	2	97.6-124	[46]
Olive oil	500	HNO_3 and H_2O_2	Cu, Na and Ca	FAAS	0.5897,0.4541 and 0.4232	N/A	53.39	[47]
Olive oil	25g	N/A	Co, Ni, Cu, Zn, Ba and Ag	ED-XRF	N/A	2.17	59.5-90.59	`[35]
Petroleum samples	N/A	N/A	Ba, B, Co, Fe, Li, Na, Rh, Sc, U, Y and K	LA-ICP-MS	1.2, 4.6, 3.1,11, 6.0,2.1.18,10,10 and 23	5	96-100	[32]
Petroleum	3	N/A	Cu, Fe and V	EAAS	0.01, 0.2 and 0,8	5	92.5	[48]
Vegetable oil	0.5	N/A	Cu and Ni	DS-GFAAS	0.001 and 0.002	5	50-144	[28]

Vegetable oils	5 000	N/A	As, Pb, Cd and Zn	ET-AAS	0.0012, 0.0011, 0.0002 and 0.0001	3-8	94.4-97.1	[22]

[N/A]- Not applicable**, [ETV-ICP-MS]-**electrothermal vaporisation inductively coupled plasma mass spectrometry**, [XRF]-** X-ray fluorescence spectroscopy, **[MP-AES]-** microwave plasma atomic emission spectrometry, **[USN-ICP-MS]-** ultrasonic nebulizer inductively coupled plasma mass spectrometry, **[ED-XFS]-** energy dispersive X-ray fluorescence spectroscopy, **[LA-ICP-TOFMS]-** laser ablation-inductively coupled plasma time-of-flight mass spectrometry

2.2.2 Sample preparation method for oily matrices

In chemical analytical processes there are four well reported crucial steps which are; sampling, sample preparation, measurement and data analysis [49]. However, out of the four steps, sample preparation is regarded as the most important stage of the chemical analysis. This is because, this step prepares the analyte to be compactable with the proposed detection technique [49, 50]. Sample preparation aimed at removing analyte of interest from the interfering species. Additionally, it can also pre-concentrates the target analytes if present in very low concentration levels [49]. The type of sample preparation method that one develops depends on many factors which include: (i) nature of the analyte, (ii) matrix type, (iii) analytical technique, (iv) sample size and (v) analyte concentration levels [49, 51]. Therefore, sample preparation is important in improving detection limits and it helps to reduce any form of chemical interference that might come from the sample matrix [51, 52]. For example, the introduction of high organic content samples into the ICP-MS/ OES is challenging, because:

(a) Polyatomic interferences might form, due to the formation of poly-atomic ions with carbon.
(b) There might be carbon deposits at the interface and on the ion lenses.
(c) A decrease in the sensitivity and ion transmission might be experienced.

(d) Matrix effects due to the introduction of organic solvents are highly expected and

(e) The occurrence of plasma extinction due to high carbon content [36].

Therefore, this section of the review highlights the various sample preparation methods that have been reported for metal extraction prior to elemental determination in oily matrices. These sample preparation methods include decomposition by using acids (digestion) or heat (combustion) and extraction (solid phase extraction, liquid phase extraction and other).

2.2.2.1 Decomposition sample preparation methods

Decomposition sample preparation methods are those methods that separate target analyte from the matrix by destroying the matrix, in order to eliminate matrix effects during analysis. There are two major types of sample preparation methods that fall under decomposition methods. The latter are digestion methods by using inorganic acids and combustion methods with the help of heat and oxygen (**Fig 2.3**).

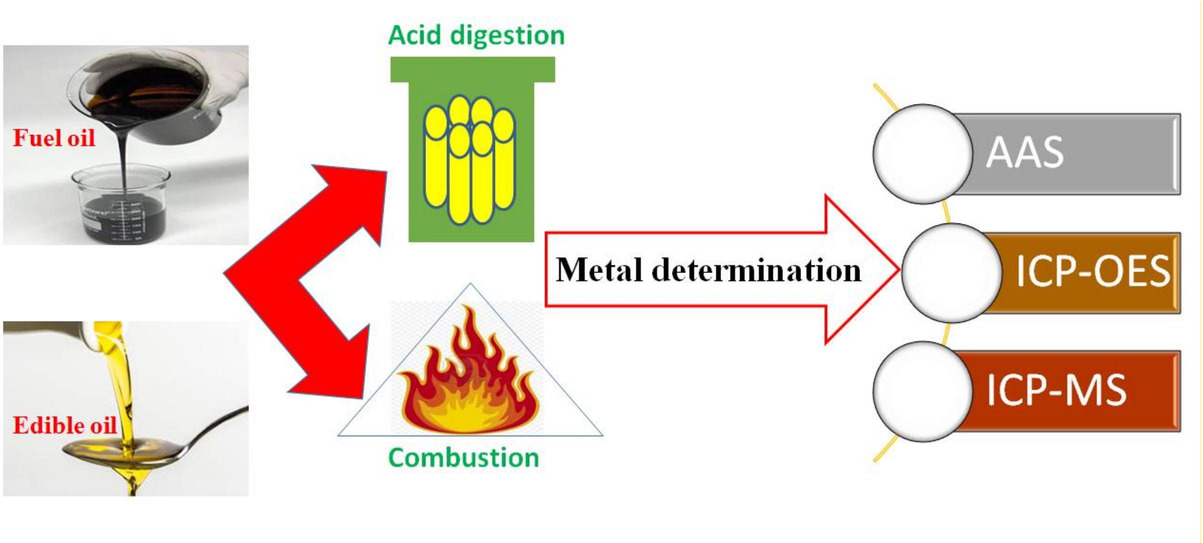

Figure 2.3: Indirect metal determination in various oily matrices using different analytical methods after matrix decomposition

2.2.2.1.1 Acid digestion decomposition

Microwave-assisted digestion sample preparation methods were mostly reported for acid digestion of oily matrices [53-55]. The microwave energy was reported to be very effective in breaking the carbon element bond in oily samples [53]. Microwave energy is a non-ionizing form of electromagnetic radiation that causes molecular motion by migration of ions and rotation of dipoles [56]. The microwave assisted processes are based on the efficient heating of materials by microwave dielectric heating effects and the efficiency depends on the ability of a specific material (reagent or solvent) to absorb microwave energy and convert it to heat [56]. Most of the microwave acid digestion methods are performed in closed vessels, with the use of concentrated acid to improve the digestion efficiency and to reduce digestion time [4, 55, 57]. The use of closed systems is advantageous as it prevent losses of volatile analytes [36, 58]. Despite the good efficiency of sample digestion observed when concentrated acids were used, the use of concentrated acids could increase the blank values and cause nebulization matrix effects in some of the analytical techniques like ICP-MS and ICP-OES [6]. The mostly used digestion vessels (digestion bombs) are constructed from polytetrafluoroethylene (PTFE) and these PTFE have several limitations. The PTFE vessels are porous and are prone to adsorption of some elements [36, 59]. This challenge can be corrected by socking the PTFE in nitric acid before use, thereby removing previously adsorbed metal ions that might cause cross-contamination [55]. The use of concentrated acids like HNO_3 and $HClO_4$ is associated with explosion during microwave acid assisted digestion [60]. Additionally, the efficiency of

MAAD is influenced by the boiling point of the acid, the sample amount, digestion time and microwave temperature. It has to be noted that, the digestion temperature is also controlled by the nature of microwave vessels used [14]. However, in most cases the maximum temperature for PTFE vessels is 250 ℃. Above these temperatures, the vessels get some deformability and that is the limitation of this sample preparation method. The use of concentrated acids like HNO_3 can also produce carcinogenic nitrous oxide gases, thereby making this sample preparation to be environmentally unfriendly [61]. Therefore, in 2015, Mketo e*t al.* developed an environmentally friendly sample preparation method where diluted hydrogen peroxide was used to assist the digestion of coal samples prior to elemental analysis. This sample preparation method (MW-AHPD) proved to be environmentally friendly, since hydrogen peroxide was converted into water at high temperatures of the microwave system. To the best of our knowledge, no study has been conducted on the use of MW-AHPD digestion in crude-oil, diesel, kerosene and gasoline.

2.2.2.1.2 Combustion decomposition

Combustion methods are referred to those methods that make use of the heat and oxygen to decompose organic reached samples. These methods include ashing (wet or dry) and microwave induced combustion (MIC). In dry ashing, the sample is weighed and heated in a hot plate and then later, the heated sample is put in a muffle furnace for further heating at temperatures that are ranging from 450 to 550 °C [62, 63]. After further heating in the muffle furnace, an acid, preferably nitric acid is added to the ash to dissolve the metals, and finally diluted with water in preparation for analysis. Wet ashing is like dry ashing except that with wet ashing, an acid is added to the sample and then heated in the hot plate until it is dry. Both dry and wet ashing sample preparation methods are prone to several draw backs which include; loss of volatile element due to open systems, sample contamination due to open-air, sample heating and time consuming as muffle furnace heating may take up to more than 12 hrs [62].

Another environmentally friendly sample preparation that was developed to overcome the problems associated with MAAD, dry ashing and wet ashing was microwave induced combustion (MIC). The latter combines the advantages of MAAD and combustion techniques. The use of MIC has been proposed for digestion of high carbon content matrices [11]. This sample preparation method reduced sample preparation time on various matrices, which include biological samples, elastomers, coal, petrochemicals and crude oil [6, 55, 64]. Microwave induced combustion (MIC) was conducted by using oxygen for combustion and ammonium nitrate for ignition aiding [65].Various samples have been reported to be efficiently decomposed and the metals ions were absorbed by using diluted acids. The operational cost of MIC is high making it not to be readily available in most laboratories. Additionally, combustion of sample mass higher than 500 mg is not favourable as the sample exceeds about 50% of maximum pressure that quartz vessels support (80 bar) [66].

A summary of the literature reported decomposition methods is presented in **Table 2.2.** Under acid digestion topic, the microwave acid assisted digestion was the mostly used sample preparation method over the other digestion methods and most reported matrices were crude and edible oils. The sample mass reported ranged from 0.05 to 2.50 g and it is worth to state that the most reported sample mass ranged from 0.100 to 0.500 g as per the information reported in **Table 2.2**. Literature has also shown that time ranging from 5 to 75 minutes was enough to give complete digestion of different oil samples and the temperature required to give complete digestion were ranging from 110 to 235 °C. Additionally, the ICP-OES/MS were the most favoured analytical technique under microwave assisted digestion.

For example, Sant'Ana et al. [60] reported for the first time the use of H_2SO_4, HNO_3 and H_2O_2 for microwave digestion of diesel sample prior to the determination of Al, Cu, Fe and Zn using ICP-OES. This study was divided into three steps which were carbonization (using H_2SO_4), oxidation (using HNO_3) and another oxidation where H_2O_2 was used. This sample preparation method reported the use of the highest sample mass (2.50 g), thereby improving sensitivity of the target analytes with good accuracy ($\geq 90\%$) and precision ($< 5\%$) for the three investigated metals. However, this method was less favoured for Zn, due to the reported poor accuracy (70-78%) [60]. Additionally, the use of several reagents might cause contamination as the sample handling time was increased. The acids used were corrosive and the gas (nitrous oxide) produced when boiling nitric acid is carcinogenic, making this sample preparation not to be greener. The use of large volume of concentrated reagents (5 ml H_2SO_4, 4 ml HNO_3 and 10 ml H_2O_2) made this sample preparation method to be expensive and to be environmentally unfriendly, as more hazardous waste was generated. Zhang [67] also reported for the first time the use of microwave digestion for hydrogenated cottonseed oil prior to Ni determination by ETAAS. This sample preparation used the smallest sample mass (0.05g), which was digested using 2 mL of concentrated HNO_3 and 0.5 mL of concentrated H_2O_2 at 120 °C for 5 minutes. This sample preparation reported excellent accuracy values ranging from 96 to 118%, precision $< 3.2\%$, and short digestion time (5 minutes), making this sample preparation one of the best reported digestion methods [67]. However, the waste generated when using concentrated acids made this sample preparation to be environmentally unfriendly. Das et al. [68] reported the determination of trace elements using ICP-MS from silicon oil samples after MAAD. This sample preparation method used three reagents (aqua regia, HF and H_2O_2) that were added sequentially at 5 minutes interval during the digestion. The accuracy (97-105%) and precision of 15 % were reported [68]. The addition of reagents at 5 minutes interval made this method to be prone to contamination and loss of volatile analytes.

In **Table 2.2** several studies have been reported on combustion methods of oily matrices. Gazula et al. [69] reported a study where several sample preparation methods were compared for their efficiency in Na determination in vacuum gas oils. Amongst the sample preparations studied were the two dry ashing sample preparations. These methods were (i) dry ashing by Bunsen burner carbonisation and muffle furnace calcination. The other sample decomposition method was dry ashing in a new piece of equipment designed and created by Institute de Teennologia Ceramica (ITC). The ITC prototype was designed in such a way that, formation of flame that can result in loss of volatile element is prevented and all the furnace material parts were Na free, thus ensuring prevention of cross-contamination. The use of dry ashing by Bunsen burner carbonisation and muffle furnace had many steps (time consuming), more prone to contamination and, therefore, was rejected for the determination of Na in vacuum gas oil. The sample decomposition by dry ashing in a new piece of equipment designed created by ITC gave acceptable accuracy ranging from 90 to110 % and low LOD (0.002 µg/g) were obtained [69]. Chauhan and de Klerk [70] also reported the use of dry ashing in oil sands bitumen samples, where 10 g sample was heated in a muffle furnace for 4 hours at 550 °C and the resulted ash was digested in 10 mL HNO_3. This sample preparation reported poor accuracy ranging from 44 to 82%, precision of $\leq$ 20% and very high detection limits (79 and 189 µg/g) for Ni and V, respectively. [70]. Additionally, for dry ashing sample preparation, the ICP-OES/MS were more favoured for analysis and this might be due to their low detection limits. Zhanghin et al. [71] reported the determination of metals in camellia oil by ICP-MS after dry ashing. The oil samples were first put in 380 °C for carbonization and then in 550 °C for ashing. The sample was heated for 110 minutes in both the 380 °C and 550 °C. Very low LOD ranging from 0.6-48 ng/g, accuracy of 85.6-98.4% and precision of 1.1-5.5% were reported [71]. Lastly, Nora et al. [65] reported the use of microwave induced combustion for the determination of Cd, Co, Cr, Cu, Mn, Ni, Pb and V in diesel oil using ICP-MS. This sample preparation method used pressurized oxygen atmosphere (20 bar) without a dangerous pressure increase or damage rick, as reported for microwave systems. This method is preferable as it avoids ricks associated with explosion and low detection limits (0.001 to 0.20 µg/g) were reported [65]. Additionally, Mohamed et al. [55] reported the use of MIC for metals and metalloids characterization and screening in crude oils prior to analysis by ICP-MS/OES. This sample preparation provided several advantages over MAAD as it used diluted acids, which helped to minimise spectral interferences encountered by ICP-OES/MS. In this study 10 metals (Hg, Au, Cu, Al, Ca, Co, K, Mg, Si and Sr) were detected using ICP-OES and the other metals and metalloids (Mo, Ti, Mn, Li, Se, Rb, Ag, Ba, Pb, As, Cd, Cr, Fe, Ni, V and Zn) were at trace levels and were detected using the ICP-MS. The relative standard deviation was less than 2% with low detection limits ranging from 144 to 172 ng/g.

Table 2. 2: Different decomposition sample preparation methods applied in oily matrixes prior to metal determination by various analytical techniques

Method	**Matrix**	**Mass (g)**	**Reagent**	**Temperature (ºC)**	**Time (min)**	**Detection Technique**	**Precision (%)**	**Accuracy (%)**	**Analyte**	**LODs (µg/g)**	**Ref.**
Dry ashing	Camellia oil	2	5 % HNO_3	380-550	140	ICP-MS	1.1-5.5	85.6-98.4	Mg, Ca, Cr, Mn, Fe, Co, Ni, Zn and Pb	0.031,0.048,0.0006, 0.004,0.022,0.0004,0.006,0.00089 and 0.0003	[72]
Dry ashing	Oil bitumen	10	Conc. HNO_3	550	240	ICP-OES	<20	44-82	Ni and V	79 and 189	[70]
Dry ashing	Vacuum gas oils	2	Conc. HNO_3 & HCl	110-750	60	ICP-OES	NA	90-110	Na	0.002	[69]
Dry ashing	Waste oil (gum deposit)	5	30% H_2O_2, aqua regia & conc. HF	700-120	28 hrs	ICP-OES	10	80.5	Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Si and Zn	6-100	[73]
MAAD	Biodiesel	0.950	7M HNO_3 & 2M H_2O_2	900 W	75	SF-ICP-MS	<6	95-108	Ba, Co, Cr, Cu, Mn, Ni, Pb, Sr and V	0.00067, 0.00063,0.00012,0.0069, 0.0048, 0.0028, 0.00014,0.0005 and 0.00012	[5]

MAAD	Cottonseed oil	0.050	Conc. HNO_3 & H_2O_2	120	5	EAAS	<3.2	99-118	Ni	0.015µg/L	[67]
MAAD	Crude oil	0.5	6 mL of 14.4 M of HNO_3	250	60	MI-ICP-MS	< 7	96-106	Mg, Sr and Pb	0.059-0.203	[74]
MAAD	Crude oil	0.3	9.1 M of HNO_3 and 2mL H_2O_2	230	50	ICP-OES	< 10	95-104.2	Fe, Ni and V	0.1, 0.03 and 0.007	[75]
MAAD	Crude oil	0.100	4M H_2O_2 & 5M HNO_3	180	40	ICP-OES	0.42-4.62	94.6-98.2	Ni and V	0.24 and 0.06	[58]
MAAD	Crude oil	1.100	Conc. HNO_3	200	NS	ICP-OES	<5	94-110	Na, Ca and Mg	0.0001 -0.002	[6]
MAAD	Diesel	2.500	Conc. H_2SO_4, HNO_3 & H_2O_2	60-210 W	40	ICP-OES	5	70-78	Al, Cu, Fe and Zn	0.12, 0.089,0.14,0.052 and 0.11	[60]
MAAD	Lubricating oil	1.000	Conc. HNO_3 & H_2O_2	NS	40	FAAS	NA	NA	Fe, Cu, Cr and Pb	0.1,0.05,0.1 and 0.05	[76]
MAAD	Lubricating oil	1ml (V)	Conc. HNO_3 & H_2SO_4	110-220C	45	ICP-MS	<8	94-109	Ca, Mg, Sr and Fe	0.92-0.115	[77]

MAAD	Fish oil	0.200	Conc. HNO_3, & H_2O_2	235	18	ICP-OES	1.86 and 3.24	94-108	Hg	0.0016 µg/L	[78]
MAAD	Fuel oil	0.100	Conc. HNO_3 & H_2O_2	170-180	50	GFAAS	1.9 and 0.8	97.9-102.9	V	0.25	[79]
MAAD	Fuel oil	0.200	Conc. HNO_3 & H_2O_2	450 W	100-150	ICP-MS	<5	NA	Al, As, Co, Cr, Ni, Pb, V and Zn	NA	[80]
MAAD	Gasoline	0.205	Triton X-100, conc. HNO_3 & H_2O_2	220	40.5	ICP-MS	5-6	99.2-100.2	S	18	[81]
MAAD	Milk and oil	0.500	Conc. H_2O_2 & HNO_3	210	47	ICP-OES	NA	NA	Na, Mg, K, Ca, P, Fe, Cu, Mn, Zn, Al, As, Bi, Cd, Co, Cr, Ni and Pb	0.1-1.6	[82]
MAAD	Olive oil	0.250	Conc. HNO_3 & H_2O_2	200	30	ICP-MS	<10	88-112	Al, V, Cr, Fe, Co, Ni, Cu, As, Cd, Sb and Pb	2-10	[83]
MAAD	Rice bran oil	0.2	5 mL conc. HNO_3 and 3 mL H_2O_2	200	30	ICP-OES	< 5	97-101	As, Pb, Cr, Cu and Zn	0.01,0.001, 0.007,0.001, 0.001 and 0.002	[84]

MAAD	Silicon oil	0.150	aqua-regia, conc. HF & H_2O_2	440-550 W	23	ICP-MS	<15	97-105	Li, Na, Mg, Al, P, Ca, Sc, V and Cr	0.1, 0.2, 0.1, 0.7, 0.1, 1.6, 4.0 and 0.1	[68]
MAAD	Tree nut oil	0.500	Conc. HNO_3 & H_2O_2	130	45	ICP-MS	<7	90.7-107.7	Cr, Mn, Fe, Ni, Cu, Ag, Zn, Cd and Pb	0.0008-0.01	[85]
MAAD	Vegetable oil	0.400	Conc. HNO_3 & H_2O_2	180-200	30	ICP-OES	<2	91-106	P and Fe	0.004 and 0.007	[86]
MIC	Crude oil	0.500	5% H_2O_2 & conc. HNO_3	1 400 W	40	ICP-OES	<5	99-101	Ni, V and S	0.2, 0.1 and 2	[87]
MIC	Crude oil	0.500	4M HNO_3 & conc. H_2O_2	200	40	USN-ICP-MS	<10	96.8-104	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm	0.0008-0.0025	[11]
MIC	Crude oil	0.250	Conc. HNO_3 & H_2O_2	190-220	40	ICP-MS	8-15	82-94	Sc, Y, La, Pr, Nd, Sm, Eu, Tb, Dy, Er, Tm and Yb	0.006-0.45	[64]
MIC	Crude oil	0.500	Conc. HNO_3 & H_2O_2	1000 W	40	ICP-OES	6-8	92-108	Cl and S	12 and 5	[88]

MIC	Crude oil	0.100	Conc. HNO_3 & H_2O_2	200	40	ICP-OES	<2	N/A	Hg, Au, Cu, Al, Co, K, Mg, Si and Sr	0.144 -151.37	[55]
MIC	Diesel	0.400	6M NH_4NO_3	120-210 W	25	ICP-MS	<5	70-78	Cd, Co, Cr, Cu, Mn, Ni, Pb and V	0.10,0.87, 0.14,0.14, 0.052 and 0.11	[60]
MIC	Diesel	0.400	Conc. HNO_3	1 400 W	30	ICP-OES	<13	95.6-98.7	S	2	[89]

Note: NS [not specified]; **V [volume], MIC-** [Microwave Induced Combustion**]; MAAD- [**Microwave Acid Assisted Digestion]

2.2.2.2 Extraction sample preparation methods

Metal extraction is whereby the metal is separated from the organic phase to the aqueous phase usually with an aid of an extracting solvent, making the analyte of interest ready for analysis [38, 90]. Extraction step is important as it eliminates the organic content in the samples which may result in low sensitivity and inefficient nebulization in spectrometric detection [38]. There are several literature reported extraction methods on elemental determination in oily samples and these methods include; liquid-liquid extraction (LLE), solid phase extraction (SPE) and other (microwave assisted extraction, ultrasound assisted extraction and combination of LLE and SPE) (**Fig. 2.4**).

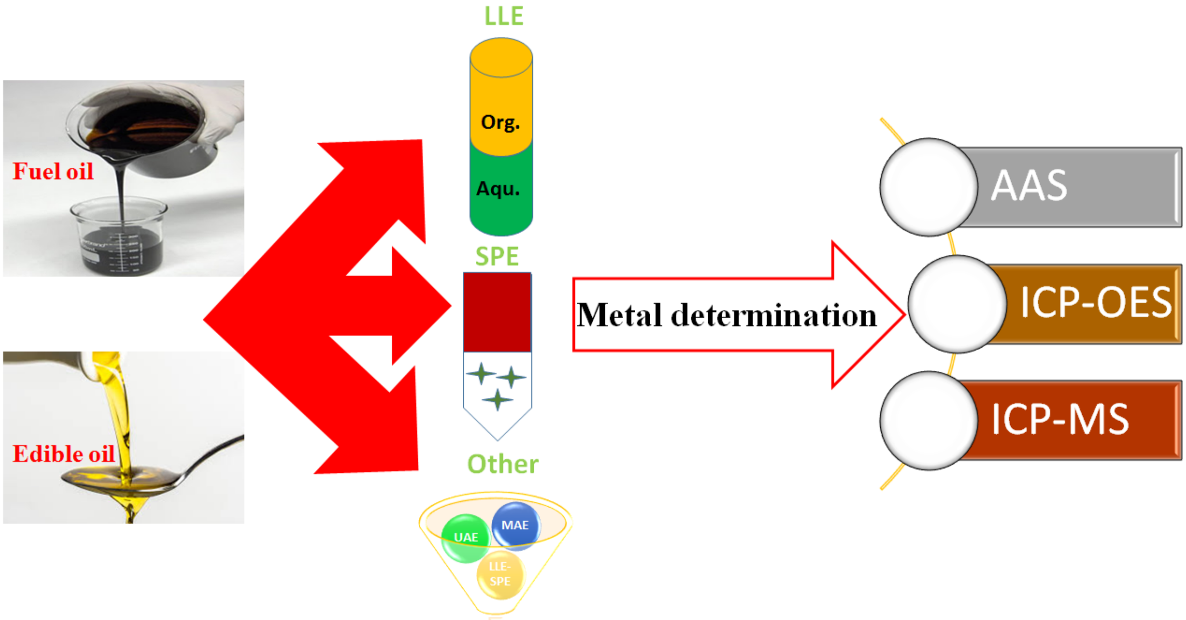

Figure 2.4: The types of extraction methods prior to their spectrometric determination

2.2.2.2.1 Liquid-liquid extraction (LLE)

Liquid-liquid extraction is a pre-treatment procedure that helps in enrichment and separation of metals from samples, independently on their form [91]. This sample preparation method separate analytes based on their relative solubilities in immiscible liquids with the aid of extraction solvent [92]. In the case of element extraction, elements move from the organic phase (oil) to the aqueous phase (analyte and acid), and the aqueous phase with analyte is then called an extract. The choice of extraction solvent affects the efficiency of the extraction method [91]. Under LLE, different extraction methods are observed, and they include the; (i) extraction induced by emulsion breaking (EIEB) and (ii) liquid-liquid micro-extraction (LLME)

(i) Liquid-liquid microextraction (LLME) can be further divided into three categories which are single drop liquid-liquid micro-extraction (SD-LLME), hallow fiber liquid-liquid micro-extraction (HF-LLME), and dispersive liquid-liquid micro-extraction (DLLME), as shown in **Fig.2.1**. Firstly, DLLME is a form of extraction, whereby an extraction solvent is mixed with a dispersive solvent and this mixture is then rapidly injected into the aqueous sample. For efficient extraction, the extraction solvent must be immiscible with water and dispersive solvent and show high affinity for the target analytes. The extraction solvent is typically denser than water, such that it will form sedimented phase, at the bottom of the extraction tube [92].

Reverse phase–DLLME is a new extraction method that is under DLLME and is characterised by its few extraction steps and cost effectiveness as very small volumes of reagents are used [93].This method allows the use of very small volume (µL) of aqueous phase (dispersant/ extracting solvent) to high volume (mL) of organic phase (oil). The RP-DLLME mainly consist of the following steps; (i) injection of dispersant/extractant mixture and this result in formation of turbid solution, (ii) then manual shaking of the mixture to ensure proper mixing of the dispersant with the oil sample for efficient extraction of target analyte, (iii) centrifugation is performed to separate the aqueous phase (analyte and disperser/extracting solvent), the aqueous phase get deposited at the bottom of the centrifuge tube, (iv) since the aqueous phase is very mall, the removal of organic phase is conducted and (v) the remaining aqueous phase is then extracted using a micropipette, transferred to a volumetric flask (preferably 5 mL) and diluted to the mark for analysis of target analytes [93-95]. The RP-DLLME is gaining some popularity as it has shown several advantages during metal extraction methods. This sample preparation method just like DLLME, uses extraction solvent at µL scale in the presence of low chain alcohol, making this method less toxic to human life. Additionally, high enrichment factor and low LOD have been reported when using this sample preparation method [93, 96] .However, the use of RP-DLLME has a limitation when metal ions are extracted from fat samples. This is because, RP-DLLME requires an agent that prevent solidification of liquified samples for fats samples [93].

The SD-LLME is also under LLME and the first study on this sample preparation method was conducted in 1996 [97]. In this method, a drop of organic solvent is exposed for a certain time to the aqueous sample that contains the target analytes. Then the organic drop pre-concentrate the analytes of interest prior to collection and determination. This sample preparation method showed advantages as it uses less extraction solvent (µL) and fast extraction time (1-15 minutes). However, the dislodging of solvent drop in SD-LLME is a major drawback of this sample preparation method [98].

In addition, Pedersen-Bjergaard and Rasmussen published a first paper on HF-LLME and this method uses hallow fiber (normally polypropylene) constitutes with a semi-permeable membrane, in which the pores are filled with a suitable organic solvent [98]. Alternatively, a different immiscible solvent is present within the fibre lumen to allow for two equilibria for the analytes between; the water and solvent in the wall, solvent and wall in the lumen thus constituting the three-phase [99]. The HF-LLME showed to be cost effective as less volume (µL) of reagents are used. In contrast, this sample preparations showed limitations which include, a need to prepare dispersible hallow fibers, clogging of hollow fiber pores and time consuming as the analyte cross the hollow fiber wall by diffusion [98]. Literature had not reported the use of HF-LLME and SD-LLME in determination of metals in oil samples (ii) Extraction induced by emulsion breaking (EIEB) is another widely investigated sample preparation method under liquid-liquid extraction and it was firstly reported in 2010. This sample preparation procedure involves the use of surfactant to reduce surface tension between the two immiscible liquids, resulting in proper mixing of the liquids by forming emulsions. After emulsion formation, emulsions are broken using water bath [57, 94, 100, 101], centrifugation [3, 102, 103] and ultrasound bath [104]. A successful separation mostly result in a formation of two layers, though three layers are also reported in some studies [105]. In the case of two layers, the top layer is the organic phase (oil) and the bottom layer is the aqueous phase (analyte and acid) [24, 100, 105]. In the case of three layers, the top layer is the organic phase, middle layer becomes the aqueous phase and the bottom layer is usually the surfactant rich phase [100]. The EIEB was introduced to avoid problems related to special equipment and long tedious time require in decomposition methods. [106]. This sample preparation has been used in different oily matrices such as lubricating oils [107], edible oils [108] and fuel oils [24]. Additionally, this sample preparation method has been used with different kinds of analytical techniques such as ICP-OES [58, 109], ICP-MS [24, 102, 110], ETAAS [111, 112], FAAS [3, 101, 113, 114],CV-AAS [8] and GFAAS [3, [115-117]. The EIEB has showed several advantages which include; cost-effectiveness, easy operation, minimal use of concentrated acids and organic solvents, prohibited plasma extinctions, and it minimizes carbon deposit build up in the plasma based techniques [24]. The advantages of EIEB made researchers to pay more attention to this sample preparation procedure [107, 118].

The different types of LLE methods applied in oily matrices for metal extraction prior to spectrometric detection are presented in **Table 2.3**. Cassela et al. [94] reported EIEB for the first time, which was applied in diesel samples followed by ETAAS analysis for the determination of Cu, Fe, Ni and Pb. These researchers optimised all the significant parameters that were affecting the extraction, which were [HNO_3], surfactant type (Triton X-114 and Triton X- 100) and the extraction temperature [94]. Very low detection limits of 0.114, 0.183, 145 and 0.294 µg/L for Cu, Fe, Ni and Pb, respectively, were observed. The same sample preparation method was also reported in crude oils [95, 119], edible oils [57, 103] and lubricating oil [102]. Despite the dominance of the use of surfactants for emulsion breaking, another study by Nunes et al. [103] also reported for the first time the use of HCl and n-propanol for micro-emulsion breaking in virgin oil. This study showed no significant differences as high percentage recoveries ranging from 89-103% for Cu, Fe, Ni and Zn were obtained, making this sample preparation similar to EIEB, which make use of Triton X-114 and Triton X-100. Valasques et al.[120] reported for the first time the use of HCl with Triton X-114 for extraction of As, Se and Hg in crude palm oil prior to analysis by HG-AFS (As and Se) and CV-AFS (Hg). The choice of HCl was because HNO_3 oxidizes $NaBH_4$, thereby, reducing the efficiency of hydride and mercury vapour generations [120]. Limits of detection for As, Hg and Se were 0.22, 0.036 and 0.46 µg/L, respectively with percentage recoveries ranging from 90-111%, making this sample preparation one of the best methods reported in literature for extraction of metal ions in oily matrices [120]. The use of HCl reported an extraction time of 40 minutes, which was a limitation (more time was used). Additionally, the use of two different analytical instruments (HG-AFS and CV-AFS) for different elements was also a disadvantage, as more time was spent during the optimization of two different techniques.

Even though, EIEB was mostly reported, there were other sample preparation procedures under LLE, which were reported. These techniques include LLME [121] and RP-DLLME [113]. These sample preparations showed short extraction time of 21 and 15 minutes, with percentage recoveries of 84-104% and 93.9-108% for LLME and RP-DLLME, respectively. Additionally, Soylak et al. [1] reported the use of deep eutectic solvent (DES) in LLME for the determination of Co, Pb, Ni and Mn in some edible oils prior to analysis by FAAS. The DES was prepared by mixing choline chloride (hydrogen bond acceptor) with urea (hydrogen bond donor) [1]. The use of DES in LLME made this sample preparation to be of low cost (as urea and choline chloride are readily available), and environmentally friendly (DES is non-toxic compared to most organic solvents). The use of DES in LLME gave percentage recoveries ranging from 97-102% for the analysed metals [1]. However, this sample preparation method showed the short coming of having high detection limits, which were 2.4, 4.6, 7.5 and 1.0 µg/L for Pb, Co, Ni and Mn, respectively [1]. Lima et al.[122], attempted to improve detectability limits by introducing the combination of EIEB and DLLME as a pre-concentration technique. Low detection limits of 0.23 and 0.24 µg/L were obtained for Cu and Pb, respectively and percentage recoveries ranging from 87-115 % were obtained [122]. It is worth in noting that, the combination of two sample preparation methods can increase chances of contamination as more reagent, sample manipulation and increased extraction time was used. Additionally, Baran et al.[123] reported the traditional LLE where a Schiff base solution (N, N'-bis(methoxy-salicylidene)-2-hydroxy-1,3-propaneldiamine) was used for extraction of Fe in edible oil prior to analysis by FAAS. Despite excellent percentage recoveries (96.75-102.30 %) observed, the use of large volumes of Schiff base solution (21 mL) and use of large volumes of concentrated HNO_3 (5 mL) made this sample preparation to be expensive and hazardous.

It is worthy to note that, **Table 2.3** shows EIEB as the mostly reported sample preparation method under LLE and the AAS was the most used analytical technique. The choice of EIEB over the other sample preparation might be due to its simplicity, less energy used, short extraction time, environmentally friendliness, etc. [100]. The choice of AAS might be due to the complexity of ICPs. Additionally, group I & II elements (Na, K, Ca, Mg etc.) from the Periodic Table easily ionize at low temperatures; hence AAS was favoured when these elements were the target analytes [124, 125, 99]. Form **Table 2.3**, it can also be observed that, the use of HNO_3 over other acids dominated. This is because, HNO_3 is compatible with many spectrometric techniques [24]. It has to be noted that, the overall LODs reported from different LLE methods ranged from 0.000037 to 294 µg/L, irrespective of the analytical technique that was used. Lastly, spiking was the mostly favoured validation method over certified referenced material (CRM). This is because, spiking methods are cost effective compared to purchasing of the costly CRMs. It is worth in noting that, some CRM are not yet available on markets, but that cannot stop the researchers from persuading and building new scientific knowledge. Lastly, **Table 2.3 (**LLE) shows that when spiking was used as the validation method, the aqueous and organometallic standards were equally used in terms of the literature reported publication numbers.

Table 2. 3: Different types of LLE methods applied in oily matrices for metal extraction prior to analysis

Matrix	**LLE type**	**Surfactant/ Dispenser solvent**	**Dilute acid**	**Emulsion breaker**	**E.T (min)**	**Validation method**	**Spiking**	**Metal ions**	**Detection technique**	**LODs µg/L**	**RSD (%)**	**%R**	**Ref.**
Biodiesel	DLLME	Isopropyl alcohol	HNO_3	Centrifugation (3600 rpm)	15	CRM (SpecSol SRM-682)	NA	Ca, Mg, Na and K	AAS	32.3, 4.3, 3.0 and 5.8	1.3-2.5	90.3 - 94.7	[121]
Engine oil, gasoline and diesel	DLLME	Magnetic ionic liquid	HNO_3	Magnet	NA	Spiking	Standard aqueous solutions	Cd	ETV	0.084 ng/g	9.6	95-110	[126]
Biodiesel	DLLME +EIEB	Ethanol (disperser solvent) and Triton X-114	HNO_3	Centrifugation (3 600 rpm)	39	CRM (NIST 2772)	NA	Cu (II) and Pb (II)	GFAAS	0.23 and 0.24	0.9-5.7	87-115	[122]
Biodiesel	EIEB	Triton X-114	HNO_3	water bath (90 °C)	10	Spiking	Organometallic std	Mg and Ca	FS-FAAS	0.047 and 0.013	7.6 and 18	88-106	[127]

Bitumen	EIEB	Triton X-100	HNO_3	Water bath (90 °C)	15	Spiking	Standard aqueous solutions	Co, Fe and Ni	HR-CS GF-AAS	0.003, 0.018 and 0.027	<10	100 - 100.7	[128]
Crude oil	EIEB	Triton X-100	NHO_3	Ultrasonication (50 Hz)	30	CRM (SRM 1634c)	NA	Co, Cu, Pb, and Se	GFAAS	ng/g 20,30, 40 and 110	2.8-4.8	102-116 106-119 98-111 95-122	[116]
Crude oil	EIEB	Triton X-100	HNO_3	Ultrasonication (40 Hz**)**	18	CRM (NIST 1085b and NIST 1634c)	NA	Ca, Mg, Sr, and Na	ICP-OES	5.6,3.9,0.12 and 9.8	3.5-10.9	92.8 - 102.2	[95]
Crude oil	EIEB	Triton X-100	HNO_3	water bath (88 ±2 °C) and centrifugation (4000 rpm)	15	CRM (NIST 1634c)	NA	Ba, Ca, Mg and Na	ICP-OES	0.12,1.2,0.14 and 5.8	0.0058-0.29	99-104	[109]

Crude oil	EIEB	Triton X-100	HNO_3	Centrifugation (4000 rpm) water bath (90 °C)	75	CRM (SRM 1634c)	NA	As, Co, Cr, Mn, Mo and Pb	ICP-MS	0.17,0.15 0.31,0.20, 0.22 and 0.27	6-10	80-115	[24]
Crude palm oil	EIEB	Triton X-114	HCl	Ultrasonication (90 °C)	40	Spiking	Standard aqueous solutions	As, Hg and Se	Vapour generator-ASF and CV-AFS	0.22,0,036 and 0.46	0.92, 2.2 and 3.7	90-111, 99-108 and 95-128	[120]
Crude palm oil	EIEB	Triton X-100	HNO_3	Water bath (90 °C)	30	spiking	Standard aqueous solutions	Cd and Pb	GFAAS	0.051 and 0.039 ng/g	1.8 and 5.4	88.5-112	[129]
Diesel	EIEB	Triton X-100 and	HNO_3	Water bath (80 °C)	15	Spiking	Organometallic standards	Cu, Fe, Pb and Ni	EAAS	114,183, 294	4.5,3.5,3.3	85.2-109	[94]

		Triton X-114								and 145	and 8.8		
Diesel	EIEB	Triton X-100	NHO_3	Ultrasonication (50 Hz)	30	CRM (SRM 1634c)	NA	Co, Cu, Pb, and Se	GFAAS	ng/g 20,24, 1320 and 110	2.8-4.8	100-113 100-117 105-117 100-116	[116]
Diesel	EIEB	TritonX-114	HNO_3	Centrifugation (3200 rpm)	60	Spiking	Aqueous standard	Al, Cu, Mn, Ni, Sn and V	ICP-MS	0.03,0.09, 0.04,0.07 0.03 and 0.05	0.59-3.30	84-113	[100]
Gasohol	EIEB	Triton X-114	HNO_3	Ultrasonication (90 °C)	10	Spiking	Organometallic standard	V and Ni	GFAAS	1.1 and 3.5	5.8 and 3.4	86-101	[104]

												91-109	
Gasoline	EIEB	Triton X-100	NHO_3	Ultrasonication (50 Hz)	30	CRM (SRM 1634c)	NA	Co, Cu, Pb, and Se	GFAAS	ng/g 320,480, 640 and 1760	2.8-4.8	91-105 83-102 72-106 82-113	[116]
Gasoline	EIEB	n-propanol (alcohol)	HNO_3	Horizontal shaker (speed **NS)**	16	Spiking	Organic standard	Hg	CV-AAS	0.9	4.8	88-109	[130]
Gasoline	EIEB	Triton X-100	HNO_3	Water bath (90 °C)	10	Spiking	Organometallic standard	Cu, Fe, and Pb	HR-CS-FAAS	3.0, 5.0 and 14.0	4.7, 3.5 and 5	98-105	[101]

Lubricating oil	EIEB	Triton X-114	HNO_3	Centrifugation (6000 rpm)	10	CRM(SRM 1084 and 1085b)	NA	Mg, Cr, Ni, Cu and Pb	ICP-MS	0.126, 0.058, 0.028, 0.078 and 0.009	1.87 - 4.01	86-110	[102]
Lubricating oil	EIEB	Triton X-114	HNO_3	Water bath (90 °C)	10	spiking	Aqueous	Cr and Mn	ETAAS	0.066 and 0.036	2.5-4.3	89-115 86-115	[131]
Lubricating oil	EIEB	Triton X-114	HNO_3	Centrifugation (3500 rpm)	30	Spiking	Organometallic standard	Cu, Fe, and Mn	FAAS	ng/g 2.9,77 and 8.2	1.3-5.6	89-109	[3]
Lubricating oil	EIEB	Triton X-114	HNO_3	water bath (90 °C)	30	Spiking	Aqueous standard	Ca, Mg and Zn	FAAS	ng/g 134,15 and 25	**0.72 - 2.67**	**NS**	[114]
Lubricating oil	EIEB	Triton X-114	HNO_3	water bath (80 °C)	7	Spiking	Aqueous standards	Fe, Cu, Cr, Ni	ICP-MS	ng/g	3	95.5 -	[132]

								and Pb		1050, 960, 1050, 1000, and 970		104.8	
Lubricating oils	EIEB	Triton X-100	HNO_3	Ultrasonication (90-140 °C)	75	CRM (SRM 1084a)	NA	V, Ni, Cu, Cr, Pb, Mo, and Ag	ETAAS	0.83, 0.77, 0.44, 0.23, 1.25, 1.34, and 0.14	1-7	94-115	[133]
Mineral oil	EIEB	Triton X-114	HNO_3	water bath (90 °C)	30	Spiking	Organometallic standard	As, Cr, Cu, Mn, Pb and V	GF AAS	0.9, 0.08, 0.16, 0.03, 0.13 and 0.8	NS	91-104	[117]

Omega-3 dietary oils	EIEB	Triton X-114	HNO_3	water bath (88±1 °C)	10	Spiking	Aqueous Standard	Cd	TS-FF-AAS	2.5	3.8	93-99	[57]
Sunflower, olive, rapeseed and cold liver oil	EIEB	Triton X-100	HNO_3	Ultrasonication (**NS**) and centrifugation (300 rpm)	70	CRM (LENvioroMAT HU-1-used oil)	NA	Al, Ca, Cd, Mg, Mn, Ni, Ti, V and Zn	ICP-MS	ng/g 2470, 2810, 37, 1370, 50, 490, 470,32 and 87	2.9-14.5	83.3–117.8	[110]
Sunflower,corn, Fish and olive oil	EIEB	Triton X-100	HNO_3	Water bath (90 °C)	60	spiking	Aqueous Standard	Sn	ICP-MS and GFAAS	0.009 and 1.1	<5	94-104	[134]
Vegetable oil	EIEB	Triton X-100	HNO_3	Water bath (90 °C)	20	spiking	Aqueous Standard	Al, Ba, Cu, Cr, P, Ni, Ti and Zn	MIP-OES	0.6-3.7	<2.5	99-104	[135]

Vegetable oil	EIEB	Triton X-114	HNO_3	Centrifugation (8 140 rpm)	12	Spiking	Organometallic standard	Mg, Mn, Fe, Zn, Ag, Ba, Pb, and Cr	ICP-MS	0.004-0.271	0,59-3.40	87-108	[136]
Virgin oil	EIEB	Alcohol	HCl	Centrifugation (3 000 rpm)	30	Spiking	Organometallic standard	Cu, Fe, Ni and Zn	HR-CS-FAAS	0.12, 0.62 0.58 and 0.12	5-11	89-103	[103]
Crude oil	LLE	Dichloromethane	HNO_3	Centrifugation (7 800 rpm)	20	CRM (NIST 981 and SRM 976)	NA	Pb and Zn	MC-ICP-MS	ng/g 2 and 100	0.1-3	95-100	[119]
Olive oil	LLE	5MSHP	HNO_3	Water bath (25 °C)	5.6	Spiking	Organometallic standard	Cu	ICP-OES	ng/g 60	2.3	92.50-	[137]

												107.72	
Olive, corn, sunflower, hazelnut and canola	LLE	Ethanol	4MSHP	Magnetic stirrer (29.7 °C)	15.4	Spiking	Aqueous standard	Ni	FAAS	0.26	2.3	93.02- 96.78	[138]
Olive and sunflower oils	LLE	Ethanol	4MSHP	Magnetic stirrer (31.1-27.3 °C)	50- 62	Spiking	Organometallic standard	Ni and Zn	FAAS	0.41 and 0.16	5	96.4-100 and 98.6-101	[139]
Sunflower, olive and corn oil	LLE	4MSHP	HNO_3	19.3	10	Spiking	Organometallic standard	Fe	FAAS	0.09	1.0	96.75-102.30	[123]
Sunflower, olive and refined oils	LLE	Xylene	HNO_3	Water bath (90 °C)	20	Spiking	Organometallic standard	Fe, Ni, Cu, Pb, Cd,	AAS	0.04, 0.01, 0.01, 0.03, 0.001	5-17	90-110	[140]

								and As		and 0.006			
Soybean, sunflower, olive and hazelnut oils	LLE	Ethanol	HNO_3	Magnetic stirrer (speed **NS**)	24 – 31.8	Spiking	Organometallic standard	Fe (III) and Cu (II)	FAAS	ng/g 67.3 and 0.0153	3.7 and 3.4	98.6	[141]
Edible oil	LLME	ChCl with urea Deep eutectic solvent	HNO_3	Centrifugation (4 000 rpm)	30	Spiking	Aqueous standard	Pb, Co Ni, and Mn	MS-FAAS	2.4, 4.6, 7.5and 1.0	0.9-4.3	97-102	[1]
Olive oil	LLME	Combination of ethanol, methanol, acetone and acetonitrile	HNO_3	Ultrasonication (60 °C)	12	Spiking	Aqueous standard	Cu, Cd, Ni, Pb and Zn	FAAS	0.8, 0.3, 0.5,1.5 and 0.5	3.6	95.2-101	[142]
Olive, sunflower, rapeseed	LLME	Lipase	HNO_3	Centrifugation (3000 rpm)	20	CRM (EnviroMAT HU-1 used oil)	NA	Al, Ba, Cd, Fe,	ICP-MS	0.46, 0.03, 0.007, 0.028,	2.8	94-116	[108]

and salmon oils								Mn, Mo, Ni, V, and Zn		0.67, 0.038, 0.022, 0.14, 0.17, 0.05 and 0.07			
Soybean, hazelnut. Sunflower and canola oils	LLME	Cyclohexyl amine (extracting solvent)	HNO_3	Water bath (60 °C) and Centrifugation (5000 rpm)	21	Spiking	Aqueous standard	Cd and Zn	FAAS	ng/g 3.8 and 0.6	2.4-1.7	84-104	[143]
Biodiesel	RP-DLLME	Isopropanol	HNO_3	Centrifugation (3600 rpm)	15	Spiking	Aqueous standard	Na, K, Ca and Mg	FAAS	ng/g 0.40, 0.02, 0.05 and 0.08	3	93.9-108.1	[96]

Fish oil	RP-DLLME	n-propanol	HNO_3	Centrifugation 5 600 g	10	Spiking	Organometallic standard	Cd, Fe, Mn, Ni, Pb and Zn	ICP-OES	ng/g 0.41, 1.98, 0.33, 0.35, 1.52 and 1.39	5	85.3 - 97.3	[93]
Vegetable oil	RP-DLLME	n-propanol and xylene	HNO_3	Centrifugation 5 600 g	10	Spiking	Aqueous standards	Ni	FAAS	ng/g 40	0.9-8.4	93.3 - 101.5	[144]

Note: **4MSHP** –[N,N``-bis (4-methoxysalycylidene)-2-hydroxy-1,3-propanediamine]; **5MSHP**- [ N,N``-bis(Methoxy-salicylidene)-2-hydroxyl,3-Propanediamine]; **NS-** Not specified; **DLLME-[** Dispersive liquid-liquid microextraction]; **EIEB-[** Extraction Induced by Emulsion Breaking]; **LLE** -[Liquid-liquid Extraction]; **RP-DLLME**-[Reverse Phase-Dispersive Liquid-liquid microextraction]; **CRM** –[Certified Reference Material]

2.2.2.2.2 Solid phase extraction (SPE)

This extraction strategy uses a sorbent to adsorb analytes of interest. The analytes move from the aqueous solution and get absorbed on the adsorbent's active sites, making these analyte to be easily removed from the solid phase (sorbent) during the elution step [145]. The traditional SPE is characterised by five major steps, which are; (i) conditioning, (ii) equilibrating, (iii) sample loading, (iv) washing and (v) elution [145]. Conditioning activates the sorbent by wetting as most extraction of the metals is highly hydrophobic. The second step is equilibrating which creates an environment of sorbent that is equilibrium to that of sample as possible. Then next step is sample loading, which deals with putting the sample to be extracted. The fourth step of SPE is sample washing whereby sorbent is washed to selectively remove contaminant species from the sorbent leaving the adsorbed analyte on the sorbent. The final step is elution step, in this step a suitable solvent is used to extract analytes that were retained from the sorbents and that solvent must be capable of disrupting all interactions between functional groups of the sorbent and the analyte [145]. The type of the sorbent used plays a critical role in adsorption, therefore an appropriate sorbent must be used to ensure maximum extraction of analyte in the sample. There are four sample preparation methods that falls under the SPE. These methods are; dispersive solid-phase extraction (DSPE), column-based solid-phase extraction, batch solid-phase extraction, magnetic solid-phase extraction (m-SPE) and solid-phase micro-extraction (SPME) [146]. Solid phase extraction sample preparation procedure has several advantages when compared to other extraction and pre-concentration methods, which include simplicity, rapidity, cheapness, selectivity, ability to achieve high pre-concentration factor and its applicability to all analytical techniques [18, 147, 148]. This research focused on the m-SPE in crude oil, gasoline and diesel as stated in **Chapter 1** under objective section. The m-SPE is a sample preparation method where a solid sorbent of magnetic character is used for adsorption of metal ions. This method was firstly reported by Towler et al. in 1996, where a magnetic sorbent made of Fe_3O_4 coated with MnO_2 was applied for extraction of Pb, Po and Ra in seawater samples [99, 149]. Magnetic solid phase extraction is considered as a simple and fast sample preparation technique used in the extraction of numerous trace elements in the environment and biological samples [150]. To the best of our knowledge, m-SPE has been conducted in diesel oils [151] and edible oil [152]. Additionally, FAAS was the most favoured technique in elemental determination.

Information presented in **Table 2.4** shows the type of sample preparation methods reported under SPE prior to metal determination by spectrometric techniques. Asci et al., for the first time developed a method where zinc-piperazinedithio-carbonate (ZnPDC) was used as a sorbent and $Hg(NO_3)_2$ was the eluent. This method showed high recovery values (93-100%) for Cd, with very low enrichment factors (10) [153]. In 2014, Mohmood et al., reported SPE for the first time, where a modified disk (octadecyl silica membrane disk) was used as a sorbent for extraction of Hg in gasoline samples prior to CV-AAS analysis. This sample preparation showed very high pre-concentration factor of 240 which becomes the highest pre-concentration factor reported under the proposed title [8]. In 2018, a combination of MSPE and Batch SPE was developed by Barreto et al., and a magnetic sorbent (Fe_3O_4) was used in the extraction of trace Cd in edible oil [154]. This sample preparation method showed high recovery values of 96-105%. However, very low enrichment factor of 9 was reported. Santos et al., developed a column SPE where a resin modified with 3,4-dihyroxybenzoic acid was used as sorbent and HCl as eluent for extraction of Cu, Fe, Pb and Zn in gasoline samples. The enrichment factors were 5.4, 5.3, 6.7 and 6.1 for Cu, Fe, Pb and Zn, respectively [155]. These were the lowest enrichment factors reported for SPE in oily matrices. Another interesting study was reported by Nunes et al., for the first time vermicompost (biosorbent) was used for extraction of Cd in edible oil. High percentage recoveries ranging from 94-100% with enrichment factor of 32 made this sample preparation to be among the best extraction methods [156]. Despite very good percentage recoveries and enrichment factor, LOD (1.7 µg/L) was the highest reported for Cd under SPE. There were no other literature reports that published the use of bio-sorbents for extraction of metal ions in oily matrices. Lastly, Nomngongo et al., compared for the first time the two strong ionic exchangers (Dowex 50W-x8 and Dowex 1-x8) for extraction of Mo, Sb and V in gasoline samples. It was reported that, the extraction of such elements favoured the use of the anionic exchanger (Dowex 1-x8) over the cationic (Dowex 50W-x8) resin. This sample preparation reported the second highest pre-concentration factor of 120 reported in SPE for metal extraction in oily matrices. Despite Dowex 50W-x8 failing to show good extraction of Mo, Sb and V, but in 2014, Nomngongo et al, reported the use of this cationic ion exchanger (Dowex 50W-x8) for the extraction of Cd, Cu, Fe, Pb and Zn in gasoline and diesel samples [157]. This sample preparation just like other reported SPE showed higher percentage recoveries (92-104%) and enrichment factor of 30. It is also worthy in noting that, Nomngongo et al., then developed a dual bed SPE where the Dowex 50W-X8 and Dowex 1-x8 were both used in the formation of the column bed. This sample preparation also showed high enrichment factors ranging from 100-150 and percentage recoveries ranging from 95-99 % [158].

Table 2. 4: Different types of SPE methods applied in oily matrices for metal extraction followed by spectrometric determination

Matrix	**SPE type**	**Analytical technique**	**Sorbent**	**Element**	**Eluent**	**Validation method**	**LOD µg/L**	**%R**	**RSD (%)**	**Enrichment factor**	**Ref.**
Corn, olive and sunflower oils	Column SPE	FAAS	Zinc-Piperazinedithio Carbamate (ZnPDC)	Cd	$Hg(NO_3)_2$	CRM (CONOS-TAN S-21)	0.028	93-100	NS	10	[153]
Crude oil	Column SPE	CV-AAS	Octadecyl silica membrane	Hg	$HClO_4$	Spiking	0.25	88-109	1.9	240	[8]
Diesel oil	Column SPE	ED-XRF	Sisal Fiber	Cu, Ni, Mn and Zn	NA	spiking	0.03,0.04,0.03 and 0.02	86 -108	3.2, 6.5, 6.8 and 6.1	10,10,39 and 12	[159]
Ethanol fuel	Column SPE	FAAS	Silica-gel (**SiAT**)	Cu, Ni, and Zn	HCl	Spiking	1.3,1.1, and 0.9	92-101	3.5, 4.4, 4.4 and 3.2	38, 35 and 52	[160]
Fuel alcohol	Column SPE	FAAS	Vermicompost (biosorbent)	Cd	HNO_3	Spiking	1.7	94-100	2.4	32	[156]
Gasoline	Column SPE	CV-AAS	Octadecyl silica membrane disk	Hg	$HClO_4$	Spiking	0.20	88-109	1.9	240	[8]

Gasoline	Column SPE	FAAS	Resin modified (**XAD-DHB**)	Cu, Fe, Pb and Zn	HCl	Spiking	3.1,2.2,2.3 and 2.6	82-99	5.8-9.7	5.4, 5.3, 6.7, and 6.1	[155]
Gasoline	Column SPE	FAAS	Silica-gel (**SiAT**)	Cu, Fe, and Ni	HCl	Comparison with other methods	0.8,3,3 and 0.1	95-100 96-100 93-97 99-102	**NS**	**NS**	[161]
Gasoline	Column SPE	ICP-OES	Dowex 50w-X8 and Dowex 1-X8	Ag, Al, As and Cr	HNO_3	Spiking	0.16-0.22 and 0.52-0.76	95-99.3-101 96.9-100 and 99.8-101 99	1.2,2.0, 1.8 and 1.3	100,130,130 and 150	[158]
Gasoline	Column SPE	ICP-OES	Dowex 1-x8	Mo, Sb, and V	HNO_3	Spiking	0.14,0.05	99.3-101	1.3-1.5	120	[162]

							and 0.03	96.9-100 and 99.8-101			
Gasoline	Column SPE	ICP-OES	Dowex 1-x8	Mo, Sb, and V	HNO_3	Spiking	0.14,0.05 and 0.03	99.3-101 96.9-100 and 99.8-101	1.3-1.5	120	[162]
Edible oils	Combination of m-SPE and batch SPE	GFAAS	Magnetic nanoparticle	Cd	HNO_3	CRM (F15C0448D)	0.006	96-105	3.3	9	[154]

Biodiesel	m-SPE	ED-XFS	$CoFe_2O_4$ nanoparticle impregnated with alizarin fluorine blue	Cd, Pb, Cr, V and Mo	NA	NA	166,106,137, 82 and 92 ng/g	85-114	1.57 - 4.50	9.3-27	[163]
Diesel oil	m-SPE	FAAS	Magnetic sorbent (Fe_3O_4 nanoparticle)	Cd	HNO_3,	CRM (NIST 1571 and NIST 1572)	0.09	96.6-104	1.7	184	[151]
Vegetable oil	m-SPE	FAAS	Fe_3O_4 nanoparticle	Cd and Pb	$[C_{4min}]$ $[FeCl_4]$	Spiking	ng/g 0.002 and 0.02	96-106 and 95-104	2.5-7.5 and 5.9-9.3	**NA**	[152]
Diesel	SPME	ICP-MS	Dowex 50w-x8	Cd, Cu, Fe, Pb, and Zn	HNO_3	Spiking	0.1,0.1,0.2 0.3 and 0.1	97-101,96-100, 96-102, 95-102 and 95-104	4.9-5.9	30	[157]

Fish oil	SPME	ICP-OES	*y*-Al_2O_3 factionalized with fluorescein	Mn, Cu, Ni, Cr, Cd and Pb	HCl	spiking	0.7, 4.1, 1.0, 1.6, 0.7 and 1.0	98.4-103.3	2.4-6.4	100	[164]
Gasoline	SPME	ICP-MS	Dowex 50w-x8	Cd, Cu, Fe, Pb, and Zn	HNO_3	Spiking	0.1,0.1,0.2 0.3 and 0.1	92-104	4.9-5.9	30	[157]

Note: **XAB-DHB-** [3,4-dihydroxybenzoic acid];**SiAT-** [Silica modified with 2-aminotiozole] NS- [not specified], %R- [percentage recoveries], RSD (%)- [relative standard deviation], SPE-[Solid phase extraction], SPME –[Solid phase micro-extraction], m-SPE-[Magnetic solid phase extraction]

2.2.2.2.3 Other extraction methods

Combination of SPE and LLE (SPE-LLE) is another promising extraction method and it offers fast and efficient extraction of target analytes [50]. The first step was the emulsion breaking and then followed by the solid phase extraction step. According to Cunha et al., [50], this sample preparation method used a magnetic nanoparticle that was added to a sample that has formed macro-emulsions. The analytes were adsorbed to the magnetic nanoparticles, a magnet was applied on the walls of the extraction system resulting in the sorbent with adsorbed analyte being attracted to the magnet. The micro-emulsions were then discarded, the sorbent was washed with deionized water and the analyte was finally eluted with diluted HNO_3. This sample preparation method proved to be very fast (40 s extraction time). Despite being very fast, a low pre-concentration factor of nine was reported [50]. It is also worth noting that, with this sample preparation method, more than 14 mg of magnetic nanoparticles was used to prevent formation of the micro-emulsions [50]. However, this method has limitations which include high cost (synthesis of nanoparticles is costly) and high chances of contamination due to use of several reagents.

Microwave-assisted extraction (MAE) was also reported in the extraction of metals in oily matrices. This extraction method combines the microwave and traditional solvent extraction [165]. The efficient heating by microwave dielectric heating effects causes the solvents to absorb microwave energy, thereby converting it to heat energy [56]. This sample preparation showed merits, which include, less risk associated with analyte loss, reduced reagent consumption and allow calibration using aqueous standards [166]. Additionally, this method is also advantageous as it allows sequential extraction as reagents can be added during extraction time and it has the ability of going through leaching cycles for efficient extraction of target analyte [167].However, this method might show limitations of severe matrix effect caused by microwave induced plasma which operates at lower power (up to 1 kW) [56] and the inability to perform simultaneous extraction of multiple samples in a single cavity [167].

Ultrasound-assisted extraction (UAE) is another extraction method reported in the extraction of metal ions in oil samples. During UAE, samples are mixed with diluted acids. It has to be noted that, diluted acid is added to transfer the metal ions from the organic phase to aqueous phase [168]. The sample is put in an ultrasound bath with controlled temperature to facilitate the extraction process and finally centrifugated for the separation of the organic and aqueous phase [169]. The latter is then diluted to the known volume and is ready for analysis with the compatible analytical instrument. Additionally, Kara et al. [108] introduced a detergentless ultrasound assisted extraction of elements from edible oils using enzyme (lipase) as an extractant. An enzyme was used in order to develop a cost-effective and greener extraction method [108]. This sample preparation just like others, showed high percentage recoveries ranging from 94-116 % and low detection limits (0.022-0.67 µg/L) for Al, Ba, Cd, Fe, Mn, Mo, Ni, V and Zn [108]. However, this sample preparation has not been applied again in any other oily matrices. This might be due to enzyme being specific on the substrate that they catalyse or the temperature and pH on which enzymes function. The UAE showed advantages which include short extraction time, operation simplicity, small reagent used and low cost [169].However, this sample preparation showed demerits which includes low sample input and very low enrichment factors which also negatively affect the limits of detection [170, 171] .

2.3 Summary of published work since 1991-2020

Several methods have been reported for the determination of the problematic elements in oil samples, which included direct and indirect analysis. Information presented in **Fig.2.5A** presents the trends in the number of publications between direct and indirect analysis in oil samples from 1991 till 2020. It can be noted that the number of publications was almost the same between direct analysis and indirect analysis from 1991 till 2005. However, from 2005 till 2020 there is a very huge difference in the number of publications between direct and indirect analysis, with the latter being the most favoured. The choice of indirect analysis over direct analysis might have come due to that, most analytical instrument requires the sample to be in aqueous state to avoid the problems that come with high organic load into different analytical instruments.

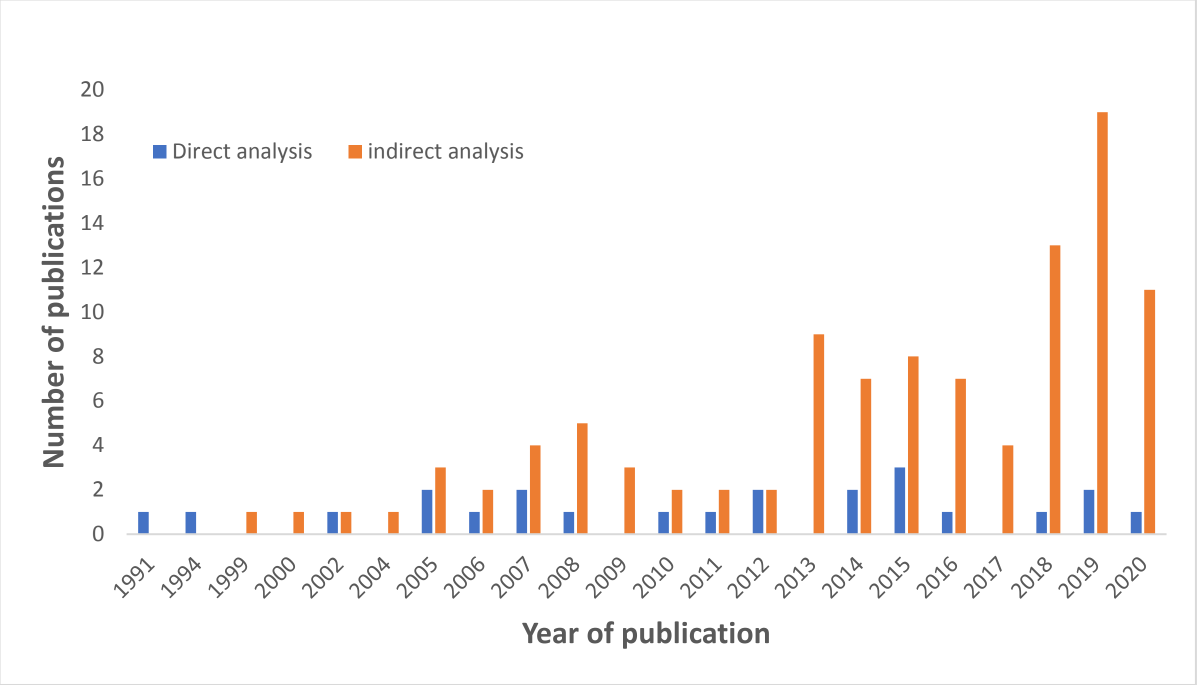

Figure 2. 5A: Trends in the number of publications under direct and indirect analysis of metals in oily matrices

As reported in **Fig. 2.5A** there use of extraction and decomposition method is something new and is getting more advanced each and every day. Therefore, the number of publications have been reported to increase over the years as presented in **Fig. 2.5B**. The use of extraction methods was much used when compared with decomposition methods. The choice of extraction methods over decomposition methods might be due to the less problems associated with most extraction methods over most decomposition methods. Decomposition methods like ashing are very prone to cross contamination and loss of volatile elements while the most digestion methods reported the use of concentrated corrosive nitric acid which at high temperatures produces too much of the deadly carcinogenic nitrous oxide. On the other hand with extraction methods over the years a huge improvement have been made to ensure that very small volume of reagents up to µL scale is used and this resulted in less hazardous waste generated into the environment in comparison to most decomposition methods that use high volumes of concentrated reagents. Additionally, very little has been reported in the other extraction methods but in 2019 and 2020 a high number of publication of up to 4 in both years have been reported up to this far which shows a great improvement.

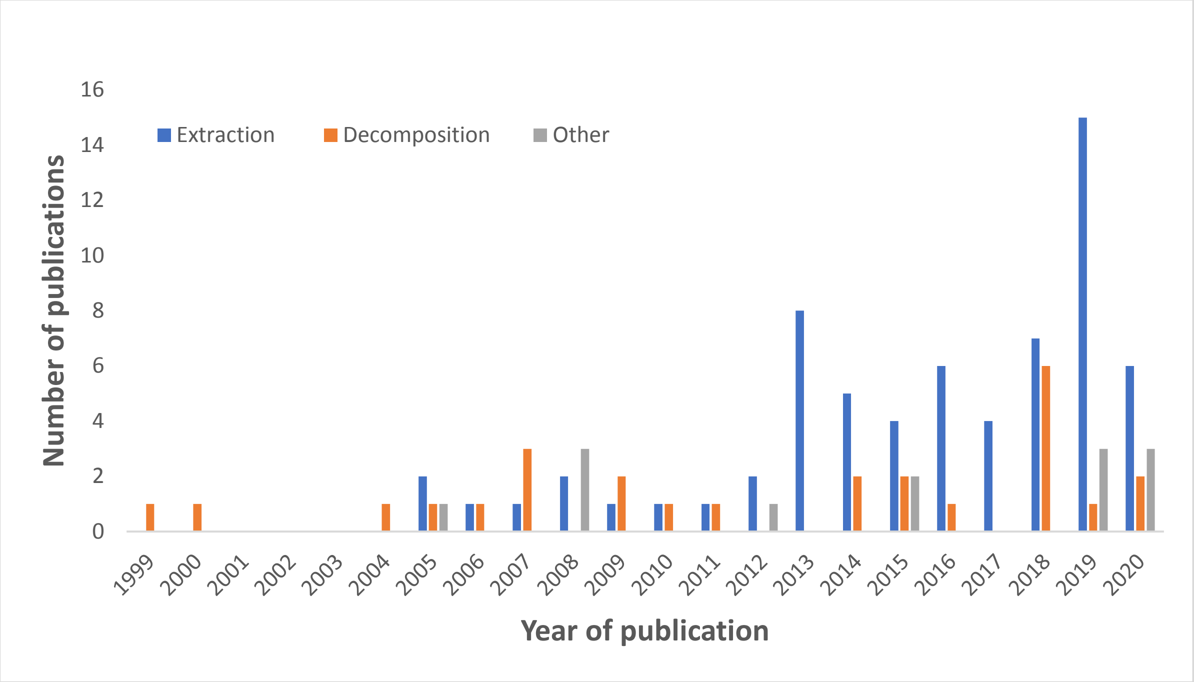

Figure 2.5 B: Trends in the number of publications for the different sample preparation under indirect analysis of metals in oily matrices

The nature of the matrix under study is very key as this create a picture of which sample is most favoured for direct analysis, decomposition, extraction and other methods. Since there were very little reports before 2005 on both direct and indirect as observed in **Fig. 2.5A**, for proper presentation of the work, matrices were studied from 2005 to 2020 for both direct and indirect sample preparation methods as presented in Fig **2.5C**. The latter shows that in direct, decomposition and extraction, the mostly studied matrix was the fuel oils. This might be due to human overreliance on fossil fuels as a source of energy. This therefore, helped to create awareness on dangers of metal present in different fuel oils from different parts of the world and ways of metal removal on the sample matrix.

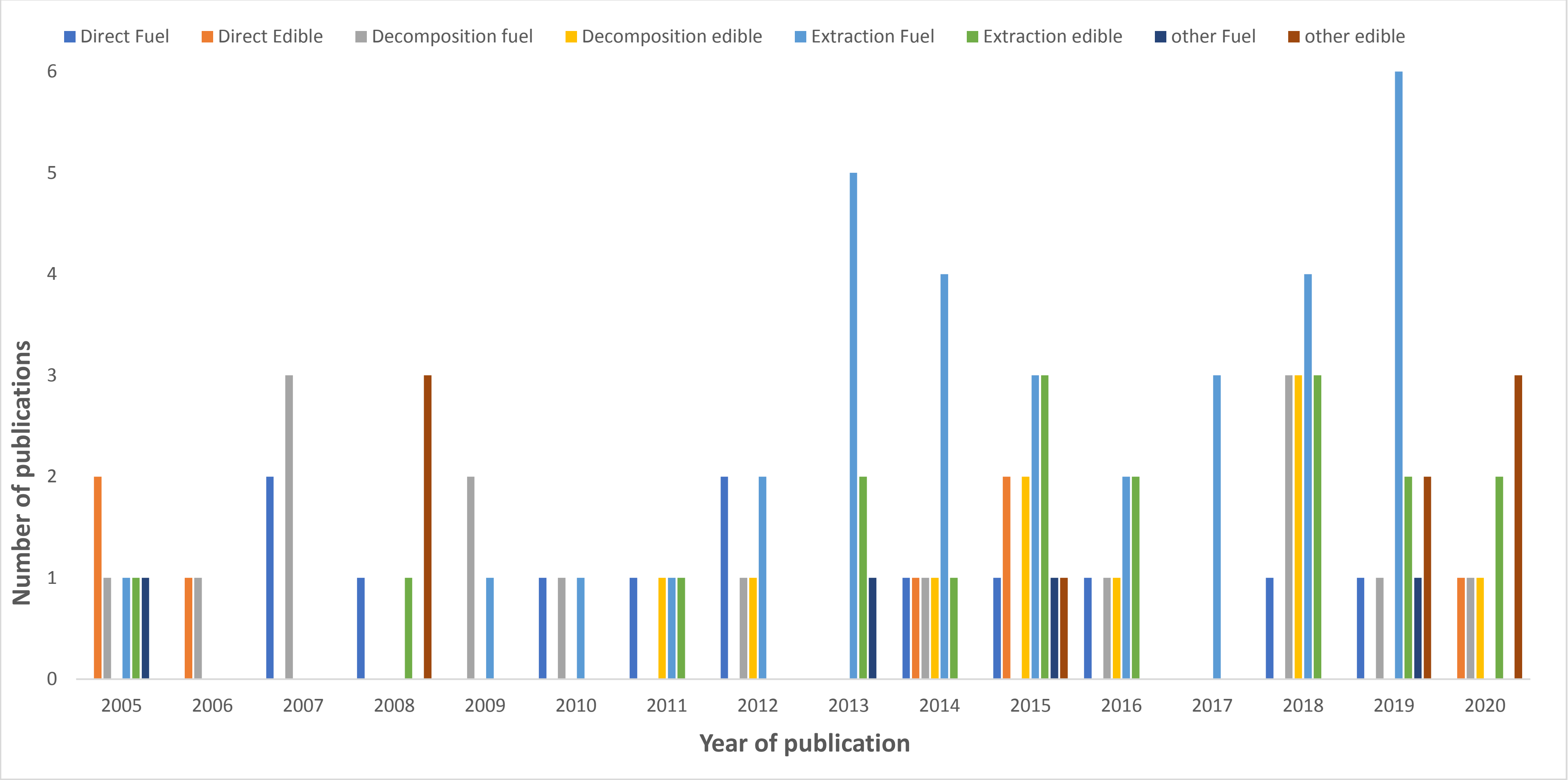

Figure 2.5 C: Trends in the number of publications under direct and indirect analysis of metals for different oily matrices

Several different elements have been determined in oil matrices, some metals were most reported between the different sample preparation methods. The information presented in **Fig. 2.6A, Fig. 2.6B**, **Fig. 2.6C and Fig. 2.6D** present the trends in metal determination under direct analysis, decomposition and extraction methods. In **Fig. 2.6A,** reported elements were determined in oil samples by direct analysis. This figure showed that metals that were most reported in fuel oils were Ni (12), Fe (10), Cu (7), Ca (6), Cr (6) and V (6). On the other hand, sulphur was the most studied non-metal reported with 4 publications.

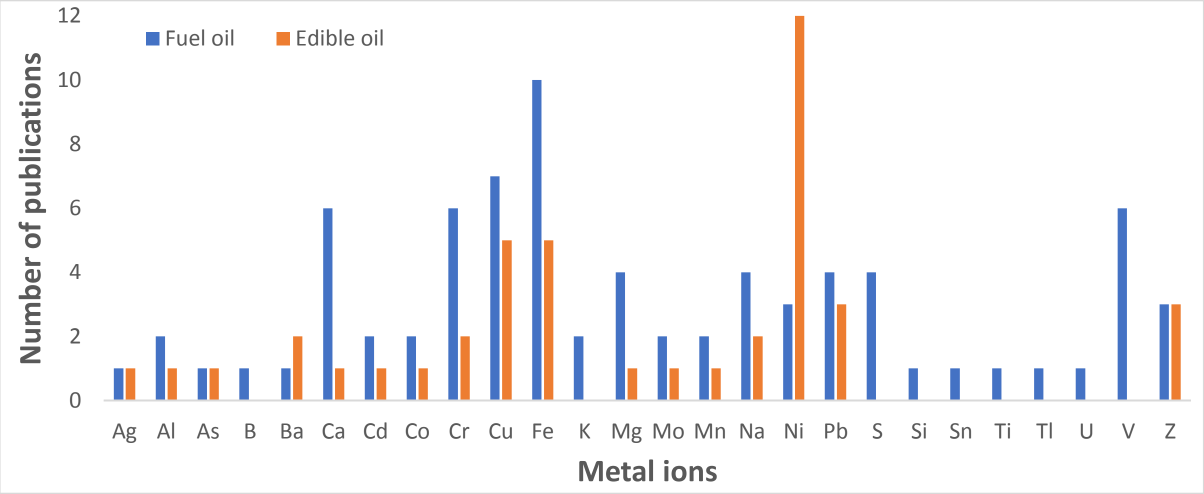

Figure 2.6 A: The different elements that were detected by direct analysis.

In **Fig 2.6B** a trend in the elements reported under decomposition of matrix, this figure reported that metals in fuel oils were most studied that in edible oils. The metals that were most reported with this sample preparation methods were Ni (10), Cu (7), V (7) and Pb (6). However, looking at the edible oils, the most reported elements were Cr (5), Zn (4), Cu (4), Fe (4) and Pb (3).

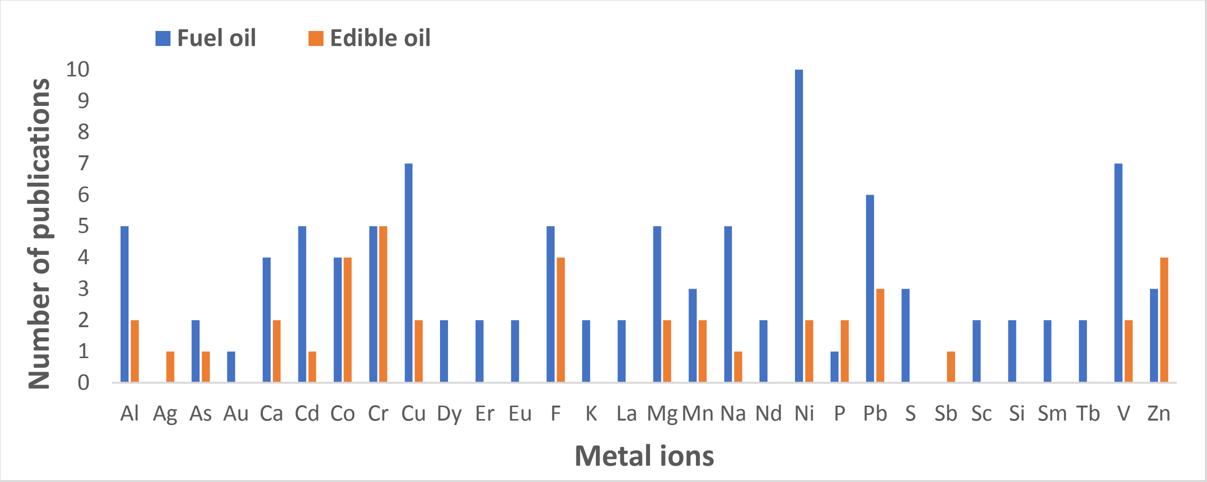

Figure 2.6B: The different element reported under decomposition prior to their analysis

When looking into **Fig. 2.6C,** the trend in the number of publications shows that fuel oils reported most on metal determination in comparison to edible oils. The metals with highest number of publications were Cu (20), Pb (15), Ni (14), Mg (10), Ca (8) and V (8). In contrast, with edible oils the trend in the number of publications ware Cd (14), Ni (12), Cu (11), Zn (11), Mn (11) and Pb 10.

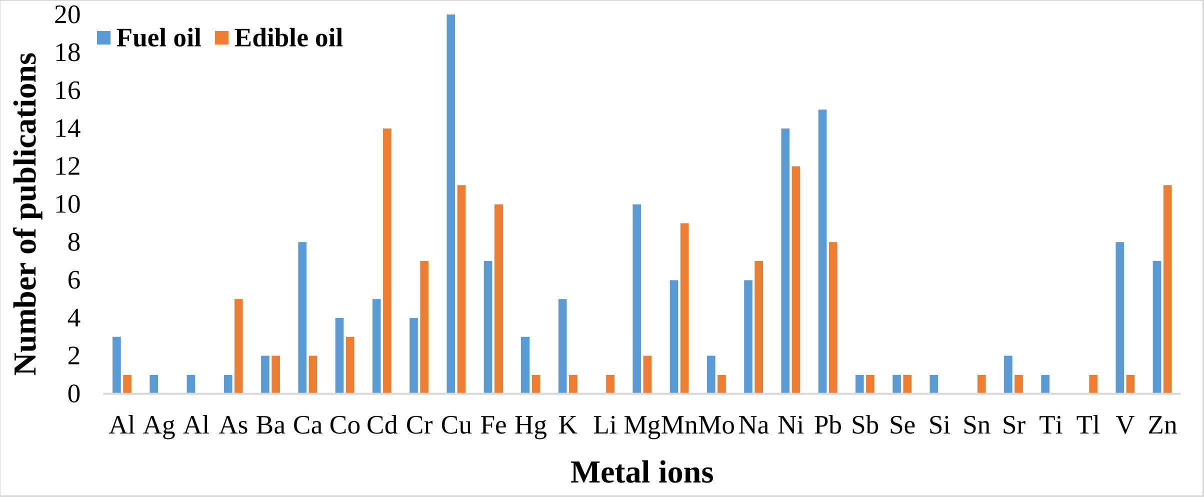

Figure 2.6 C: The different metals extracted under extraction methods prior to their analysis

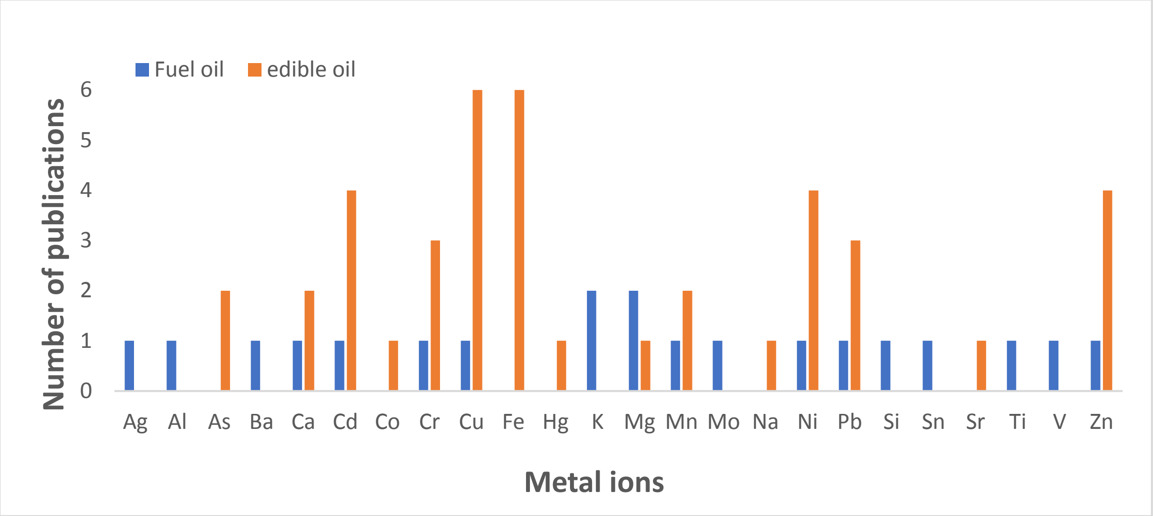

Figure 2.6 D: The different element reported under other extraction methods prior to their analysis.

In other extraction methods, most metal analysis was done in edible oils in comparison to fuel oils and very little has been reported. Additionally, when looking at the **Fig 2.6A, Fig 2.6B, Fig. 2.6C and Fig.2.6D** there is that consistency in terms of the metals that are most studied with Pb, Ni, Cu, V, Fe and Mg being mostly reported in all. In **Figure 2.7** an overall picture of the metals that were most studied from both edible and fuel oils is painted. Therefore, it can be concluded the Ni, Pb, Cd, Na, Fe and Cu were the most favoured metals in both fuel and edible oils. However, Zn, Fe, Cd, Cu, Pb, Ni and Zn were the most reported metals under the above-mentioned figures for edible oils. These metals especially Cu, Fe and Zn accelerate the oxidative degradation of edible oils even at low concentration levels and therefore calling for the need to monitor the levels to ensure the quality of the oil [71]. The elements (Ni, V, Cu, Pb, Fe and Mg) that were most reported in fuel oils were studied based on the negative impacts they have on the environment, oil refinery industry, plants and animals. The ratio of V/Ni provide information on the classification and source of crude oils [173]. When looking on to the overall picture, there was very little that has been reported on several elements which include As, Hg, Se, Si, Sr, Ti, Tl, Sb, Tb, B, Te and At therefore, a need for the study of these elements.

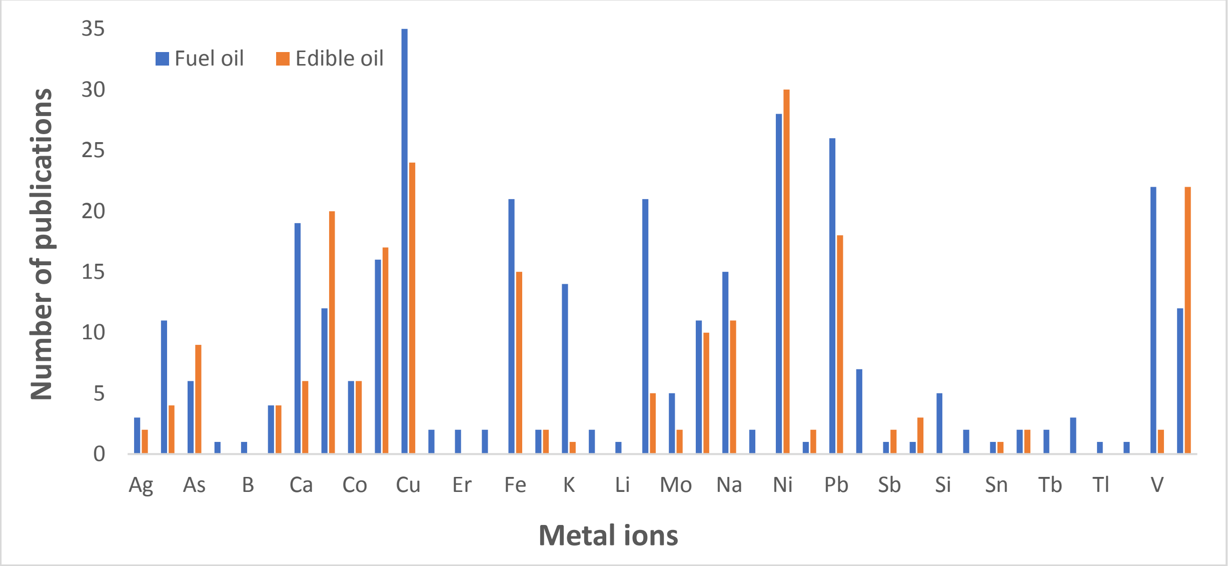

Figure 2.7: The different element reported under other extraction methods prior to their analysis.

Different analytical instruments have been reported for mental determination in oil matrices. **Fig. 2.8A**, reported that several analytical instruments have been used for direct analysis which include XRF, ICP-OES, ICP-MS, AAS, MP-AES and others (LIBS, LA-ICP-TOFMS and ICP-ID-MS). In direct analysis the most reported analytical instruments were AAS with 8 papers, XRF with 6 papers and ICP-MS with 5 papers. The ICP-OES was least reported under direct analysis, as 1 publication was produced. The XRF was only reported in direct analysis as this instrument can overcome the problems of matrix match effect which was most problematic with other analytical instruments [172]. In **Fig. 2.8B** it has been reported that the ICP-OES and ICP-MS were the most reported analytical instrument. This was due to the low detection limits and multi-elemental capabilities of the ICP-OES/MS. Additionally, since decomposition is not a preconcentration sample preparation method, an instrument with a very low detection limit was needed. With the extraction (**Fig. 2.8C**) sample preparation methods, more papers were reported for ICP-MS, AAS and little was reported on ICP-OES and other techniques.

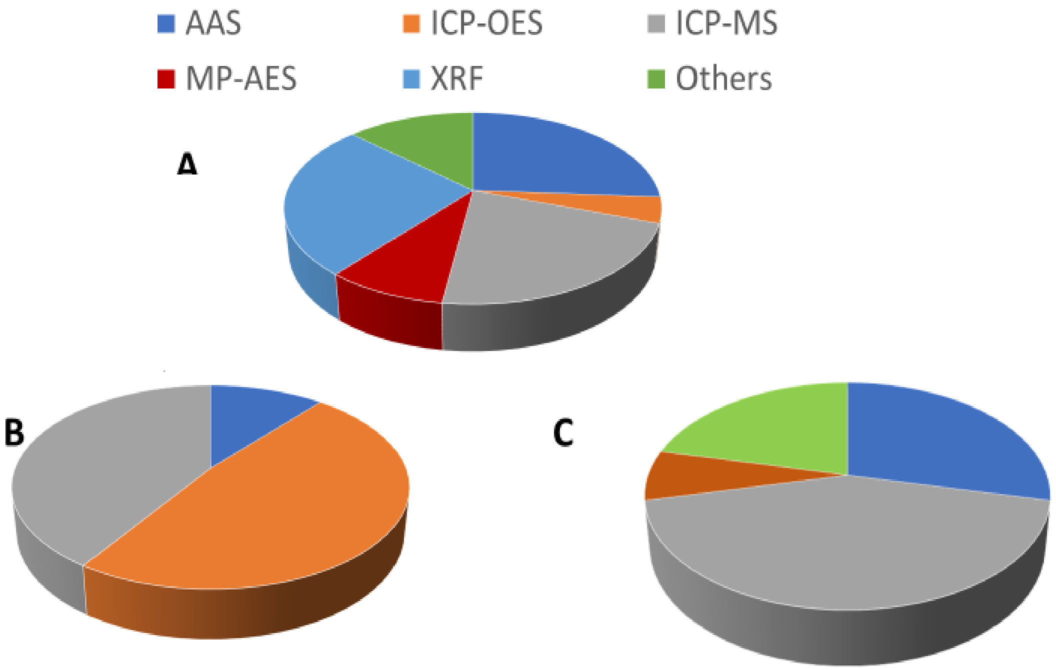

Figure 2.8: A, B and C: Analytical techniques that have been reported for direct and indirect analysis of metals in oily matrices.

2.4 Conclusion

This chapter reviews studies that have been conducted in oily samples using different sample preparation methods. The MAAD was also most reported under decomposition sample preparation as per information gathered from literature. This sample preparation method mostly reported the used concentrated acids and 30% hydrogen peroxide for digestion of samples prior to analysis. Therefore, this proposed study aims at using diluted nitric acid and hydrogen peroxide for digestion of oily samples. Literature has not reported this study in oily samples, it was only reported by Mketo et al, in coal samples in 2015 [61]. The proposed study will use the smallest concentration of acid that can bring complete digestion in the oily samples. This aims at minimizing the risks that are associated with the use of concentrated acid which may be corrosive and in the case of nitric acid, the production of nitrous oxide that is carcinogenic. Secondly, in the solid phase extraction, several studies have been reported but there are still some gaps. For example, with MSPE, only two metals (Cd and Pd) have been studied in edible oil and fuel oils. The SPME also used the Fe_3O_4 nanoparticles only for the extraction of the metals making this to be wide open for further investigations. The use of SPME has reported good recoveries (96-104%) and high enrichment factor of 184 when applied in diesel. The proposed study aimed at using MSPE in gasoline, diesel and crude oil to preconcentrate the metals since they are in trace levels. To the best of our knowledge MSPE had never been applied for metal determination in crude oil and gasoline samples. The ICP techniques have never been applied with this MSPE therefore a need to do further investigation of different metals and use different detection techniques. Lastly, the EIEB has been also well reported for the past 10 years and this sample preparation has been reported to be among the environmentally friendly sample preparations. However, the use of organic solvents like hexane, xylene and toluene for dilution of viscous oils like crude oil is a major drawback as these solvents are carcinogenic. The proposed study aimed at using the ionic liquid for dilution of viscous crude oil and this ensured the environmentally friendliness of the sample preparation.

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CHAPTER 3 (METHODOLOGY OR EXPERIMENTAL PROCEDURES)

Preamble

This chapter elaborates on the experimental standard operation procedures that were followed for washing glassware, obtaining real samples and certified reference materials, screening of the metal ions present in fuel samples (crude oil, diesel, kerosene and gasoline) and the pre-concentration methods that were conducted prior to spectrometric metal determination in fuel oils. Furthermore, the procedures that were followed for multivariate optimization and the instrumentation are discussed.

3.1 Sample collection

The crude oil samples A, B and C were used and were supplied by one of the South African petrochemical company. The diesel, kerosene and gasoline samples were purchased from three different filling station around Johannesburg, South Africa. The three sampling sites were chosen to eliminate biasness of the study. The total number of crude oil, diesel, kerosene and gasoline samples that were analysed are presented in chapters 4, 5 and 6.

3.2 Material and methods

All glassware were socked in 5% nitric solution for 24 hours and then washed with soap and water and rinsed with deionised water. After washing and drying, the glassware were put in lockers to prevent dust accumulation, which might cause several contaminations. The Teflon vessels used for sample digestion were washed by digesting 5 mL concentrated HNO_3 at 180 °C for 20 minutes, followed by washing with soup and water, and finally were rinsed with deionised water. The centrifuge tubes used throughout the experiments were also soaked in 5% acid solution for overnight, to ensure complete removal of metal ions, and rinsed with deionised water prior to oven drying.

3.3 Standard operational procedure

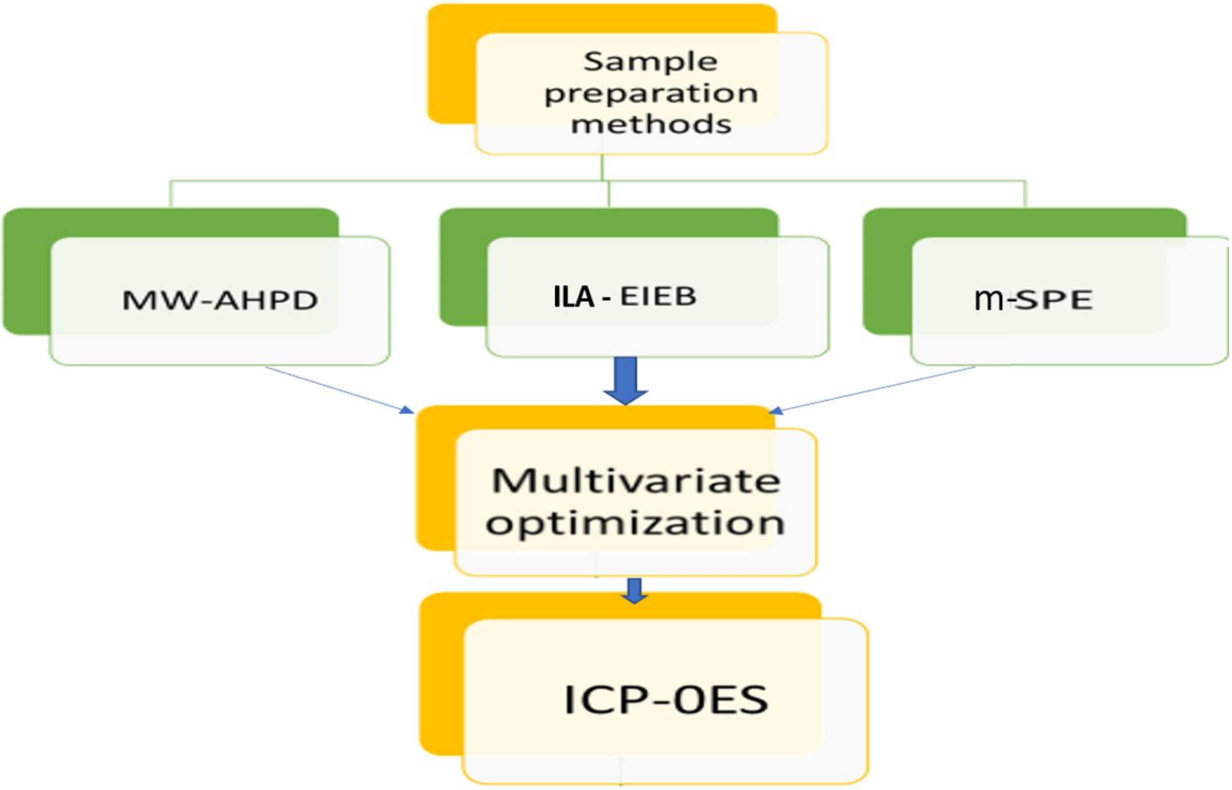

Figure 3.1: Sample preparation procedures followed prior to plasma-based spectrometric determination of metal ion in fuels sample.

Fuel samples were firstly digested by using microwave-assisted hydrogen peroxide digestion (MA-HPD) method, followed by ICP-OES analysis, for screening purposes, just to see which metals were present. Then, the two pre-concentration techniques (magnetic solid phase extraction and ionic liquid assisted -emulsion induced by emulsion) were developed to enhance the detection of the trace elements that were undetectable with MA-HPD method. However, sample preparation procedures for MA-HPD, ILA-EIBE and m-SPE are detailed in chapters 4, 5 and 6, respectively.

3.4 Multivariate optimization

There are two well documented types of optimisation, which are univariate and multivariate optimisation. In univariate optimisation, all the other factors are kept constant and one variable is optimised at a time. This type of optimisation is very time consuming, requires large quantities of reagents, thereby increase optimization costs [11]. On the other hand, the multivariate procedures evaluates several parameters simultaneously, by using mathematical tools. Furthermore, the effect of variable integration can also be optimised [12]. The multivariate procedures can be categorised as first order and second order designs. The first order designs are for screening purposes, to see which variables show significant change on the experimental response when varied from low to higher levels [13]. In this current study, the two-level full factorial design (first order design) was used for the screening optimization step. The second order designs are commonly used for further optimisation, to check the levels at which significant variables affect the response of the experiment [14]. The well reported second order experimental designs are Central composite [15], Box-Behnken [16] and Doehlert matrix [17]. For this current project, Central composite was used for further optimization of significant variables.

3.5 Plasma based metal ion detection

The plasma-based detection techniques are known for their multi-elemental detection and for their low detection limits (ppm-ppt) [18]. These detection techniques include inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES). These techniques require the analytes to be in aqueous state so that the problems that comes with high organic content load are eliminate and to facilitate nebulisation sample introduction. This is because, high organic load lead to serious problems which include plasma extinguishment or carbon deposition in the sampler cone, especially if the sample uptake rates are higher than 100 µL [19]. For this research, the ICP-OES was used for metal analysis.

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CHAPTER 4 (RESULTS PAPER 1)

Multivariate optimization of a greener microwave-assisted hydrogen peroxide digestion method followed by inductively coupled optical emission spectroscopic analysis for the determination of metal ions in selected fuel oils

Abstract

A green and cost-effective microwave-assisted hydrogen peroxide digestion (MA-HPD) was successfully developed for decomposition of crude-oil, diesel, gasoline and kerosene samples prior to determination of selected metal ions (Al, Ba, Co, Cu, Mg, Na, Ni, Sb, Ti and V) by inductively coupled plasma-optical emission spectroscopic (ICP-OES). After multivariate optimization with NIST1634c oil, it was observed that 245 ℃ microwave temperature, 25 minutes digestion time, 0.1 g sample mass and 5 M H_2O_2 were the optimum digestion conditions with accepted accuracy (104.8-117.7%) and precision (≤ 4.1%). The proposed MA-HPD method resulted in MDL of 0.046, 0.030, 0.408 and 0.057 µg/g for Ba, Na, Ni and V, respectively. The concentration levels of the selected metals (Al, Ba, Cd, Co, Cr, Cu, Mg, Na, Ni, Pb, Sb, Ti and V) ranged between 1.21-58.86 µg/g, 0.55-36.37 µg/g, 0.56-47.0 µg/g and 0.6-35.1 µg/g for crude oil, diesel, kerosene, and gasoline, respectively. In overall, the metals that reported high concentrations in the fuel oils were Na (51.94-58.86 mg/kg) and Mg (36.08-47.4 mg/kg), while Cu reported the least (0.55-2.89 mg/kg). When comparing these results with other literature reports, a conclusion can be drawn that South Africa is currently using good quality crude oil in terms of metal contamination, therefore, these fuel oils are safe to be used.

4.1. Introduction

The determination of metals and metalloids in fuel oils has been the subject of study in the last decade. This is because, metal contaminants in fuel oils have several positive and negative impacts [1]. For example, the presence of different metals and their concentration levels can help to classify the crude-oil type and the origin of the crude-oil in terms of the geochemical characterization of source rocks and the oil basin [2, 3]. Additionally, the presence of metals like Ni and V enhance the prediction of oil maturity [4]. However, some metal ions (Fe, Na, Ca, Mg, Sr, V and Ni) in crude oil are associated with corrosion of oil refinery equipment [5, 6]. Other metals like Cr, Fe, Ni, As, and V enhance catalyst poison by attaching to the active site of the catalysts during hydrotreatment, making the catalyst inactive [1, 7-9]. If these metals are present in crude-oil, so are crude oil derivatives (diesel, gasoline, kerosene, etc.) and this also introduces some negative impact. When gasoline and diesel burn, the presence of Cu, Fe, Co and Mn can catalyse the oxidation of gasoline and diesel, thereby causing low combustion efficiency [7, 10]. Additionally, when the fuel oils burn, several toxic elements (Pb, Cr, Hg and As) are released into the atmosphere and become hazardous to human health, since these metal ions are known to be mutagenic and carcinogenic [11]. It is worthy to indicate that, metals in crude oil and its derivatives occur naturally and can also be introduced as additives to improve mechanical, chemical and physio-chemical properties of the fuel oils [7].

Therefore, there is an urgent need for the development of accurate and effective analytical techniques for the determination of metal ions in fuel oils. Literature reports have proved that inductively coupled plasma based techniques (ICP-OES and ICP-MS) are the best option for elemental analysis, due to their multi-elemental capabilities and low detection limits [12-15]. However, fuel oils contain high carbon content and therefore they require mineralization method prior to spectrometric analysis of metal ions [1, 16]. Therefore, several digestion methods have been reported for mineralization of oily matrices. These methods include, microwave assisted acid digestion (MAAD) [17-21], microwave assisted-single reaction chamber (MA-SRC) [22] and microwave induced combustion (MIC) [2, 23, 24]. However, literature reported several limitations associated with the above-mentioned sample preparation methods. For example, the use of concentrated $HClO_4$ and H_2O_2 is associated with explosion, concentrated HNO_3 produce carcinogenic nitrous oxide, HCl and HF are corrosive and can dissolve glass optics of the spectrometric techniques, very toxic acid waste generated can cause environmental pollution and concentrated acids can be costly during MAAD [25-27]. Additionally, digested samples containing concentrated acids can cause matrix effect challenges during spectrometric quantification using external aqueous calibration standardization method [9]. On the other hand, MIC makes use of dilute acids, therefore overcome limitations of MAAD. The main limitations of MIC are the use of expensive oxygen, quartz vessels and the additional reflux step, which prolongs the digestion [28]. Lastly, MASRC make use of one digestion vessel at a time, which is a huge disadvantage when running a large population sample. In 2015, the use of a novel and green microwave assisted-hydrogen peroxide digestion (MA-HPD) method followed by ICP-OES and ion- chromatography for quantitative determination of total sulfur in coal samples [29]. This sample preparation method corrected some limitations of MAAD, which included, production of hazardous waste, matrix effects caused by concentrated acids and was proven to be cost-effective and environmentally friendly, since dilute H_2O_2 used gets converted to H_2O and O_2 during digestion. The ICP-OES results showed accepted sulphur recoveries of 89-102%, excellent precision of $\leq$1.5% and low detection limits of 0.014 µg/g. Another study on the use of dilute H_2O_2 and dilute HNO_3 was reported for the digestion of coal samples for quantitative extraction of trace elements with low detection limits of detection (0.003-3.5µg/g) and high accuracy (92-114%) for most of the investigated elements [28].

For the optimisation of the best digestion parameters, multivariate optimisation have been used over univariate optimisation. During univariate optimisation a single parameter is optimised at a time while keeping the other parameters constant. In contrast, multivariate optimisation investigates several parameters simultaneously and this helps to save time and reduce reagents as less experiments are conducted in comparison to univariate. Dos Anjos et al. [17] reported multivariate optimisation for microwave-assisted digestion for determination of Ni and V in crude oil prior to ICP-OES analysis. The two-level full factorial was used for screening and the central composite design was used for response surface methodologies (RSM). The central composite design was chosen based on its easy operation when compared to the other RSM [17]. Additionally, multivariate in microwave assisted digestion was also reported by Barela et al. [30], where a two-level full factorial was only used to optimize for [HNO_3] and [H_2O_2] prior to analysis Ba, Co, Cr, Cu, Mn, Ni, Pb, Sr and V in biodiesel samples using Sector Field Inductively Coupled Plasma Spectrometry (SF-ICP-MS). The expression for a full factorial is 2^n, where n is the number of parameters to be optimised.

Therefore, the current study proposed the use multivariate optimisation for obtaining the best operating conditions for the four digestion parameters (time, temperature, H_2O_2 concentration and sample mass). After optimisation, dilute H_2O_2 was used during MA-HPD method of fuel oils (crude oil, diesel, kerosene, and gasoline), prior to ICP-OES analysis of metal ions.

4.2. Experimental methods

4.2.1 Reagents and glassware

All reagents used were of analytical grade purity and Milli-Q water obtained from a water purification system (USA**)** with water conductivity of 18.2 µS/cm, which was used for rinsing and making up solutions. Multi-element standard of 100 mg/L (purchased from Sigma-Aldrich, South Africa) was used in the preparation of different concentrations of standard solution**.** Standard reference material (SRM/NIST 1634c) with trace elements in fuel oil was also purchased from Sigma-Aldrich, South Africa. The 70% (v/v) ACS grade HNO_3, and suprapure 30% (v/v) H_2O_2 were purchased from Merck, South Africa. Crude oil samples were obtained from a petrochemical company. Alternatives, crude oil derivatives (diesel, gasoline, and kerosene) were purchased in three different filling stations labelled as A, B and C. Polyvinylidene difluoride (PVDF) microfilters size of 0.45 µm pore diameter were purchased from Anatech instrument (South Africa). All glassware were washed using soapy water, then soaked in 5% nitric acid solution for 24 hrs, rinsed with deionized water and allowed to dry in the oven (EcoTherm Labotec) for overnight.

4.2.2 Instrumentation

An Anton Paar Multiwave 5000 microwave digester was used for digestion of fuel oil samples. The microwave was equipped with a rotor (20SVT) which holds a total of 20 polytetrafluoroethylene- Teflon vessels (PTFE-TFM) at a time. It is worthy to indicate that any of the vessels can be used as a reference unlike in some microwaves where only the vessel with a temperature probe is used as a reference. The microwave was equipped with a temperature programme where the ramping and holding durations were controlled. The microwave system was set to ramp for 10 minutes to 245 ℃ and holding time was 15 minutes at 245 ℃. After the holding time of 15 minutes, the microwave was allowed to cool to 70 ^{0}C and the vessels were removed from the rooter for further cooling until they were at room temperature. The resulted digests were analysed for metals by using Agilent Technologies 700 Series ICP-OES with an axial orientation of the torch. Additionally, an Agilent Technologies SPS 3 autosampler was used for sample uptake. The optimum operational conditions for analysis are presented in **Table 4.1**.

Table 4. 1: Operating parameters of the ICP-OES for metal and metalloids analysis

ICP-OES instrumental parameters	Condition
RF Power	1200 W
Auxiliary gas Flow	1.5 L/min
Plasma gas (Ar) flow rate	15.0 L/min
Pump speed	85 rpm
Peri-pump speed analysis	15 rpm
Sample uptake delay (s)	15 s
Stabilization time (s)	15 s
Nebulizer	0.75L/min
Elemental wavelengths	Al 396.52, Ba 234.759, Co 201.151, Cr 206.550, Cu 327.395, Ni 216.55, Mg 279.553, Na 588.995, Pb 283.30, Sb 217.582, Ti 336.122, and V 292.299

4.2.3 Microwave assisted hydrogen peroxide digestion (MA-HPD)

Microwave digestion system uses microwave energy to break the carbon and metal bond [4]. This is a form of energy that is non-ionizing from electromagnetic radiation resulting in molecular motion caused by migration of ions and rotation of dipoles [31]. It is of paramount importance to state that, higher temperatures ranging from 220 to 250 °C have been reported to cause deformation of the polytetrafluoroethylene (PTFE) vessels and have high risk of creating explosions and therefore Teflon vessels were favoured [32, 33]. The use of dilute H_2O_2 was preferred, because this reagent makes the proposed MA-HPD method to be greener, since high temperatures of the microwave are known to convert H_2O_2 to hydrogen, oxygen and water [29]. In the current study, a method reported by Mketo et al. [29] was followed. Briefly, known amount (0.1 g) of oil sample (crude oil, diesel, kerosene and gasoline), 9 mL of dilute H_2O_2 (5M) and 1 mL concentrated HNO_3 were transferred into 50 mL polytetrafluoroethylene-Teflon vessels (PTFE-TFM). Then, the samples were subjected to high temperatures (245 ℃) of the microwave to break the metal carbon bond for easy extraction of the metal’s presence in the oil matrix. The digestion was allowed for 25 minutes, and the resulted digest were transferred to a 25 mL volumetric flask and filled up to the mark with Milli-Q water. Each of the samples was in triplicates with a blank as the fourth. The samples from the 25 mL volumetric flask ware then filtered using 0.45 µm pore diameter sized PVDF and transferred to a 15 mL centrifuge tube for analysis using the ICP-OES. The percentage recoveries (%R) of each element (Ba, Na, Ni and V) were also calculated using the equation 1 (**Eq.4.1**). The experimental value is the obtained from multiplying the ICP-OES value with analyte volume, all divided by mass of the sample.

$$\%R = \frac{Experimental\ value}{NIST1634c\ value} \times 100\% \qquad Eq. 4.1$$

Analytical features and validation of this method were investigated by using certified reference standard material (SRM 1634c). The major steps that were followed for the proposed MA-HPD are presented in **Fig. 4.1** below.

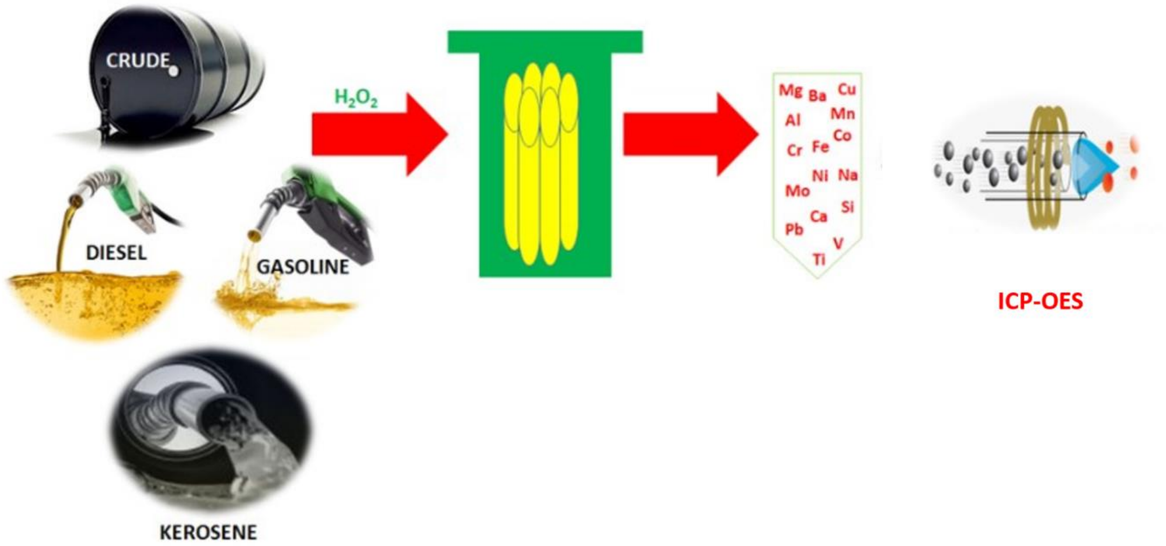

Figure 4.1: Key steps in MA-HPD sample preparation method

4.2.3 Multivariate optimisation

The multivariate optimisation approaches were used for the determination of parameters that greatly affected microwave assisted hydrogen peroxide digestion (MW-AHPD). The parameters that were optimised were digestion time, digestion temperature, sample mass and hydrogen peroxide concentration, these parameters were optimized using the full factorial design (2^n). The variable was given the lower level (-) and the higher level (+), and the central point was not included in these experiments as presented in **Table 4.2**. The central composite design was used for further optimisation of the most significant parameters. For both two-level full factorial and central composite design, the Minitab 2018 statistical software was used for the generation of the experiments and analysis of data.

Table 4. 2: The parameters that were investigated and their levels for two-level full factorial design

Variable	Low level (-)	High level (+)
Sample mass (g)	0.05	0.2
H_2O_2 concentration (M)	1	5
Digestion time (minutes)	20	60
Digestion Temperature (°C)	180	240

4.2.3.1 Full factorial design

A two-level full factorial design was used for the screening of optimised factors (sample mass, digestion time, digestion temperature and hydrogen peroxide concentration). The full factorial design was carried in way that the parameters were varied simultaneously for the optimised parameters. The 16 designed experiments generated by Minitab 2018 statistical software had the following ranges, temperature (180-240 °C), digestion time (20-60 minutes), sample mass (0.05-0.2g) and H_2O_2 concentration (1-5 M) for the optimised parameters. It is worth noting that from these experiments generated, all the experiments that were conducted at 180 °C did not give proper digestion even if the time, H_2O_2 concentration, and sample mass were varied. Therefore, digests generated at 180 °C were not taken for analysis as minimal digestion was observed indicating high organic content on the digest. High organic content in samples is not compatible with ICP-OES as it causes plasma extinction [29]. However, all samples conducted at 240 °C were taken for analysis as they showed clear or very close to clear digest. These results with clear digest were analysed and the percentage recoveries were calculated as shown in **Eq.4.1**. Additionally, these recoveries were then run in Minitab 2018 statistical software to analyse the response of each parameter. The response of each parameter was expressed in terms of Pareto chart and these parameters predicted the most significant factors.

4.2.3 Microwave assisted acid digestion (MA-AD) a standard method

The mineralisation of NIST1634c was carried under the same Anton Paar Multivariate 5000 microwave. In a 50 mL PTFE-TFM vessel, approximately 0.1 g NIST1634c was weighed and 10 mL concentrated HNO_3 was added. The vessels were then tightly sealed and sampled were subjected to high microwave temperatures for digestion. The temperature ramped from room temperature to 245 °C in 10 minutes and it was held at the temperature for 15 minutes. It must be noted that the temperature was not 245 °C exactly in all vessels but it was in the range 245 ±5 °C. Blanks were also digested in the same way as that of NIST1634c, however, in this condition the NIST1634c was not added (only concentrated acid was added). After digestion, the blanks and SRM samples were allowed to cool to room temperature, transferred to 25 mL volumetric flask and diluted to the mark. Filtering of digest was also done using 0.45 µm pore size PVDF before being transferred to 15 mL centrifuge tubes for ICP-OES analysis.

4.3 Results and discussion

4.3.1 Two level full factorial design

The screening process of the most significance parameters in MA-HPD was achieved using the two-level full factorial design (2^n). The factors that were statistically significant were further optimised using the central composite design (CCD). The experimental results from the two-level full factorial design are presented in **APPENDIX Table 1**. The results were examined by using the analysis of variance (ANOVA) at 95 % confidence level (p=0.05). The ANOVA results were then present in form of Pareto charts for each metal as presented in **Fig. 4.2 A-D**. The results indicated that digestion time and digestion temperature ware statistically significant at 95% confidence level for the determination of Ba, Na and V in NIST1634c digest. However, with Ni, in addition to digestion temperature and time, the concentration of H_2O_2 proved to be also significant at 95% confidence level. For all the metals, increasing digestion temperature and digestion time resulted in an increase in percentage recoveries. The results in **APPENDIX Table 1** indicated that digestion temperature was the most significant factor. At high temperatures the carbon-carbon bonds and the carbon-metal bonds proved to be breaking much faster as a result there was that observed increase in percentage recoveries when temperatures were at 240 °C. Additionally, the combination of increased digestion time and digestion temperature proved to be much significant, when looking at the digests, the ones at high temperatures and increased digestion time were much clear in comparison to short digestion time and same temperature. The most significant parameters (digestion time and temperature) at 95% confidence level were then taken for further optimisation using the central composite design. It is worth noting that even though H_2O_2 concentration was significant for Ni recoveries but it was not taken for further optimisation as it showed to be significant in only one metal.

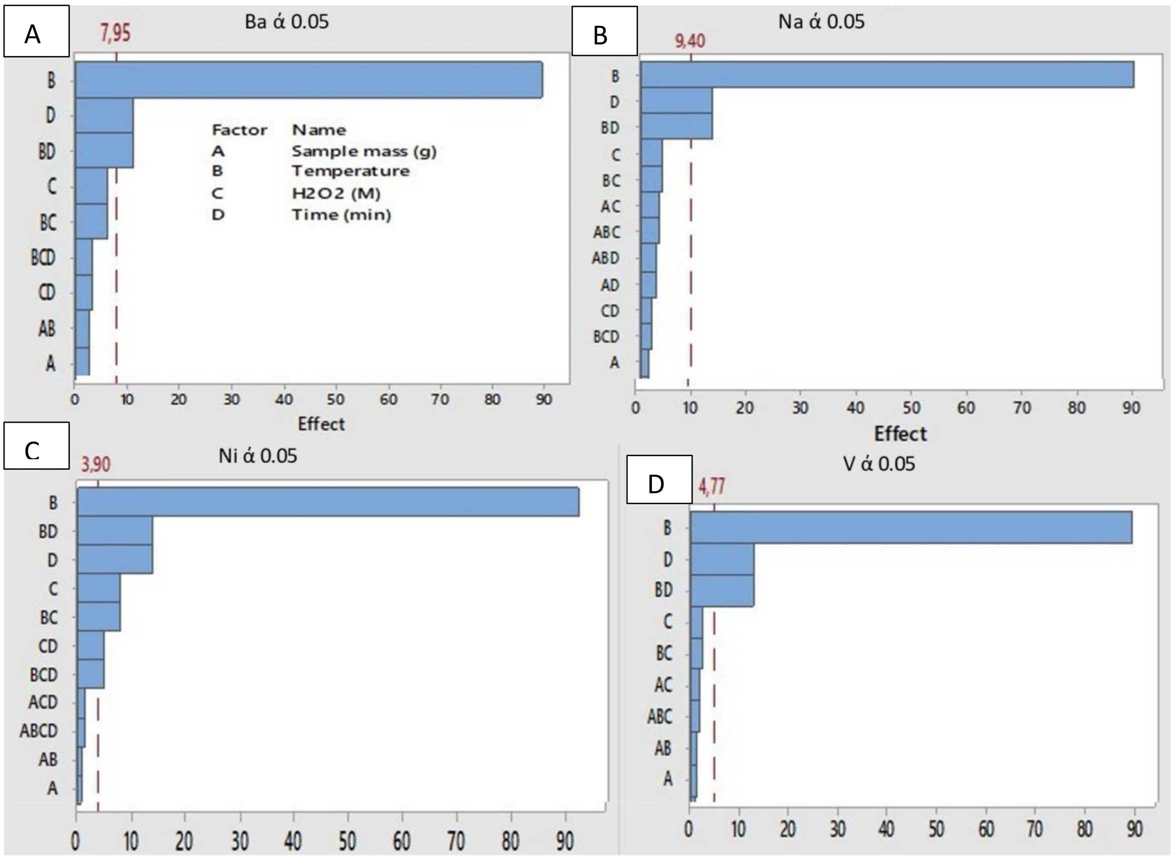

Figure 4. 2A-D: Pareto charts A (Ba), B (Na), C (Ni) and D (V) for level 2 full factorial design (2^n) at 95% confidence level for optimisation of sample mass, H_2O_2 concentration, digestion time and digestion temperature (n=3).

4.3.1 Response surface methodology (RSM)

Response surface methodology (RSM) are chemometric tools that helps in establishing quadratic models. These models assist to determine the critical conditions of factors under study. Several RSM have been reported in literature which include BBD, CCD, three level factorial design and Doehlert matrix [35, 36, 38]. Digestion temperature and digestion time was further optimised using the central composite design. The parameters that were statistically insignificant, were kept at 0.1 g and 5 M for sample mass and H_2O_2 concentration respectively. The 0.1 g sample was chosen for this digestion as 0.05 g was not giving good precisions, while 0.2 g was giving good precisions but more time was needed for it to complete digestion. In contrast, the choice of 5 M of H_2O_2 was based on hydrogen peroxide being a significant parameter with recoveries of Ni. The parameters, number of experiments, experimental conditions and results from the central composite design (CCD) are presented in **APPENDIX Table 2**. The CCD was chosen based on being mostly reported in literature and its most reliability [36]. The response surface plots (**Fig. 4.3A-D**) were used to evaluate the effects of digestion time and digestion temperature on the analytical response. Based on the quadratic equations and the surface plots, the most optimum digestion conditions were chosen to be 0.1 g (sample mass), 245 °C digestion time, 25 minutes digestion time and 5 M of H_2O_2. The surface plots showed that increasing digestion temperature reduced the digestion time needed to obtain high recoveries of the target analyte. The quadratic equations are presented from **Eq. 4.2A- D**. The optimum conditions were then used on the NIST1634c and the percentage recoveries were from 104.8-117.7 % for Ba, Na, Ni and V. The results for each analytes were confirmed by the quadratic model (**Eq. 4.2A- D**), where A and B represent digestion time and digestion temperature respectively.

$$Ba = -561 + 0.92A + 4.91B - 0.1058A^2 - 0.00933B^2 + 0.0010AB \qquad \boldsymbol{Eq. 4.2A}$$

$$Na = -1047 + 0.39\,A + 9.17B - 0.00265A2 - 0.00933B2 + 0.00156AB \qquad \boldsymbol{Eq. 4.2B}$$

$$\mathrm{Ni} = -1530 + 2\,506\mathrm{A} + 13.37\,\mathrm{B} - 0.0054\,\mathrm{A2} - 0.02757\mathrm{B2} - 0.0831\,\mathrm{AB} \qquad \mathbf{Eq. 4.2C}$$

$$\mathrm{V} = -1327 + 1.44\mathrm{A} + 11.56\mathrm{B} + 0.00468\mathrm{A2} - 0.02339\,\mathrm{B2} - 0.00694\mathrm{AB} \qquad \mathbf{Eq. 4.2D}$$

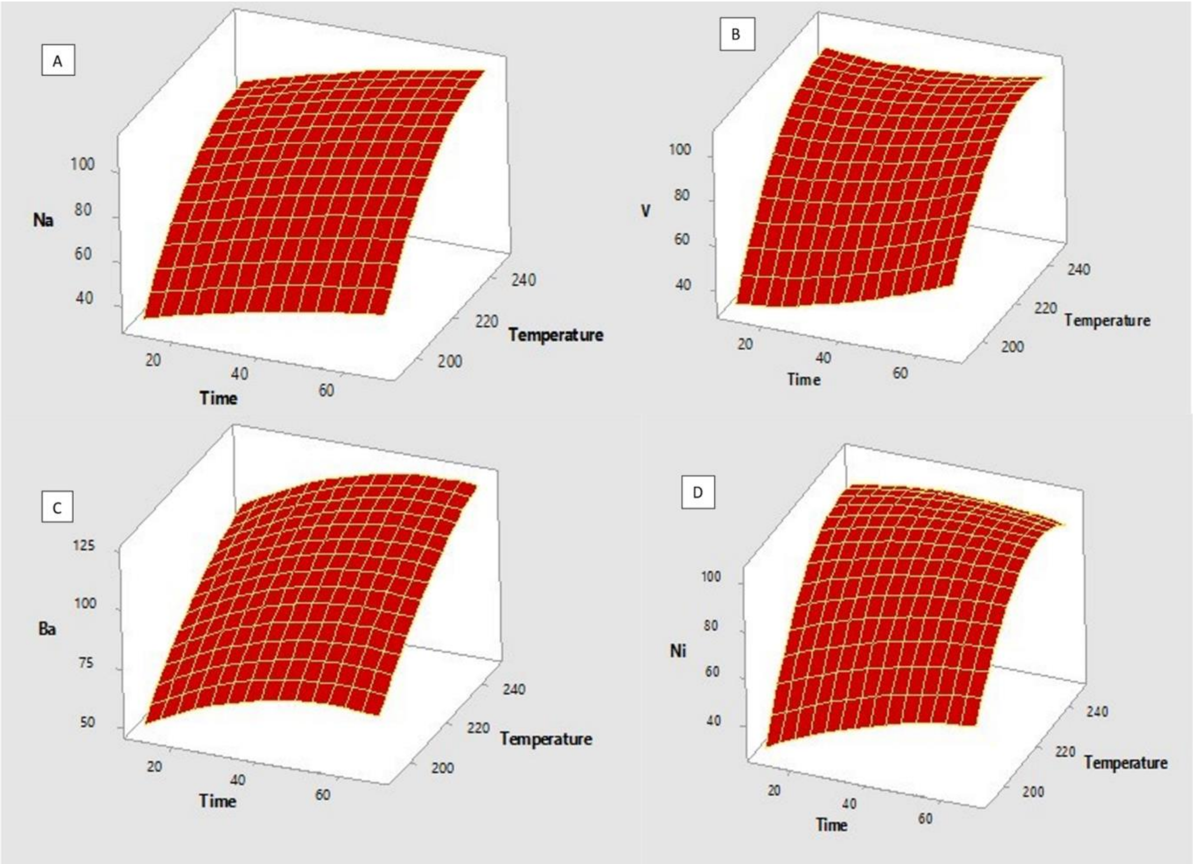

Figure 24. 3 (A-D): Response surfaces A (Na) B (V), C (Ba) and D (Ni) Versus Time. Temperature obtained from central composite design. Experimental conditions: 0.1g of the sample and 5M H_2O_2 (n =3).

4.3.2 Analytical figures of merit

For every developed analytical method, it is vital to determine analytical figures of merits which include method detection limits (MDL), method quantification limits (MQL) sensitivity, accuracy, precision, and correlation coefficient, just to name the few. These analytical merits help in drawing a conclusive decision on whether the newly developed method is better than the literature reported methods [6]. In this study, the optimum conditions generated by the RSM were used for investigating the analytical features of the proposed MA-HPD method. This was achieved by digesting 0.025, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g of NIST1634c in triplicates and the digests were analysed using ICP-OES. The concentration of each metal ion in weighed mass (0.0, 0.025, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g) of NIST1634c CRM was calculated and plotted against intensity. The plotted graphs were able to provide information which included R^2 and method calibration gradient (which is equivalent to the sensitivity of each metal). The metal ion that showed very high sensitivity was Na (2.03×10^5 cps L mg^{-1}) and the least sensitive metal was Ni (1.01×10^4 cps L mg^{-1}). The R^2 ranged from 0.9992- 0.9999 for all the metals **(see Table. 4.3).** The standard deviation of 20 blanks was also obtained by digesting 20 blank samples (only 5 M of 9 mL H_2O_2 and 1 mL conc. HNO_3). The gradient (slope) was then used to calculate limit of detection (LOD) and limit of quantification (LOQ) **(see Eq. 4.3 and 4.6).** The LOD is referred to as the lowest concentration likely to be reliably distinguished from a blank sample and at which detection is feasible [39]. On the other hand, LOQ is referred to as the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy. The LOQ is equal to ten times the standard deviation of the blanks and all is divided by the method calibration (slope). The calculated LOD and LOQ were used to calculate the method detection limit and method quantification limit (**see Table 4.3**). Additionally, it is worth in noting that the LOD and LOQ provides the detection and quantification limits of the elements close to ideal conditions, where there are few other alloying elements. Since this happen in a very clean matrix, this LOD and LOQ are referred to as instrument detection and quantification limits, respectively. Therefore, the method detection limits and quantification limits were also calculated as these consider real-life matrices [40].

$$Limit\ of\ detection\ (LOD) = \frac{3 * SD}{Method\ calibration\ slope} \qquad \boldsymbol{Eq. 4.3}$$

$$Limit\ of\ quantification\ (LOQ) = \frac{10 * SD}{Method\ calibration\ slope} \qquad \boldsymbol{Eq. 4.4}$$

$$Method\ detection\ limit\ (MDL) = \frac{LOD * Final\ volume}{Optimum\ mass} \qquad \boldsymbol{Eq. 4.5}$$

$$Method\ quantification\ limit\ (MDQ) = \frac{LOD * Final\ volume}{Optimum\ mass} \qquad \boldsymbol{Eq. 4.6}$$

Table 4. 3: Analytical features of the MA-HPD method for quantitative extraction of Ba, Na, Ni and V in NIST1634c: digestion conditions; microwave temperature (245 ℃), [H_2O_2] (5 M), sample amount (0.1 g), digestion time (25 min), replicates (n =3).

Metal	**SD of blank intensity (cps) (n=20)**	**Sensitivity (cps L mg^{-1})**	**Accuracy (%)**	**Precision (%)**	**LOD (µg/L)**	**LOQ (µg/L)**	**MDL (µg/g)**	**MQL (µg/g)**
Ba	4.6045	7.4 x 10^4	107.1	2.9	0.187	0.622	0.046	0.155
Na	8.2014	2.03 x 10^5	117.7	0.8	0.121	0.404	0.03025	0.101
Ni	5.513	1.01 x10^4	110.4	2.7	1.63	5.434	0.408	1.36
V	2.9983	3.92 x10^4	108.4	4.1	0.23	0.7658	0.057	0.1915

4.3.1 Comparison of the proposed MA-HPD with literature reports

The newly developed greener MA-HPD method was compared with other digestion methods in terms of its figures of merits and the findings are shown in **Table 4.4**. Shirlei et al.[41] reported a study on the digestion of crude oil for the determination of Ni and V prior to ICP-OES analysis. The reagents used for digestion were, 5 M of HNO_3 and 4 M hydrogen peroxide. This method reported very low MDL of 237 and 60 ng/g for Ni and V, respectively. These results were almost in line with the ones reported in the current study (408 and 57 ng/g) for Ni and V, respectively). Barela et al.[30] reported a study on the digestion of Ba, Co, Cr, Mn, Ni, Pb, Sr and V in biodiesel prior to analysis using SF-ICP-MS. This method reported very good accuracy (95-108%), precision (<6%), and MDL (0.12, 2.8 and 0.12 ng/g) for Ba, Ni and V respectively. The newly developed method showed to be an appropriate alternative for digestion of fuel samples as the use of diluted reagent results in minimal generation of secondary waste. At high temperatures, H_2O_2 gives off water which is environmentally friendly. In contrast, most of literature reported acid digestions were using high volumes of concentrated acids which resulted to generation of high volumes of carcinogenic nitrous oxide. It is worth noting that the high concentrations of nitrous oxide results in permanent stains on digestion vessels which might result to reduction in lifespan of the vessels. The use of diluted H_2O_2 helped to reduce the chances associated with explosion as high concentrations of H_2O_2 have been reported to cause explosions. Additionally, the new method is envisaged to be cost effective due to use of less reagents compared to other methods.

Table 4.4: Comparison of MDL (ng/g) and precision (% RSD) achieved by MW-AHPD prior to analysis by ICP-OES with other literature reported digestion methods for Ba, Na, Ni and V in fuel samples.

Fuel Matrix	**Sample preparation methods**	**Metal ions**	**Reagent**	**Accuracy**	**Precision**	**MDL µg/g**	**Detection technique**	**Ref.**
SRM 1634c	MA-HPD	Ba, Na, Ni and V	9 mL of 5 M H_2O_2 and 1 mL of conc. HNO_3	104.8-117.7	≤ 4.1	0.03-0.408	ICP-OES	This work
Biodiesel	MAAD	Ba, Ni and V	10 mL of 7 M HNO_3	95-108	<6	0.00012,0.002.8 and 0.00012	SF-ICP-MS	[30]
Crude oil	MAAD	Ni and V	5mL of 4 M H_2O_2 and 10 mL of 5 M HNO_3	94.6-98.2	<4.62	0.237 and 0.060	ICP-OES	[42]
Diesel	MAAD	Ni	4 mL conc. HNO_3, 5 mL H_2SO_4 and 5 mL H_2O_2	70-78	<5	0.052	ICP-MS	[20]
Fuel oil	MAAD	V	1 mL conc. HNO_3 and 1 mL H_2O_2	NA	<5	0.250	GFAAS	[18]
Crude oil	MIC	Ni and V	6 mL of 5% H_2O_2 or 6 mL HNO_3	99-101	<5	0.200 and 0.100	ICP-OES	[24]

NB: MAAD [Microwave acid assisted digestion], MIC [Microwave induced combustion]

The proposed environmentally friendly MA-HPD method was also validated by using Anton Paar Multiwave 5000 Microwave standard method for fuel samples (NIST1634c) and the ICP-OES results were compared (**see Fig. 4.4**). It is worth in noting that for the standard method, 10 mL of concentrated HNO_3 was used while with MA-HPD, used 9 mL of 5 M H_2O_2 with 1 mL concentrated HNO_3. It was observed that in terms of metal recoveries for Ba, Na, Ni and V, there were no significance difference between the two digestion methods. However, the newly proposed method was environmentally friendly as it is used dilute hydrogen peroxide and less volumes of nitric acid, making the MA-HPD much cost effective compared to the standard digestion methods. The latter used concentrated HNO_3 and generating much of the carcinogenic nitrous oxide. Additionally, concentrated HNO_3 also resulted to permanent stains (yellow / orange) on the walls of Teflon vessels.

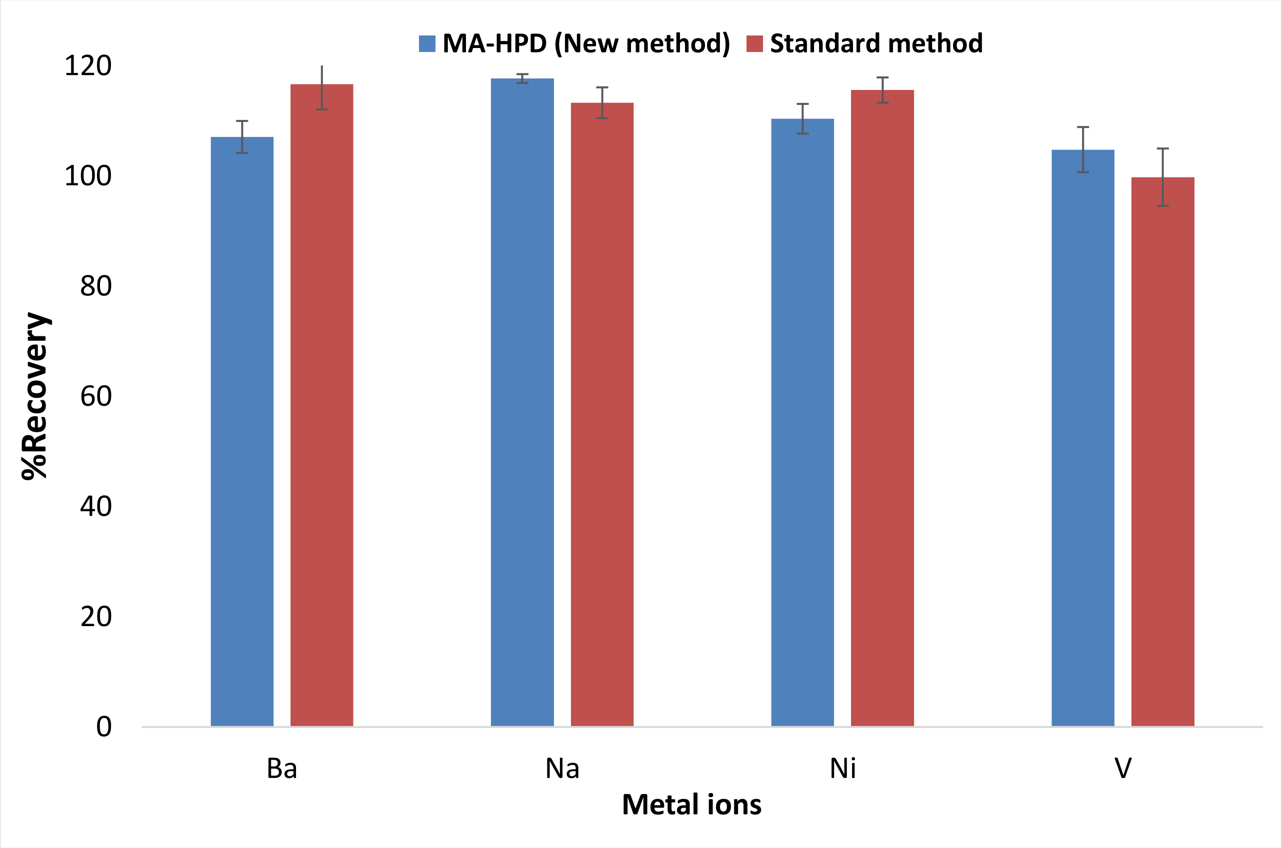

Figure 4. 4: Comparison of percentage recoveries of target analytes (Ba, Na, Ni and V) when digesting using dilute H_2O_2 with dilute HNO_3 (new method) and when concentrated acid is used (standard method).

The student *t*-test (at 95 % confidence level, with ά =0.05) was used for testing for any statistical differences between MA-HPD and MAAD based on analyte percentage recoveries of the two methods. The tabulated t was 3.182 indicating that for one to accept the null hypothesis calculated *t*-value must be within -3.182 < X> 3.182. The calculated *t*- value of 0.78974 was obtained. Therefore, the null hypothesis was accepted (H_0 is the null hypothesis and H is the alternative hypothesis).

H_0 =No difference in the methods

H ≠ There is a difference in the methods

This therefore means that there were no statistical differences between the newly developed MA-HPD and the standard MA-AD methods which used concentrated acids, and for that reason the MA-HPD can be considered as an alternative method for digestion of fuel oils in the future.

4.4.1 Application of MA-HPD in fuel sample

The optimised and validated MA-HPD method was then applied in real fuel samples (crude oil, diesel, gasoline and kerosene). There were three samples for each fuel oil and were assigned as A, B and C. For the crude oil derivatives (diesel, gasoline and kerosene), A, B and C meant different filling stations and the different labelling in crude oil samples meant different crude oil type. The samples were digested under the optimum conditions (245 ℃, 25 minutes, 9 mL of 5 M H_2O_2, 1 mL conc. HNO_3 and 0.1 g sample) and analysed for the determination of Al, Ba, Cd, Co, Cr, Cu, Mg, Na, Ni, Pb, Sb, Ti, and V using the ICP-OES. The concentration levels of investigated metals are reported in **Table 4.5**. The latter has indicated that there is no significant difference in concentrations between the crude oil samples. However, it was observed that for most metals (Cr, Cu, Mg, Na, Ni and V) there was a decrease in concentration levels from the crude oil to crude oil derivatives. The reduction in concentration levels might have happened during crude oil refinery. However, Ba, Al and Pb showed increase in concentrations from the crude-oil to crude oil derivatives. This might be due to corrosion of refinery and storage equipment of the crude oil derivatives [7]. However, some metals (Al: 1.21-2.36 and Cu: 2.05-2.89 µg/g) showed to be least present the crude oil samples. Additionally, in station C the concentration of Mg was not detected in gasoline, diesel and kerosene and this might be due to proper maintenance of the storage tanks. Despite absence of Mg in station C of the crude oil derivatives, it must be noted that the metals that reported high concentrations included Mg (36.08-47.40 µg/g) and Na (51.94-58.86 µg/g). The presence of

Na and Mg is not favoured mostly in diesel and gasoline as these metals promotes rapid ash build up in vehicle engine which in turn leads to corrosion [43]. The concentration levels of Cu were very small in all the investigated filling stations. This is good, because Cu is mostly known for causing sediments and deposit formation resulting to clogging of automotive filters [43, 44].

The overall concentration levels of metals in crude oil and crude oil derivatives purchased in different felling stations of South Africa proved to be low in comparison to literature reports. For example, Shirlei et al.[17] reported a study where determination of Ni and V was conducted in crude oil from three sampling sites of Brazil. These sampling sites reported Ni concentrations of 33.21, 15.76 and 29.52 µg/g, which were much higher that the Ni concentrations (2.2-8.19 µg/g) of the current study. For V, the concentrations were 1.07, 9.0 and 19.42 µg/g which were also higher than the ones obtained from the current research (1.9-4.73 µg/g). Mello et al.[24] also reported the determination of Ni, V and S in Brazilian crude oil samples. The concentration of Ni and V ranged from 30.43-181 µg/g and 36.9-763 µg/g, respectively. Sant'Ana et al. reported a study on the demineralization of diesel samples prior to ICP-OES and the concentrations of the metals that were under study were 0.7-1 µg/g (Al), 0.1-0.11 µg/g (Cu), 0.36-0.41 µg/g (Fe), 0.36-0.57 µg/g (Zn) and Ni was found to be below the detection limit [20]. These concentrations were much lower in comparison to those reported in the current study for diesel. It is worth in noting that very little was reported on microwave -assisted digestion on crude oil derivatives.

Table 4. 5: Concentration levels of metal ions expressed as µg/g in the real crude oil samples, diesel, gasoline and kerosene (A, B and C) after digestion using MA-HPD and analysis by ICP-OES.

Metal	**Crude oil samples (µg/g)**			**Diesel samples (µg/g)**			**Kerosene samples (µg/g)**			**Gasoline samples (µg/g)**		
	A	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
Al	2.36±0.4	1.21±0.02	2.13±0.1	4.1±0.04	36.75±1.2	<DL	47.0±1.2	<DL	26.8±0.7	7.5±0.05	6.5±0.01	<DL
Ba	3.15±0.2	1.83±0.05	6.09±0.5	7.7±0.1	7.2±0.9	9.2±0.01	8.4±0.8	6.2±0.1	7.3±0.02	8.3±0.1	3.0±0.03	9.2±0.03
Cd	6.2±0.1	6.8±0.08	5.5±0.07	4.9±0.08	4.8±0.03	4.99±0.2	5.0±0.05	4.9±0.2	5.7±0.09	5.1±0.08	4.9±0.02	5.0±0.02
Co	12.60±0.6	12.3±0.18	14.1±0.1	7.8±0.09	8.8±0.04	14.6±0.5	14.6±0.02	9.5±0.3	16.7±0.18	8.4±0.3	9.4±0.01	14.6±0.01
Cr	7.39±0.8	8.19±0.08	8.49±0.4	3.4±0.02	2.9±0.07	1.7±0.03	1.8±0.06	2.0±0.09	1.1±0.001	2.0±0.06	1.5±0.006	1.3±0.006
Cu	2.05±0.08	2.75±0.04	2.89±0.09	0.8±0.002	0.8±0.001	0.55±0.001	0.56±0.001	0.62±0.001	0.6±0.003	0.8±0.002	0.86±0.001	0.6±0.001
Mg	47.4±1.4	36.08±1.1	47.39±1.2	11.2±0.01	10.3±0.08	<DL	<DL	10.9±0.02	<DL	11.2±0.2	10.3±0.08	<DL
Na	58.86±1.1	52.70±0.9	51.9±1.6	18.7±0.1	10.3±0.1	34.3±1.0	4.9±0.07	2.5±0.08	4.6±0.07	34.3±0.9	12.4±0.1	35.1±0.8
Ni	8.19±0.08	6.14±0.1	8.09±0.1	2.4±0.03	2.4±0.02	4.9±0.03	8.0±0.02	2.2±0.01	6.3±0.06	4.9±0.08	2.5±0.08	4.6±0.01
Pb	5.81±0.1	5.06±0.09	4.89±0.06	2.7±0.04	2.1±0.01	8.0±0.06	9.5±0.1	1.6±0.007	12.6±0.6	2.0±0.06	8.0±0.001	2.0±0.001
Sb	8.70±0.2	3.3±0.04	4.67±0.03	1.9±0.01	1.5±0.07	9.5±0.2	1.4±0.08	1.5±0.003	1.4±0.01	1.4±0.09	1.9±0.02	1.6±0.003
Ti	3.99±0.05	4.42±0.07	4.17±0.08	1.5±0.01	1.5±0.05	1.5±0.08	2.3±0.1	2.5±0.08	2.9±0.08	1.4±0.02	1.4±0.008	1.4±0.008
V	4.70±0.06	4.67±0.1	4.73±0.04	1.9±0.03	1.9±0.03	2.0±0.1	2.0±0.05	1.9±0.002	2.0±0.06	2.1±0.01	1.9±0.006	2.0±0.005

4.5 Conclusion

The proposed MA-HPD method showed very good digestion results (accuracy: 104.8-117.7 %, precision: ≤ 4.1 % and MDL: 0.03 -0.408 µg/g), which were obtained by using a much cost-effective and environmentally friendly method. Therefore, this method can be further investigated for demineralization of other carbon based matrices, because it has been proven to solve most of the challenges associated with the conventional acid digestion methods. The newly developed MA-HPD can be used as an alternative digestion method for the future in fuel oils. When looking into the concentration of metals in the crude oil samples, this is a very good crude oil as it reported low concentrations of Ni (2.2-8.19 µg/g) and V (1.9-4.73 µg/g) while other literature reported crude oils reported high concentrations for Ni (15.76-33.21 µg/g) and V (36.9-763 µg/g). The crude oil derivatives when compared to other literature reports showed very little very low concentrations. The little difference observed within the crude oil derivatives, might be due to improper maintenance of other sampling sites.

APPENDICES

Table S1: The effect of varying sample mass, hydrogen peroxide concentration, digestion time and temperature on the digestion of NIST1364c to achieve high percentage recoveries of Ba, Na, Ni and V. Replicates (n=3).

Optimized Parameters				**Extraction Recoveries (%)**				**% RSD**			
Sample mass (g)	H_2O_2 conc. (M)	Digestion time (min)	Digestion temperature (°C)	Ba	Na	Ni	V	Ba	Na	Ni	V
0.05	1	20	180	0	0	0	0	0	0	0	0
0.2	1	20	180	0	0	0	0	0	0	0	0
0.05	1	20	240	80.3	80.6	79.0	76.0	9	6.7	2.8	8.9
0.2	1	20	240	70.1	70.0	71.4	72.9	4.5	4.7	1.5	5.4
0.05	5	20	180	0	0	0	0	0	0	0	0
0.2	5	20	180	0	0	0	0	0	0	0	0
0.05	5	20	240	81.2	77.5	77.8	76.6	11.5	5.5	5.5	13.4
0.2	5	20	240	80.7	81.5	82	79.1	6.4	2.8	6.2	4.1
0.05	1	60	180	0	0	0	0	0	0	0	0
0.2	1	60	180	0	0	0	0	0	0	0	0
0.05	1	60	240	94.5	95	92.8	103.6	8.2	1.8	2.8	4.8
0.2	1	60	240	88.2	92.8	92.0	93.6	4.2	1.8	2.5	1.8
0.05	5	60	180	0	0	0	0	0	0	0	0
0.2	5	60	180	0	0	0	0	0	0	0	0
0.05	5	60	240	112.7	101.7	120.0	104.6	2.5	1.4	0.7	4.8
0.2	5	60	240	107.1	101.7	117.7	110.4	1.9	0.8	2.7	4.1

Table S2: The effect of varying digestion time and temperature while keeping sample mass and H_2O_2 concentration constant in further optimization using on the digestion of central composite design. Experimental conditions: 0.1g of the sample and 5M H_2O_2 (n =3).

Optimised parameters		**Extraction recoveries (%)**				**% RSD**			
Digestion temperature (°C)	Digestion time (min)	Ba	Na	Ni	V	Ba	Na	Ni	V
220	40	115.7	88.6	89.5	83.3	1.8	0.3	2.4	5.2
220	40	109	87.0	92.5	88.7	2.4	0.6	2.6	4.7
220	40	108.8	81.3	92.9	85.2	1.6	0.6	2.3	5.3
240	60	104.0	100.0	104.4	99.2	2.2	1.0	1.8	4.1
191	40	73.0	52.5	49.0	39.3	4.9	5.1	4.9	7.1
200	20	78.8	56.7	68.4	69.3	5.1	6.9	7.1	8.9
200	60	76.0	69	90	82.6	4.4	4.4	4.2	6.4
248.3	40	110	109	102	109.8	2.9	0.8	1.9	4.1
220	40	108.8	81.3	92.9	85.5	09	3.1	2.0	4.8
240	40	111.3	87.7	92.6	98.3	2.1	2.7	1.6	3.9
220	40	102	82	87	83	1.8	2.1	1.7	4.7
220	11.7	80	74	68	61	6.1	0.9	1.9	4.9
220	68.3	106.2	106.2	108.1	103.3	4.1	0.7	2.4	5.4

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CHAPTER 5 (RESULTS PAPER 2)

Ionic liquid assisted extraction induced by emulsion breaking procedure prior to ICP-OES analysis for metal determination in crude oil, diesel, kerosene and gasoline samples

Abstract

A rapid, greener and cost-effective extraction ionic liquid assisted extraction induced by emulsion breaking (ILA-EIEB) has been developed for extraction of As, Ba, Pb, Sb, Sn, Tb and Te in crude oil, kerosene, diesel and gasoline samples. The extracts ware analysed using inductively coupled plasma optical emission spectrometry (ICP-OES). The optimum extraction conditions were achieved through the use of multivariate optimisation, where the two-level full factorial design was used for screening and the Box-Behnken design was used as the response surface methodology. The optimum conditions for ILA-EIEB were found to be 0.035% of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl), 18% nitric acid, 15% Triton x-100 and 0.1 g sample mass. The emulsions were broken by heating at a controlled water bath at 80 ±2 °C for 30 ±4 minutes and a further centrifugation step was completed for 15 minutes at 3 500 rpm. The optimum conditions were able to give good accuracy and precision of 80.1-101% and 1.9- 4.7%, respectively. This method was also able to report very low MDL for Ba, Na, Ni and V which were 0.107, 0.013, 3.494 and 0.560 µg/g, respectively. The overall concentration levels of the metals and metalloids (As, Ba, Pb, Sb, Sn, Tb and Te) analysed in this study reported a range from 0.072-8.610 µg/g. The concentrations of As reported in this study (0.084-0.46 µg/g) were in line with other literature report. From this study, it can be concluded that fuel oils around Johannesburg do not contain much metal and metalloids contaminants.

5.1 Introduction

The study of metal ion in fossil fuels remains key as this helps to create awareness on metal concentration levels and to develop proper measures of metal removal. Some of these metal ions (As, Ge, Te, Sb, Sn, and Se) appear in very trace levels, but their negative impacts associated in fuels and surrounding environment can never be overlooked [1]. For example, trace concentration levels of As and Sb in crude oil are associated with major catalyst poisoning [1]. These elements are semi-volatile, therefore are expected to be emitted into the atmosphere during crude oil refinery, combustion of gasoline/diesel in motor vehicles, thereby cause environmental pollution [2]. Additionally, other trace elements like Sn, Tl, Te, Ge and Si have been reported to be carcinogenic, cause liver damage, malfunctioning of the immune system, chromosomal damage, depression, and brain damage in animals [3-6]. In plants, these elements can reduce the synthesis of chlorophyll, resulting to poor growth [7].

Therefore, several liquid-liquid extraction (LLE) methods have been developed for the preconcentration of metal ions that are in very trace levels. These LLE methods include, traditional liquid-liquid extraction (LLE) [8,9], liquid-liquid microextraction (LLME) [10-12], dispersive liquid-liquid microextraction (DLLME) [13-15], extraction induced by emulsion breaking (EIBE) [16-20], and reverse phase-dispersive liquid-liquid microextraction (RD-LLME) [12, 21-23]. In terms of enrichment factor, time and the operational cost reported, the EIEB has been more favoured over the other LLE methods. Cassella et al. [24] reported for the first time the extraction of Cu, Fe, Pb and Ni from diesel samples using EIEB. This new extraction method reported percentage recoveries from 85.2-109 % with precision of ≤8.8 and limits of detection were 114, 183, 294 and 145 µg/g for Cu, Fe, Pb and Ni, respectively. Since then, EIEB gained more popularity and it was applied for metal extraction in both fuel (crude oil, diesel, gasoline, lubricating oil etc.), and edible oils [5, 17, 18, 21, 25, 26]. The EIEB involves the breaking of emulsion resulting in the separation of organic phase from the aqueous phase. The aqueous phase can be extracted by micropipette and taken for analysis with any compatible analytical instrument. Several studies have reported that two layers form after emulsion breaking, however, in rare cases a third layer maybe formed. The three layers are normally observed when too concentrated surfactant was used. Therefore, in the presence of the third layer, the upper phase contains the organic phase, middle layer contains acidic aqueous phase and lower phase is normally rich in surfactant [26]. The latter is a substance that reduces surface tension between two immiscible liquids, to enhance enough mixing. Literature reports have indicated the surfactants that have been used are Triton X-100 and Triton X-114. These surfactant surfactants show no significant difference, the only difference is that with Triton X-114, the emulsions take a shorter time to break [18]. Additionally, the acids that were reported for metal extraction were HNO_3 and HCl. It is worth noting that HCl was reported in few studies in comparison to HNO_3. The choice of HNO_3 was based on nitric acid being very good in the extraction of metals [24]. The EIEB reported in literature are environmentally friendly as a majority of them reported the use of diluted reagent. However, to the best of our knowledge no study have reported the use of ionic liquid to facilitate extraction of metals and these elements (As, Ba, Pb, Sb, Sn, Tb and Te) have not yet been reported in most fuel samples. The use of ionic liquid eliminates the generation of secondary waste when compared to the traditional EIEB and further enhanced the formation of stable emulsions which improved interaction time of the phases, which in turn improve extraction efficiency.

Luiz et al. [26] reported the use of EIEB sample preparation in the extraction of Co, Cu, Pb and Se in crude oil samples. In this EIEB, Triton X-100 was used as a surfactant and reported limits of detection of 20, 30, 40 and 110 ng/g for Co, Cu, Pb and Se, respectively. The percentage recoveries and precision reported were 95-122% and 2.8-4.8%, respectively. The extraction of metals (Ca, Mg, Sr, and Na) using EIEB was also reported by Vieira et.al.[21] in crude oil samples prior to ICP-MS analysis. Metal extraction was achieved in 18 minutes with excellent percentage recoveries of 92.8-102.2%. The EIEB, has also been reported in diesel samples, where Al, Cu, Mn and Ni were extracted in diesel prior to ICP-MS analysis. The percentage recoveries reported were 84-113% with precision of 3.3% [5]. The EIEB was also reported for the extraction of Hg in gasoline by Vicentino et al. [18]. In this sample preparation method, n-propanol and HNO_3 were used for the formation of emulsions while a horizontal shaker was used for breaking the emulsions. This sample preparation just like the other EIEB gave excellent Hg recoveries (88-109%) and precision of 4.8%. Additionally, EIEB was also reported for the extraction of Cu, Fe and Pb where a water bath at 90 °C was used to break the emulsions. Excellent recoveries of Cu, Fe and Pb ranged from 98-105% [18]. Literature, therefore, have shown that a lot of research can be done on EIEB as most of the elements that normally appear at very trace levels in fuel oils are not discussed with this sample preparation method. It must also be noted that, highly viscous oils are less favoured under EIEB and therefore these oils commonly require a dilution step where organic solvents like toluene, hexane and xylene are used as diluent. The use of organic solvents is a limitation for EIEB, as most of these solvents have been reported to be highly carcinogenic and large volumes of the dilutant results in unstable emulsion [27, 26].

Therefore, the current study aims to investigate the use of small volumes (500 µL) of p-xylene as a diluent, combined with ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) to solve the challenges of unstable emulsions. If the emulsions are not stable, the interaction between the organic and aqueous phase becomes minimal resulting to reduction in extraction efficiencies [21]. Additionally, to the best of our knowledge, Sb, Te, Si, Ge and Ba have never been extracted using EIEB in fuel oils. Elements like As, Sr, Sn and Se have been studied in crude oil and diesel but not in gasoline and kerosene. Additionally, in developing method for metal extraction prior to analysis, multivariate optimization have been used over univariate optimization. In univariate optimization, a single factor is controlled at a time while keeping the other factors constant [28]. The major problem with univariate is the number of experiments and the effect of one variable can be dependent on the levels of other factors involved in the optimization [29]. Therefore, to overcome the limitations of univariate, multivariate optimization has been employed for optimization of parameters. In multivariate optimization, there are two steps which are screening of factors and response surface methodology. In screening, only the factors that have an effect in the optimization are shown while the response surface methodology helps to attain the optimum operating conditions for the optimized variable [30]. Under response surface methodology, Doehlert matrix (DM), central composite design (CCD), Box-Behnken design (BBD) and three-level design have been reported [21, 29, 31, 32]. Literature has indicated that based on efficiency of DM, BBD and CCD there is no significant differences so in this research, the BBD was used for response surface response methodology.

5.2 Experimental procedures

5.2.1 Reagents and glassware

The glassware (beakers, volumetric flasks, centrifuge tubes etc.) used were washed using soap and water, then socked in 5% nitric acid and finally rinsed with deionized water prior to drying and storage in lockers. Metal and metalloids standards were prepared from dilution of 100 mg/L multi-element standard solution (Sigma-Aldrich, South Africa**)**. Standard reference material (NIST1634c) which contain trace elements in fuel oil, 1-ethyl-3-methylimidazolium bis(trifluromethylsulfonyl) and 70% ACS grade HNO_3 were purchased from Sigma-Aldrich, South Africa. Real gasoline, diesel and kerosene samples were purchased from local filling stations around Johannesburg, South Africa. Nylon microfilters (0.45 µm) were purchased from Anatech instrument (South Africa). Crude oil samples came from one of the crude oil refinery companies in South Africa.

5.2.2 Instrumentation

The vortex mixer (Velp Scientifica) was used to mix the surfactant, oil and extractant solution. After a homogenous mixture was formed a water bath was used to break the emulsions. Later a bench top centrifuge machine (NEYA16R) was used to ensure proper phase separation. After the phase separation, the aqueous phase was extracted and taken for analysis in the Agilent Technologies 700 Series ICP-OES (see **Table 5.1**).

Table 5.1: Operating parameters of the ICP-OES for metal and metalloids analysis

ICP-OES instrumental parameters	Condition
RF Power	1200 W
Auxiliary gas flow	1.5 L/min
Nebulizer	0.75L/min
Peri-pump speed	15 rpm
Pump speed	85 rpm
Plasma gas (Ar) flow rate	15.0L/min
Sample uptake delay (s)	15 s
Stabilization time (s)	15 s
Element wavelenghts	As 188.980, Ba 234.759, Pb 283.30, Sb 217.582, Sn 189.925, Tb 350.914 and Te 190.802

5.2.3 Ionic liquid assisted extraction induced by emulsion breaking procedure

To a 15 mL centrifuge tube, 0.1g of sample was weighed and diluted with 500 µL of p-xylene. A mixture of 0.035% of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) (ionic liquid) and 18% nitric acid of 5 mL volume was added to the diluted sample. On to the mixture, 2 mL of Triton X-100 (15%) was then added and the mixture was thoroughly mixed using the vortex mixer for 3 minutes. After mixing, the test tubes were put in a test tube rack for 15 minutes. This was to ensure maximum interaction of the two phases and to see if the formed emulsions were stable or not. Finally, the emulsions were broken by heating at a controlled water bath at 80 ±2 °C for 30 ±4 minutes. The sample was later taken to bench top centrifuge for centrifugation for 15 minutes at 3 500 rpm. This step was conducted to ensure maximum phase separation. The two phases which were the organic phase (top layer) and the aqueous phase (bottom layer) were separated by the use of a micropipette. The aqueous phase was accurately collected with a micropipette and the analytes were transferred into new 15 mL centrifuge tubes for ICP-OES analysis. The aqueous multi-element standards were used for producing calibration curves for each element (As, Ba, Pb, Sb, Sn, Tb, and Te). The concentrations of the calibration standards were 0.01, 0.05, 0.1, 0.3, 0.8, 1, 1.5, 1.8, 2, and 2.5 ppm.

5.2.4 Multivariate optimization

The multivariate optimization approaches were used for the determination of parameters that greatly affected the Ionic liquid assisted extraction induced by emulsion breaking (ILA-EIEB). The parameters that were optimized were sample mass, ionic liquid [1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)] concentration, Triton x-100 concentration and HNO_3 concentration. These parameters were optimized using the full factorial design (2^n). The variable was given the lower level (-) and the higher level (+) as presented in **Table 5.2**. The Box-Behnken design (BBD) was used for further optimisation of the most significant parameters. For both two-level full factorial and BBD, the Minitab 2018 statistical software was used for the generation of the experiments and analysis of data.

Table 5.2: The parameters that were investigated and their levels for two-level full factorial design

Factor optimised	**Low level (-)**	**High level (+)**
Nitric acid concentration (%)	10	20
Triton x-100 (%)	5	20
Ionic liquid concentration (%)	0.02	0.05
Sample mass (g)	0.05	0.1

5.2.4.1 Full factorial design

A two-level full factorial design was used for the screening of optimised factors (sample mass, digestion time, digestion temperature and hydrogen peroxide concentration). The full factorial design was carried in way that the parameters were varied simultaneously for the optimised parameters. The optimum condition of the ILA-EIEB were achieved using multivariate mathematical tool with NIST1634c fuel oils. The parameters that were optimised with lower and upper limits were as follows: (i) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) concentration (0.02 -0.05%), (ii) Triton X-100 concentration (5-20%), HNO_3 concentration (10-20%), and sample mass (0.05-0.1 g), see **APPENDIX Table 3.** These lower and upper limits were then used in creating a two-level full factorial design on Minitab software 2018. This design had one number of blocks and for that reason a total number of 16 experiments were generated. It is worth in noting that the experiments were not randomised for easy handling of experimental work and data generated. In each experiment approximately the same ma**ss (see APPENDIX Table 3**) was weighed into three separate 15 mL centrifuge tube. It is also worth noting that for every experiment a blank was made under the same conditions of the experiment but without NIST1634c. Additionally, these recoveries were then run in Minitab 2018 statistical software to analyse the response of each parameter and the response was presented in the form of Pareto charts. The parameters that proved significant at 95% confidence level were further taken for further optimization using the BBD.

5.3 Results and discussion

5.3.1 Multivariate optimization of ionic liquid assisted extraction induced by emulsion breaking parameters

5.3.1.1 Full Factorial Design

The results were then run in Minitab software for analysis and Pareto charts were generated (see **Fig. 5.1A-D)**. The Pareto charts assisted to confirm those parameters that were more significant at 95% confidence level. The concentration of nitric acid, Triton X-100 and ionic liquid concentration proved to be significant for the extraction of Ba, Na and Ni. However, with V the most significant factors were ionic liquid and nitric acid concentration. The multivariate optimization procedure proved to be a great success for Ba, Na and Ni as the percentage recoveries reached 100% for some of the experiments. In contrast, for V 85.4% was the highest percentage recorded in all the 16 experiments. The low recoveries of V might have caused by failure to extract vanadium that had +5 oxidation state (VO_3^-) from the organic matrix. The +5 oxides would be acidic in nature and reaction with H+ would not be most favoured. In fact, a basic medium would be probably extract those better [33]. Additionally, the most significant factors were then taken for further optimization using Box-Benhern design which falls under the response surface methodology (RSM) which helped to predict the most optimum condition for ILA-EIEB. Additionally, the mass of sample was insignificant at 95% confidence level and 0.1 g was used for further optimization. The choice of 0.1 g was based on results that used 0.1 g showing very good precision in comparison to those experiments that used 0.05 g.

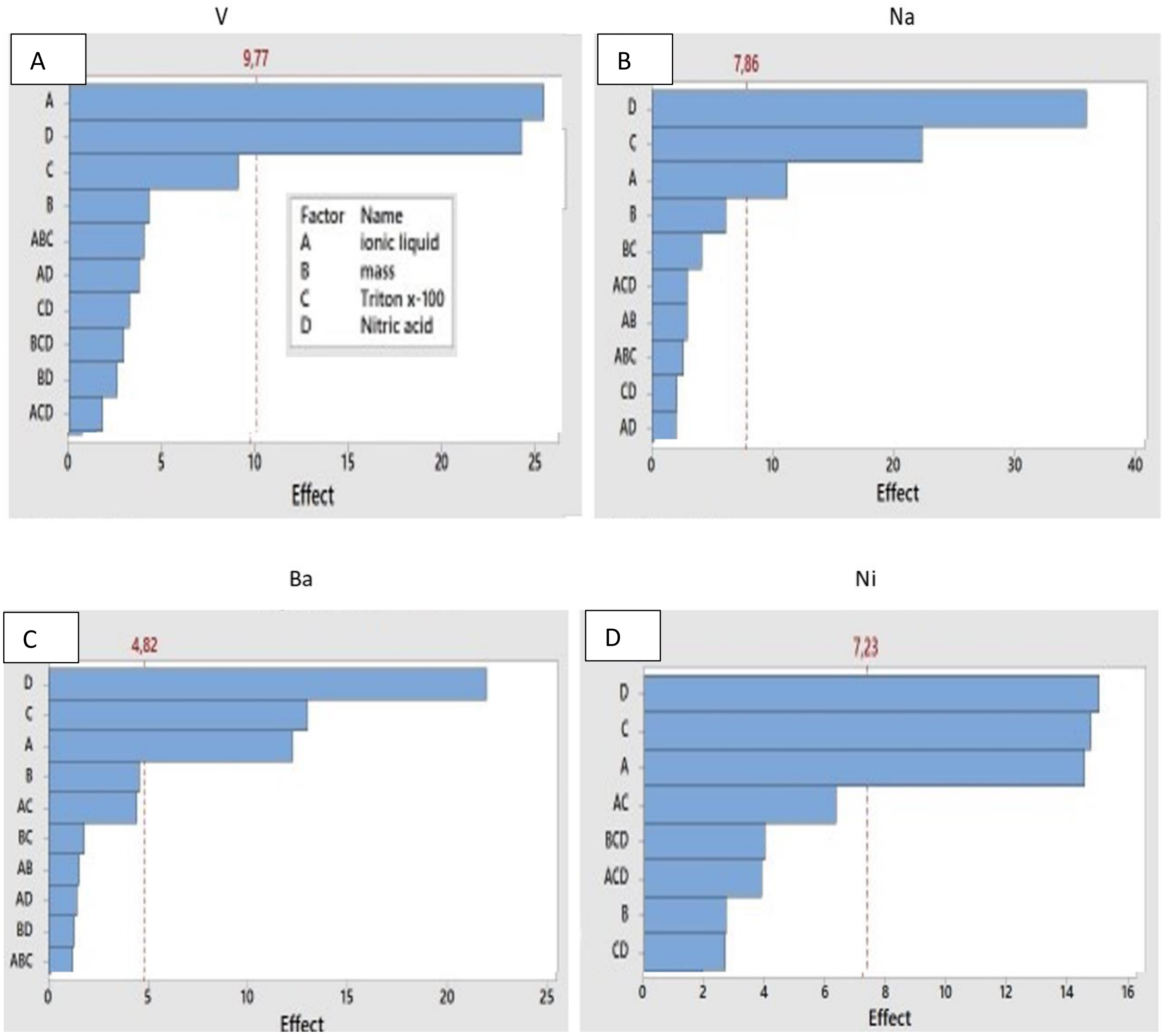

Figure 5. 1 (A-D): Pareto charts A (V), B (Na), C (Ba), and D (Ni) for a level 2- full factorial design (2^4) at 95 % confidence level for optimization of sample mass, nitric acid, ionic liquid and Triton X-100 concentration for extraction of metals using EIEB (n=3).

5.3.1.2 Box- Behnken design (BBD)

The parameters (ionic liquid, nitric acid and Triton X-100 concentrations) that proved to be significant in the two-level factorial design were further optimised using the Box-Behnken design. The latter was chosen as literature reported that it is one of the best response surface methodology for 3 factors going upwards [29]. The Box-Behnken was designed in a way that there was one block design resulting to 15 experiments generated. The RSM helped to predict the most optimum conditions for the proposed extraction method. These optimum conditions were also confirmed by the quadratic equations generated RSM (**see Eq. 5.2A-D**). The interactions of the factors amongst each other were also presented in the form of surface plot (**see Fig. 5.2A-D).** From all the figures it was discovered that keeping ionic liquid at 0.035% was enough to give high extraction recoveries when both the Triton X-100 and nitric acid concentration were above 15%. The surface also indicated that increasing the concentration of HNO_3 and Triton X-100 showed an increased percentage recoveries (see **Fig.5.2A-D**). The surface response and quadratic equations confirmed the optimum conditions for ILA-EIEB to be 0.035% of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl), 18% nitric acid, 15% Triton X-100 and 0.1 g sample mass.

$$Ba = -145.4 + 3965A - 2.47B + 21.07C - 46667A^2 + 0.0373B^2 - 0.633C^2 + 8.4AB - 32.3AC + 0.157BC \qquad \boldsymbol{Eq. 5.3A}$$

$$Na = -6.9 + 1064A + 2.03B - 7.63C - 15148A^2 - 0.0748B^2 - 0.2043C^2 + 13.3AB - 6.0AC + 0.0120BC \qquad \boldsymbol{Eq. 5.3B}$$

$$Ni = -90.4 + 1173A + 2.25B + 17.75C - 4907A^2 - 0.0650B^2 - 0.461C^2 + 0.20AB - 46.7AC - 0.0213BC \qquad \boldsymbol{Eq. 5.3C}$$

$$V = -49.4 + 475 + 2.69 + 11.23C - 8907A^2 - 0.0774B^2 - 0.3482C^2 - 0.7AB + 17.0AC - 0.0073BC \qquad \boldsymbol{Eq. 5.3D}$$

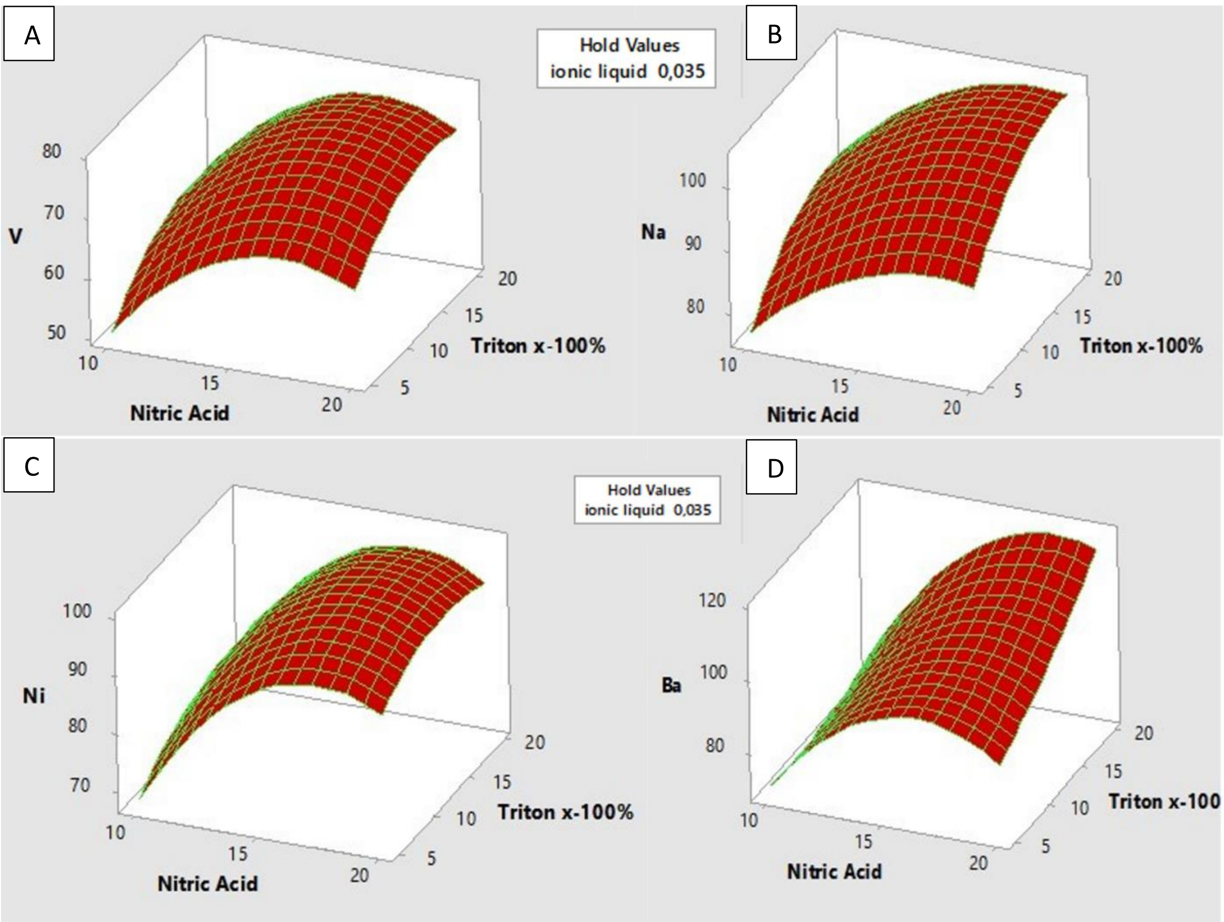

Figure 5. 2(A-D): Response surfaces A, B, C, and D for Ba, Na, V and Ba, respectively Versus Time.Temperature obtained from Box-Behnken design. Experimental conditions: 0.1 g of the sample and all the other factors were varied (n =3).

5.3.2 Analytical figures on merit

The optimum parameters (HNO_3, Triton X-100 and ionic liquid concentrations) obtained from the RSM were used in the investigation of analytical features for the current extraction procedure. The analytical features that were investigated included method detection limit (MDL), method quantification limit (MQL), correlation coefficient (R^2), and sensitivity (gradient). The linear graph that produced the correlation coefficient and sensitivity was achieved by weighing 0.025, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.325 g (NIST1634c in triplicates) into 15 mL centrifuge tubes. These masses were then dissolved in the mixture of 500 µL of p-xylene, 0.035% ionic liquid, 18% nitric acid and 15% Triton X-100. After extraction and emulsion breaking the aqueous phase was analysed using the ICP-OES. The intensity of each metal at a given mass was plotted against the expected concentration (Theoretical value) [37]. Additionally, for the determination of standard deviation of 20 blanks, same procedure as above was followed except for mass. Only 500 µL p-xylene, 0.035% ionic liquid, 15% Triton X-100, and 18% nitric acid was used subjected to the optimum conditions of the proposed ILA-EIEB. The standard deviation of blanks, limits of detection, limit of quantification, sensitivity, method detection limit and method quantification limits are presented in **Table 5.3.** The R^2 showed very good linearity as they were ranging from 0.9983-0.9997. The most sensitive metal in this method was Na which reported MDL of 0.013 µg/g, in contrast with Ni, which showed to be less sensitive with this method as it reported very high MDL of 3.494 µg/g. The low sensitivity of Ni might be due to Ni being bonded to organic structures in the oil. The Ni are bonded to the organic molecules present in the oil through more stable interactions than the other elements under study [5].

Table 5. 3: Analytical features of the ILA-EIEB method for quantitative extraction of Ba, Na, Ni and V in NIST1634c: ILA-EIEB conditions; ionic liquid (0.035%), Triton X-100 (15%) and HNO_3 (18%) replicates (n =3).

Metal	**Correlation coefficient (R^2)**	**SDV of intensity (cps)**	**Sensitivity (cps L µg^{-1})**	**Accuracy (%)**	**Precision (%)**	**LOD (µg/L)**	**LOQ (µg/L)**	**MDL (µg/g)**	**MQL (µg/g)**
Ba	0.9983	2.71	3.0299	95	3.2	2.6833	8.9441896	0.107	0.357
Na	0.9991	5.59	515.407	101	4.7	0.0325374	0.108458	0.013	0.043
Ni	0.9990	3.14	1.0783	98	1.9	8.736	29.11	3.494	13.12
V	0.9997	1.67	3.5801	80.1	3.3	1.3994023	4.6647	0.560	1.866

5.3.3 Comparison of the proposed ILA-EIEB with literature reports

This newly developed ILA-EIEB method was then compared with other EIEB methods from literature (**Table 5.3**) and it is worth noting that the limit of detection (LOD) was selected as this analytical figure is directly linked with sensitivity. The method detection limit (MDL) was not picked for comparison in **Table 5.3** as most literature did not report it. Viera et al. [34] reported the extraction of metals from crude oil by EIEB, this method reported very good percentage recoveries ranging from 92.8-102.2% with precision less than 10%. The MDL of was reported to be 3.3 µg/g for Na which was slightly higher than the one reported in the current study, making the proposed ILA-EIEB method to be more sensitive. Carballo et al. [35], reported the determination of metals in lubricating oil after EIEB. This method reported acceptable accuracy of 94-115% with precision (< 7). The MDL for Ni and V were 0.77 and 0.83 µg/g, respectively, which were comparable with the current method, except for Ni.

Table 5. 4: Comparison of method sensitivity, precision, and accuracy between the ILA-EIEB and other EIEB reported from literature

Fuel matrix	**Sample preparation**	**Metal**	**Reagents**	**LOD (µg/L)**	**Accuracy (%)**	**Precision (%)**	**Detection Technique**	**Ref**
Bitumen	EIEB	Ni	Triton X-100 HNO_3	9	100	< 10	GFAAS	[36]
Crude oil	EIEB	Na	Triton X-100 HNO_3	9.8	92.8-102.2	3.5 -10.9	ICP-OES	[34]
Diesel	EIEB	Ni	Triton X-100 HNO_3	145	85.2 - 109	8.8	EAAS	[24]
Diesel	EIEB	Ni	Triton X-114	0.07	84-113	<3.30	ICP-MS	[5]
Lubricating oil	EIEB	Ni and V	Triton X-100 HNO_3	0.77 and 0.83 µg/g	94-115	<7	ETAAS	[35]
NIST1634c	ILA-EIEB	Ba, Na, Ni and V	Triton X-100 HNO_3	2.68, 0.03, 8.74 1.399	95,101, 98 and 80.1	3.2, 4.7,1.9 and 3.3	ICP-OES	This work

5.3.6 Application of extraction induced by emulsion breaking in real fuel samples

After optimization and validation of the ILA-EIEB sample preparation method, the optimum parameters were applied into the different samples which were crude oil, diesel, gasoline and kerosene. There were five different samples for crude oil which were labelled A, B, C, D, and E. However, for diesel, kerosene, and gasoline the samples were labelled as A, B and C. The optimum condition for ILA-EIEB were 18% of HNO_3, 15% of Triton X-100, 0.1 g sample and 0.035% of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl). The aqueous extracts were taken for analysis of As, Pb, Sb, Sn, Tb and Te using ICP-OES. The investigated metals and their concentration are reported in **Table 5.5.** The concentration of Arsenic reported in this study were very small and there were slight differences in concentration levels obtained between crude oil, diesel, gasoline and kerosene. The obtained concentrations were 0.012-0.015 µg/g for crude oil, 0.08-0.1 µg/g for kerosene, and 0.084-0.116 µg/g for gasoline and 0.1-0.25 µg/g for diesel. However, the highest concentrations of As were reported in diesel (0.1-0.25 µg/g). Additionally, the concentration of As in this study were compared with other literature studies on other fuel matrices. Wuyke et al.[27] reported EIEB for the determination of As, Co, Cr, Mn, Mo and Pb in heavy and extra heavy crude oil. The concentration of As ranged between 0.082- 0.180 µg/g. Cassella et al. [5] also reported EIEB for Al, Cu, Mn, Ni, Sn, and V determination in diesel oil by ICP-MS. The concentration of Sn reported were very small in the five samples of the diesel compared to the current study as they were 1.70, 1.57, 1.60, 1.86 and 1.55 µg/L. It is worth in noting that most of the studied elements including Sb, Te, Ge and Ba were not reported in literature on EIEB on fuel samples and so this is the first study to report on such elements using ILA-EIEB. When looking at the overall tread in metal concentrations from the samples, it can be noted that Ba reported lowest concentrations in crude oil (1.76- 6.6 µg/g) when compared to the crude oil derivatives such as kerosene (6.8-89 µg/g), diesel (7.3 -8.0 µg/g) and gasoline (2.95- 8.7 µg/g). The concentration of Tb in all the samples was much lower than for the other elements as it ranged from 0.067-0.590 µg/g. It can be highly recommended that the levels of these metals can be further monitored and reduced in the crude oil and crude oil derivatives as these trace metals can cause severe air and water pollution, increasing health risk to both plant and animals.

Table 5. 5: Concentration levels of metal ions expressed as µg/g in the real crude oil samples, diesel, gasoline and kerosene (A, B and C) after digestion using ILA-EIEB and analysis by ICP-OES.

Element	**Crude oil samples (µg/g)**					**Diesel samples (µg/g)**			**Kerosene samples (µg/g)**			**Gasoline samples (µg/g)**		
	A	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
As	0.123±0.002	0.167±0.002	0.109±0.002	0.107±0.0	0.178±0.0	0.25	0.21±0.0	0.100±0	0.1±0.00	0.08	0.95±0.0	0.104	0.12±0.0	0.084±0.
Ba	3.0±0.08	1.76±0.01	6.1±0.08	4.2±0.1	2.51±0.0	7.3±0.0	7.4±0.2	8.0±0.2	8.9±0.5	6.8	6.9±0.5	8.0	2.95±0.1	8.7±0.4
Pb	6.09±0.03	4.624±0.03	5.257±0.08	6.12±0.06	5.2±0.02	6.35±0	6.9±0.1	5.89±0.5	8.61±0.3	5.81	4.2±0.1	5.87	7.1±0.6	5.4±0.2
Sb	6.27±0.02	5.047±0.02	6.852±0.05	3.458±0.01	1.104±	1.03±0.	0.548	0.37±0.0	0.94±0.01	0.92	0.89±0.0	0.53	1.0±0.1	1.0±0.01
Sn	0.818±0.004	1.174±0.03	0.848±0.004	0.839±0.0	1.1±0.01	1.14±0	1.14±0.0	0.925±	0.645±0.0	0.64	0.64±0.0	0.810	0.513±0.	1.5±0.08
Tb	0.457±0.002	0.515±0.006	0.481±0.002	0.533±0.0	0.51±0.0	0.541±0.	0.487±0	0.483±	0.075±0.0	0.067	0.072±0.	0.466	0.590±0.	0.53±0.0
Te	2.765±0.06	1.42±0.01	3.85±0.03	3.23±0.01	4.2±0.02	2.12±0	3.8±0.01	3.95±0.1	0.95±0.0	0.92	0.85±0.0	<DL	1.54±0.1	2.12±0.1

5.4 Conclusion

The newly proposed ILA-EIEB which used 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) for extraction of metals and metalloids reported very good extraction efficiencies with good LODs: 0.033-8.74 µg/L, accuracy: 80.1 -101% and precision: 1.9 -4.7%. This method proved to be environmentally friendly as an ionic liquid and very small volumes (µL) of carcinogenic organic solvents was used throughout the study. This newly developed method which used ionic liquid solved the problem of unstable emulsions that are associated with the traditional EIEB. The extract in the form of aqueous phase also ensured that very minimal carbon content goes with the sample for analysis. This method therefore was advantageous as it is postulated to reduce carbon overload into the torch, which might result in extinction of the plasma. The concentrations of the metals under study when compared with literature report indicated that the locally used crude oil and crude oil derivatives have very small metal contaminant. This therefore means that South Africa is importing quality crude oil and producing quality crude oil derivatives.

APPENDICES

Table S1: The effect of varying sample mass, ionic liquid , nitric acid and Triton x-100 concentration during EIEB on NIST1364c to achieve high percentage recoveries of Ba, Na, Ni and V. Replicates (n=3

Exp	Ionic liquid (%)	Mass (g)	Triton x-100 (%)	Nitric acid (%)	Ba (%R)	Na (%R)	Ni (%R)	V (%R)	Ba (%RSD)	Na (%RSD)	Ni (%RSD)	Ni (%RSD)
1	0.02	0.05	5	10	67.8	40.9	76.6	51.0	14.5	17.1	9.2	18.1
2	0.05	0.05	5	10	50.8	30.2	55.7	17.60	16.3	19.2	14.2	15.2
3	0.02	0.10	5	10	75.8	43.6	80.1	63.40	10.5	17.5	8.14	14.3
4	0.05	0.10	5	10	56.5	32.4	64.0	31.7	16.2	10.2	16.7	12.9
5	0.02	0.05	20	10	76.8	68.4	87.7	67.90	8.3	7.1	6.2	5.4
6	0.05	0.05	20	10	67	43.9	78.5	37.7	7.3	8.4	7.7	3.4
7	0.02	0.10	20	10	81.7	69.0	87.9	72.2	5.4	4.3	5.2	5.9
8	0.05	0.1	20	10	72.5	62.3	69.8	43.8	6.8	6.1	8.2	2.3
9	0.02	0.05	5	20	86.1	80.1	91.3	80.60	3.4	4.6	4.8	5.1
10	0.05	0.05	5	20	75.4	67.0	69.5	62.30	5.1	5.2	5.0	6.7
11	0.02	0.10	5	20	96.3	81.3	93.8	83.50	2.0	1.9	1.3	2.5
12	0.05	0.10	5	20	76.8	69.4	70.4	54.40	4.8	4.9	4.4	5.1
13	0.02	0.05	20	20	100.2	93.1	96.0	84.80	1.2	2.4	3.5	3.8
14	0.05	0.05	20	20	94.2	85.2	93.5	61	6.4	6.5	6.9	7.1
15	0.02	0.10	20	20	101.4	101.8	103.3	85.4	2.3	2.7	1.9	4.7
16	0.05	0.10	20	20	94.1	98.2	100.2	72.2	3.5			

Experiment	Ionic-liquid	Triton x-100	HNO_3 %	% R				%RSD			
				Ba	Na	Ni	V	Ba	Na	Ni	V
Exp 1	0.02	5	10	83.3	84.4	88.9	65.6	6.2	4.7	5.3	7.1
Exp 2	0.05	5	10	87.7	85.4	89.3	68.8	5.1	4.6	5.4	6.9
Exp 3	0.02	20	10	95.4	94.1	94.6	69.1	4.7	3.1	5.1	6.5
Exp 4	0.05	20	10	103.7	100	95.1	72.0	4.9	2.1	4.3	5.8
Exp 5	0.02	5	20	45.4	79.8	62.7	56.6	6.7	6.3	3.1	4.9
Exp 6	0.05	5	20	62.9	81.6	77.2	56.9	6.3	4.8	5.6	8.1
Exp 7	0.02	20	20	90.9	99.9	97.9	69.6	4.2	2.9	1.8	4.7
Exp 8	0.05	20	20	98.9	100	98.5	75.3	1.9	2.5	1.8	3.1
Exp 9	0.01	12.5	15	74.8	79.4	72.9	49.2	5.1	4.8	3.9	6.1
Exp 10	0.06	12.5	15	82.2	90.5	78.2	64.9	4.7	4.6	4.1	5.0
Exp 11	0.035	12.5	15	80.4	88.0	86.5	60	3.9	4.3	3.8	4.8
Exp 12	0.035	12.5	17.5	111.3	100	88.6	74.6	1.9	0.8	1.4	4.9
Exp 13	0.035	12.5	17.5	103.8	98.7	97.3	76.3	2.2	1.3	4.1	5.1
Exp 14	0.035	15	17.5	99.1	99.2	96.8	75	1.3	2.6	4.9	4.8
Exp 15	0.035	12.5	17.5	99.8	98.7	96.0	74.4	3.2	0.6	3.6	4.2

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CHAPTER 6 (RESULT PAPER 3)

Magnetic solid phase extraction based on $Fe_3O_4@Al_2O_3$ adsorbent for simultaneous preconcentration of selected metal ions from crude oil, diesel, kerosene and gasoline samples followed by ICP-OES determination

Abstract

In this study, $Fe_3O_4@Al_2O_3$ nanoparticles were synthesised, characterized and applied as magnetic adsorbents for simultaneous magnetic solid phase extraction (m-SPE) of As, Ba, Cd, Cr, Cu, Mn, Mo, Ti, V, Pb, Sb, Sn, Tb, Te and Zn in selected petroleum samples prior to analysis using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The adsorbent was characterized using FTIR, SEM, EDS and XRD. Fourier transform infrared spectra showed 580 and 630 cm^{-1} stretching frequencies, which were attributed to Al-O and Fe-O stretching vibrations, respectively. Scanning electron microscopy and energy dispersive X-ray spectroscopy confirmed that Fe_3O_4 elemental distribution was composed of Fe, O and C at 63.5, 30.6 and 5.9 wt%, respectively. While $Fe_3O_4@Al_2O_3$ metal composition included O, Al, C and Fe at 40.1, 31.1, 17.3 and 11.0 wt%, respectively. The particle size of $Fe_3O_4@Al_2O_3$ ranged between 37 and 74 nm, as shown in the transmission electron microscopy images which is in line with literature report for magnetite nanoparticles. Strong diffraction peaks with 2ϴ values of 30.2°,35.5°, 43.5°, 53.8° and 57.3° were attributed to $Fe_3O_4@Al_2O_3$, which were also reported in literature.

Thereafter, various experimental parameters affecting the proposed m-SPE method were investigated by using CONOSTAN oil analysis standard-custom bled containing Ag, Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Ti, V and Zn metal ions. Additionally, two multivariate mathematical tools, two level fractional factorial design (FrFD) and the central composite design (CCD) were used for the optimization. The optimization results showed that $Fe_3O_4@Al_2O_3$ adsorbent exhibited excellent preconcentration of selected metal ions when 40 mg adsorbent mass, 35 minutes extraction time, 6.5 pH, 20 µg/L spike concentration and 1.0 mol/L eluent concentration were used. Under optimum conditions, the developed m-SPE displayed good accuracy (86-96%) for all metals with exception of Zn at 74%, precision (0.9-4.8%) and low method detection limits (0.114-0.62 µg/g). The proposed m-SPE method also reported preconcentration factors of 168, 166, 152, 165, 164, 150 and 150 for Co, Cr, Cu, Mn,

Mo, Pb and V, respectively. Additionally, the enrichment factors were 30, 24, 11, 20, 26, 10 and 8 for Co, Cr, Cu, Mn, Mo, Pb and V, respectively, which were quite comparable with other literature reported SPE methods.

The optimised and validated m-SPE method was then applied in real fuel oil samples. Some of the metal ions were less than 1 µg/g (As, Tb and Mn) while the rest of the analytes were above 1 µg/g but below 10 µg/g. The rapidness of the proposed m-SPE method was facilitated by the easy separation of the adsorbent using external magnet. Therefore, this method can be used as an alternative for preconcentration and removal of metal ions in fuel oils.

6.1 Introduction

Solid phase extraction (SPE) is a a sample preparation method that is characterized by using adsorbent for preconcentration and separation of target analyte from a complex matrix [1, 2].The traditional SPE is characterized by five steps which are; conditioning, equilibrating, sample loading, washing and elution [3-5]. It is worth in noting that when choosing the elution solvent, one must choose a solvent that can disrupt all interactions between different functional groups of the adsorbent and the target analyte [6-8]. Therefore, the selection of an appropriate adsorbent is also a key in SPE, as this ensures maximum extraction of target analyte. The SPE sample preparation method has therefore been applied in extraction of various analytes from different samples such as water, food, pharmaceutical and fuels, just to name a few [9-11]. Additionally, SPE sample preparation method has reported several advantages when compared to other preconcentration techniques. These advantages include cost effectiveness, good selectivity, simplicity, rapidity and high enrichment factors [12, 13]. However, traditional SPE methods have several limitations which include, large volume of carcinogenic organic solvent, time consuming due to challenging separation steps and labour intensiveness [14]. Therefore, several new sample preparation methods that fall under SPE have been developed to overcome these challenges. The newly developed SPE methods included; dispersive solid-phase extraction (d-SPE) [9], magnetic solid-phase extraction (m-SPE) [15] and solid-phase micro-extraction (SPME) [11, [16-20].

The d-SPE method was developed to allow for the direct addition of a sorbent into the analytical solution, resulting in a strong interaction between the sorbent and the analytes. When the process is finished, the sorbent containing the analytes is retained on the surface [9]. The analytes are then separated using a mechanical process, typically centrifugation or filtration.

This technique has several advantages over traditional SPE, including shorter time, lower cost, ease of operation, and low organic solvent consumption [21]. Additionally, d-SPE is also regarded as one of the best SPE method, however, this method normally uses a lot of carcinogenic solvents for washing of adsorbent and sometimes have a lot of extraction steps with increases the chances of contamination [5].The SPME is another sample preparation method that has gained popularity in the analytical and bioanalytical fields due to its improved partition coefficient and diffusion properties, as well as its high selectivity for trace-level target analytes [22]. As a result, various nanostructured materials have been integrated with different types of SPME (e.g., fibre SPME, in-tube SPME, in needle SPME, thin-film SPME and in-tip SPME). The advantage of SPME is that, very little (µL) reagents are consumed making it much cost effective, however, this method reported the short comings as it is not applicable in samples with complex matrix composition like fuel oils [23]. The m-SPE is characterised by the use of magnetic nanoparticles (MNPs), which are mainly made from three metals (cobalt, nickel and iron), and their oxides. [22]. The MNP sizes normally ranges from several nanometres to microns [24]. The m-SPE is characterised by few extraction steps which reduces chances of contamination, it makes use of deionised water for washing of the adsorbent instead of carcinogenic solvents (e.g. hexane) and the rapid separation step due to the use of external magnet is the most attractive feature for m-SPE [25]. The latter has been previously applied during the extraction of metals in several matrices, which include water, fuel and biological samples [9, 26]. To the best of our knowledge very little has been reported about m-SPE in fuel oils. For example, Ebrahimzadeh et al [27] reported a new magnetic polymeric Fe_3O_4 nanoparticles for extraction and determination of Cd content in diesel oil samples using flame atomic absorption spectroscopy (FAAS). This method reported very good accuracy (96.4-104%), limit of detection (0.09µg/L), precision (1.7%) and enrichment factor (184).

For the first time, this study then explored the use of $Fe_3O_4@Al_2O_3$ magnetic adsorbent for the preconcentration and extraction of As, Ba, Cd, Cr, Cu, Mn, Mo, Ti, V, Pb, Sb, Sn, Tb, Te and Zn in crude oil, gasoline, kerosene, and diesel samples prior to analysis using ICP-OES. Most influential experimental factors affecting m-SPE were optimised using multivariate approaches.

6.2 Experimental methods

6.2.1 Reagents and glassware

Glassware (beakers and volumetric flask) used were washed using soap and water, then socked in 5% nitric acid and finally rinsed with deionized water prior to drying in an oven at

100 ^{o}C for overnight. Metal and metalloid standards were prepared from appropriate dilution of 100 mg/L multi-element standard solution (Sigma-Aldrich, South Africa). Standard reference material (NIST 1634c) which contained trace elements in fuel, 70% ultra-pure HNO_3, iron(II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron(III) chloride hexahydrate ($FeCl_3.6H_2O$), aluminium isopropoxide, sodium dodecyl sulfate (SDS), 1-(2-pyridylazo)-2-naphthol (PAN) and ethanol were purchased from Sigma-Aldrich, South Africa. Real gasoline, kerosene and diesel samples were purchased from local filling stations around Johannesburg and the crude oil samples were supplied by a petrochemical company from South Africa. The 99% xylene used to reduce sample viscosity in crude oil and neodymium-iron-boron alloy magnet for removal of magnetic nanoparticles were both purchased from Sigma-Aldrich, South Africa.

6.2.2 Instrumentation

6.2.2.1 Inductively coupled plasma optical emission spectroscopy

The multielement capability and sensitivity of the ICP-OES made it to be favourable for trace elements determination in m-SPE extracts. The operating parameters for the instrument, and wavelengths monitored for each element are presented in **Table 6.1**. The resulted digests were analysed for metals by using Agilent Technologies 700 Series ICP-OES with an axial orientation of the torch. Additionally, an Agilent Technologies SPS 3 autosampler was used for sample uptake.

Table 6. 1: Operating parameters of ICP-OES for metal and metalloids analysis.

Agilent ICP-OES instrumental parameters	Conditions
RF Power	1200 W
Auxiliary gas Flow	1.5 L/min
Plasma gas (Ar) flow rate	15.0 L/min
Pump speed	85 rpm
Peri-pump speed analysis	15 s
Stabilization time (s)	15 s
Nebulizer	0.75L/min
Elemental wavelengths	As 188.980, Ba 234.759, Co 201.151, Cr 206.550, Cu 327.395, Ni 216.55, Mg 279.553, Na 588.995, Pb 283.30, Sb 217.582, Sn 189.925, Tb 350.941, Te 190.802 Ti 336.122, and V 292.299

6.2.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was carried out using a Jeol JEM-2100F Field Emission Electron Microscope at an acceleration voltage of 200 kV (JEOL Inc., Akishima, Japan) equipped with a LaB6 power source. The TEM samples were then prepared as follows: A small amount of synthesized magnetic nanocomposite was dropped onto a TEM grid (Cu-grid, 200 mesh) coated with a lacy carbon film. Then, the pictures of a digital charge coupled device were used to test the nanoparticles.

6.2.2.3 Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX)

The scanning electron microscope (SEM) measurements were performed on a Tescan Vega 3 LMH at a voltage of 20 kV, with a secondary electron detector (SED) and energy dispersive X-ray spectroscopy (EDX). Prior to measurement, the samples were carbon-coated with the Agar Turbo Carbon coater to improve their conductivity.

6.2.2.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) measurements were taken with a PAN ayltical X'Pert Pro powder diffractometer. The latter was outfitted with a 1D X'Celerator detector (PHD lower level and higher level), upper levels of 6.67 and 12.78 keV, respectively, as well as programmable divergence slitting (10 mm radiation length). The measurements were taken with Cu K radiation in the 2 range from 5 to 90^o at 40 kV and 40 mA operational conditions, the wavelength was 0.15405 nm. The diffractometer was set up with a sample spinner (Spinner PW3064) and a rotation time of 1 s to get the preferred orientation of crystallites. Predictions for the raw P-XRD patterns were made using High Score (Plus) software and ICDD PDF-4+ 2015.

6.2.2.5 Ultraviolet-Visible (UV-Vis)

The Genesys 180 UV-Visible spectrophotometer was used for confirmation of the nanoparticles of Fe_3O_4 and $Fe_3O_4@Al_3O_4$. The dissolved solid samples (Fe_3O_4 and $Fe_3O_4@Al_3O_4$,) were first put in centrifuge tubes and diluted to make it less concentrated Blank samples were also prepared prior to analysis of real samples. The samples were then run with wavelength range of 200-1200 nm.

6.2.2.6 Fourier transform infrared spectroscopy (FT-IR)

The KBr wafer technique was used to measure the Fourier transformed infrared (FTIR) spectra with a Bruker Tensor 27 FTIR spectrophotometer. The synthesized samples were combined with KBr before being compressed into pellets. During the analysis, data was collected from 400 to 4000 cm^{-1}.

6.2.3 Synthesis of Fe3O4@Al2O2 core-shell magnetic nanocomposite

The synthesis of Fe_3O_4@Al_2O_3, followed two steps: (1) synthesis of Fe_3O_4 magnetic nanoparticles (MNPs) and (2) the incorporation of the Al_2O_3 into the Fe_3O_4 as support to form Fe_3O_4@Al_2O_3 magnetic nanoparticles (MNPs).The synthesis of Fe_3O_4 MNPs was achieved via chemical coprecipitation method as reported by Kang et al. [28]. Briefly, 2.0 g $FeCl_24H_2O$ and 5.2 g $FeCl_36H_2O$ and 0.85 mL concentrated HCl were all dissolved in 25 mL deionized and deoxygenated water at room temperature. This was followed by the dropwise addition of 250 mL of 1.5 mol/L NaOH into the solution under vigorous stirring in inert environment (achieved by purging nitrogen gas (99.9%) through the reaction vessel) and heated at 80 °C for 2 hours. This resulted in the formation of a black precipitate (Fe_3O_4 MNPs) and was separated from the solution by neodymium-iron-boron alloy magnet and washed with 50 mL deionized water five times and later dried at 60 °C for 2 hrs. Thereafter, the newly synthesised Fe_3O_4 MNPs were used to prepare Fe_3O_4@Al_2O_3 core-shell following the method described by Barreto et al. [20]. Aluminium isopropoxide (1 g) was dissolved in 60 mL of ethanol to form a clear solution. This was then followed by the addition of 0.1 g Fe_3O_4 MNPs. Then 100 mL of a mixture of deionized water and ethanol in 1:5 ratio (v/v) was added dropwise to the suspension of Fe_3O_4 MNPs under vigorously stirred for 30 minutes. Then separation and washing with ethanol was done 5 times. The resulted Fe_3O_4@Al_2O_3 core-shell MNPs product was dried and calcined in muffle finance at 500 °C for 1 hour and allowed to cool at room temperature. The functionalization of Fe_3O_4@Al_2O_3 core-shell was carried out as follows; 1.5 g of the newly synthesized MNPs, 100 mg of sodium dodecyl sulfate (SDS) and 1.0 mL of 2.5 g/L of 1-(2-pyridylazo)-2-naphthol (PAN) solution were added into 100 mL ethanol at controlled pH of 2 (adjusted using 3 mol/L HCl). The mixture was further stirred for 15 minutes and then the factionalized Fe_3O_4@Al_2O_3 core-shell MNPs were then separated by external magnetic field. The resultant product was washed three times with 50 mL ethanol. The functionalization, helped to enhance the adsorption capacity [29]. The characterization of Fe_3O_4 and Fe_3O_4@Al_2O_3 core-shell MNPs were done using the scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), UV-visible spectrometer, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR).

6.2.3Magnetic solid phase extraction (m-SPE)

The m-SPE procedure was carried out as follows: a 5 mL of model sample spiked with 20 µg/L of multielement (Ag, Al, Cd, Co, Cr, Cu, Mn, Mo, Pb, Ti, V and Zn) and blank samples were placed in a small beaker containing 40 mg of Fe_3O_4@Al_2O_3 coreshell magnetic nanoparticles . Manual shaking the beaker was performed to ensure proper mixing of sample and adsorbent. The mixture was then sonicated for 25 minutes at room temperature (25 °C). For separation of adsorbent from sample, a neodymium-iron -boron alloy magnet was used, where the magnet was put below the beaker. The oil sample was then decanted into a small beaker leaving behind the adsorbent and with the target analyte. The $Fe_3O_4@Al_2O_3$ core-shell magnetic nanoparticles were then washed with deionised water for removal of oil and finally eluted with 1 M of HNO_3. The analytes ware then taken to the ICP-OES for analysis while the remaining adsorbent was reused. The major steps of m-SPE are presented in **Fig. 6.1**

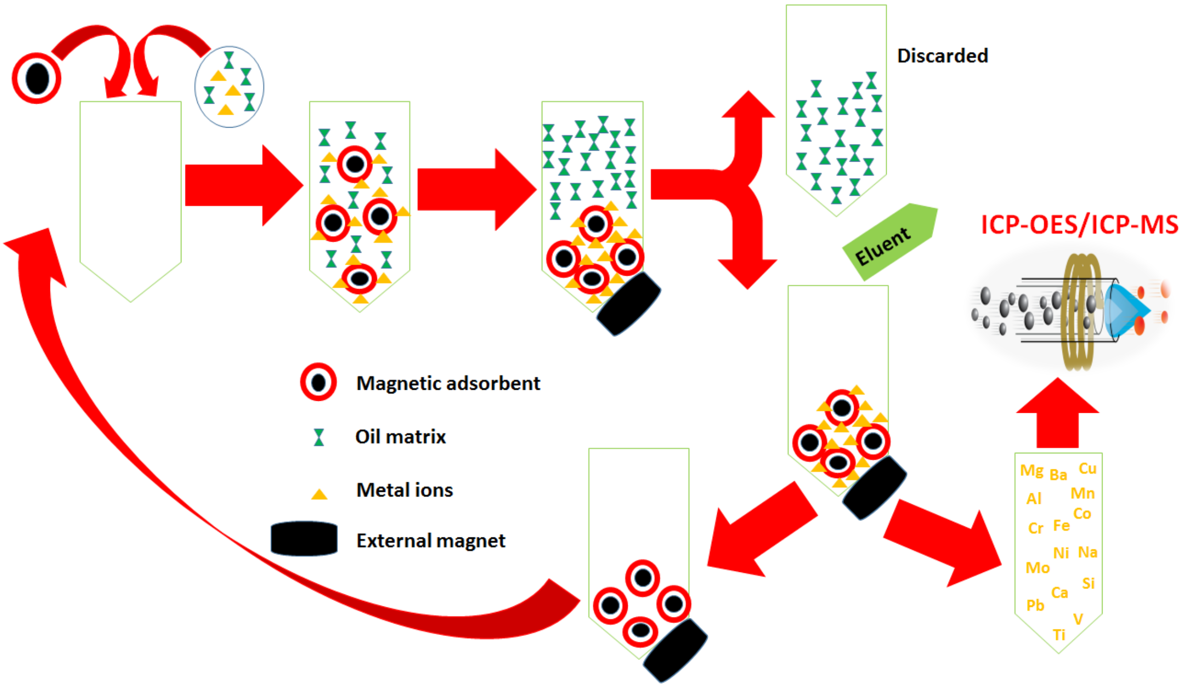


Figure 6.1: The steps involved in m-SPE prior to metal and metalloid analysis by ICP-OES

6.2.3 Multivariate optimization

The optimum conditions that greatly affected m-SPE were achieved by using multivariate optimization approaches. The parameters that were optimised were sorbent mass, sonication time, pH, spike concentration and eluent concentration. A two level fractional factorial design (FrFD) was used for generating the experimental conditions. The variables were given the lower level (-) and the higher level (+), as presented in **Table 6.2**. The central composite design (CCD) was used for further optimisation of the most significant parameters. For both FrFD and CCD, the Minitab 2018 statistical software was used for the analysis of data.

For screening purposes, parameters such as sorbent mass, eluent concentration, sonication time, pH and spike concentration were optimised. The 16 designed experiments had the following ranges, sorbent mass (10- 50 mg), eluent (HNO_3) concentration (0.1-1mol/L), sonication time (20-60 minutes), pH (6-9) and spike concentration (10-50 µg/L). The response of each parameter was expressed in form of Pareto chart and these parameters predicted the most significant factors. The most significant parameters were then further optimised using central composite design.

Table 6. 2: The parameters that were investigated and their levels for ½ fractional factorial design

Variable	Low level (-)	High level (+)
Sorbent mass (mg)	10	50
Eluent HNO_3 (M)	0.1	1
Sonication time (minutes)	20	60
pH	6	9
Spike concentration (µg/L)	10	50

The most significant parameters were further optimised using the central composite design. The optimised parameters were sonication time and sorbent mass. The CCD generated 13 experiments and one block was picked for the experimental design. The lower and higher values for adsorbent mass were 20 and 50 mg respectively with 35 mg central point. Additionally, 10 and 40 minutes were the lower and higher values for extraction time while 25 minutes was the central point.

6.3 Results and discussions

6.3.1 Characterization of the Fe_3O_4 and Fe_3O_4@Al_2O_3

The synthesized Fe_3O_4 and Fe_3O_4@Al_2O_3 magnetic nanoparticles were then characterised using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), UV-visible spectrometer, Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD).

6.3.1.1 Transmission electron spectroscopy (TEM)

The TEM images for Fe_3O_4 and Fe_3O_4@Al_2O_3 are presented in **Fig. 6.2 (a)** and **(b)**, respectively. In terms of particle size, there was a significant difference between the Fe_3O_4 and Fe_3O_4@Al_2O_3. The Fe_3O_4 reported a wide range (50-251 nm) in particle sizes, which is normally associated with agglomeration of the unsupported Fe_3O_4 MNPs [30]. However, a reduction in particle size was observed for $Fe_3O_4@Al_2O_3$ nanoparticles, ranging between 37and 74 nm. It is worthy to indicate that, the smaller size of these nanoparticles ensured a high surface area which is a key to increase the rate of adsorption of the target analytes [29]. Additionally, the particle size of the synthesised MNPs were comparable with literature reported ones. For example, Peng et al [31] reported the characterization of Fe_3O_4 MNPs with a size of 6.5 nm. Zhu et al [30] also did surface modification on Fe_3O_4 MNPs and the particle size was within the range of 14.1-20 nm. Lastly, Husain et al [32] reported the synthesis and characterization of Fe_3O_4 MNPs from iron ore and reported a particle size ranging from 50 to70 nm.

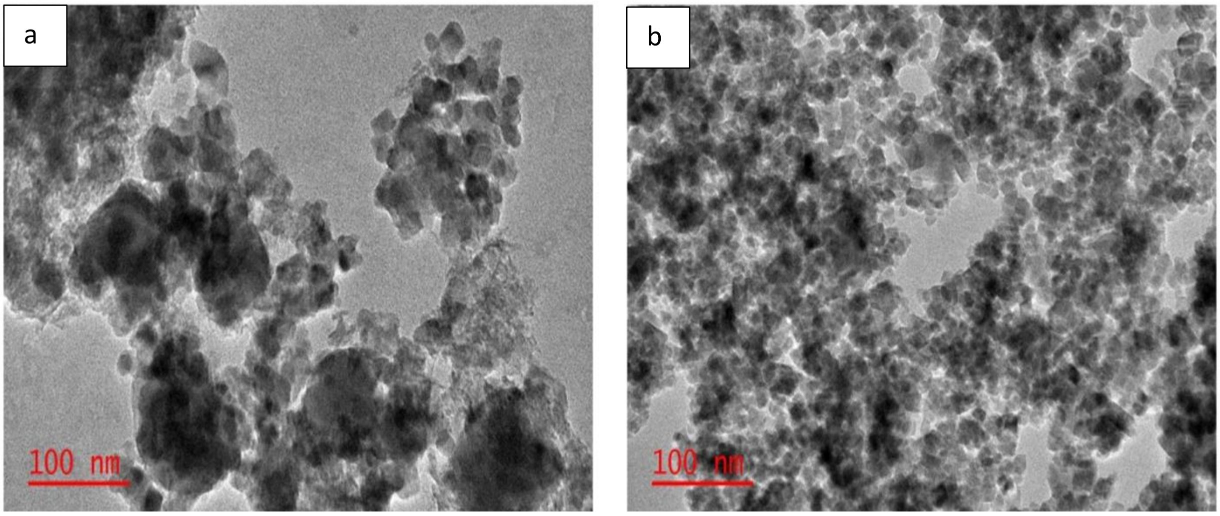


Figure 3.2: Transmission electron microscopy (TEM) images of (a) Fe_3O_4 and (b) $Fe_3O_4@Al_2O_3$ core shell magnetic nanoparticles

6.3.1.2 Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX)

The SEM images and EDX spectra of the naked Fe_3O_4 and $Fe_3O_4@Al_2O_3$ MNPs are shown in **Fig. 6.3 (a-d)**. The images in **Fig. 6.3 (a)** and **(c)** have shown the spherical shape of both Fe_3O_4 and $Fe_3O_4@Al_2O_3$, respectively. From the EDX spectra, the chemical composition and the proportions of element making up the compound are reported. The EDX spectrum for Fe_3O_4 is in **Fig. 6.3 (b)** and the elemental distribution is composed of Fe, O and C at 63.5, 30.6 and 5.9 wt%, respectively. However, the EDX spectrum for $Fe_3O_4@Al_2O_3$ is illustrated in **Fig. 6.3 (d)** and the metal composition include O, Al, C and Fe at 40.1, 31.1, 17.3 and 11.0 wt%, respectively. Therefore, when comparing Fe_3O_4 with $Fe_3O_4@Al_2O_3$ MNPs, the latter is composed with mainly Al while the former is mainly Fe. Additionally, both spectra reported a small portion of carbon, which was due to carbon coating during sample preparation step [6, 35].

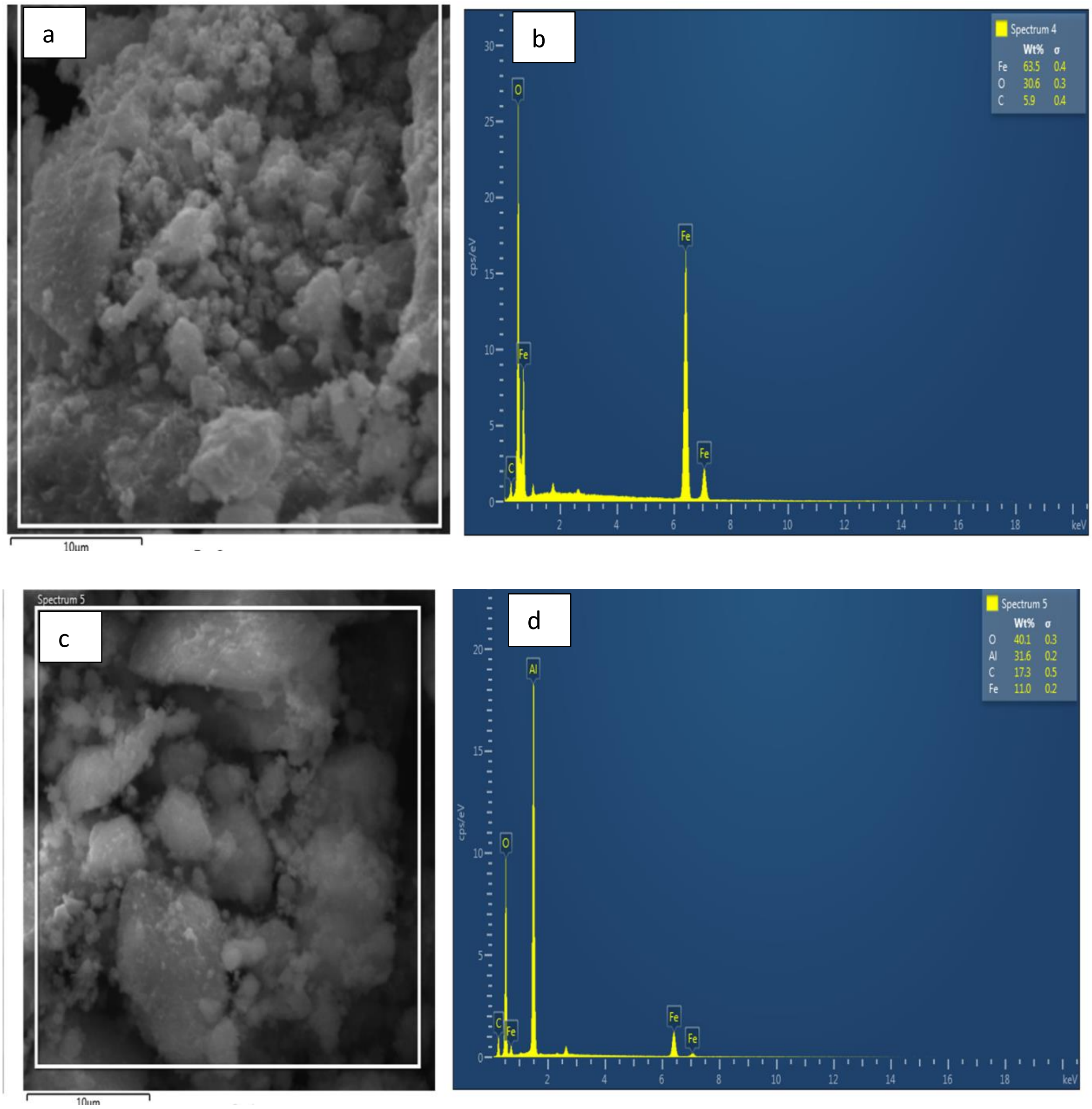


Figure 4.3 (a-d): Fe_3O_4 a) SEM image and c) EDX spectrum and $Fe_3O_4@Al_2O_3$ b) SEM image and d) EDX spectrum

6.3.1.2 Ultraviolet-visible spectroscopy (UV-vis)

The presence of the $Fe_3O_4@Al_2O_3$ nanoparticles was also confirmed by using the UV-visible spectrophotometer. The peaks that were reported were around wavelength of 500-520 nm, which was in line with other literature report by Chingsungneon et al[33] on Fe_3O_4 and $Fe_3O_4@Au$ MNPs. However, there was no significant difference in the absorption peaks of Fe_3O_4 and $Fe_3O_4@Al_2O_3$ magnetic nanoparticles. The d-d transitions were responsible for the absorption bands between 500 and 520 nm for Fe_3O_4 and $Fe_3O_4@Al_2O_3$ nanoparticles. The difference in the absorption intensities were slightly due to the difference in concentrations between the two samples, Fe_3O_4 being more concentrated than $Fe_3O_4@Al_2O_3$. The UV-visible spectra are reported in **Fig 6.4.**

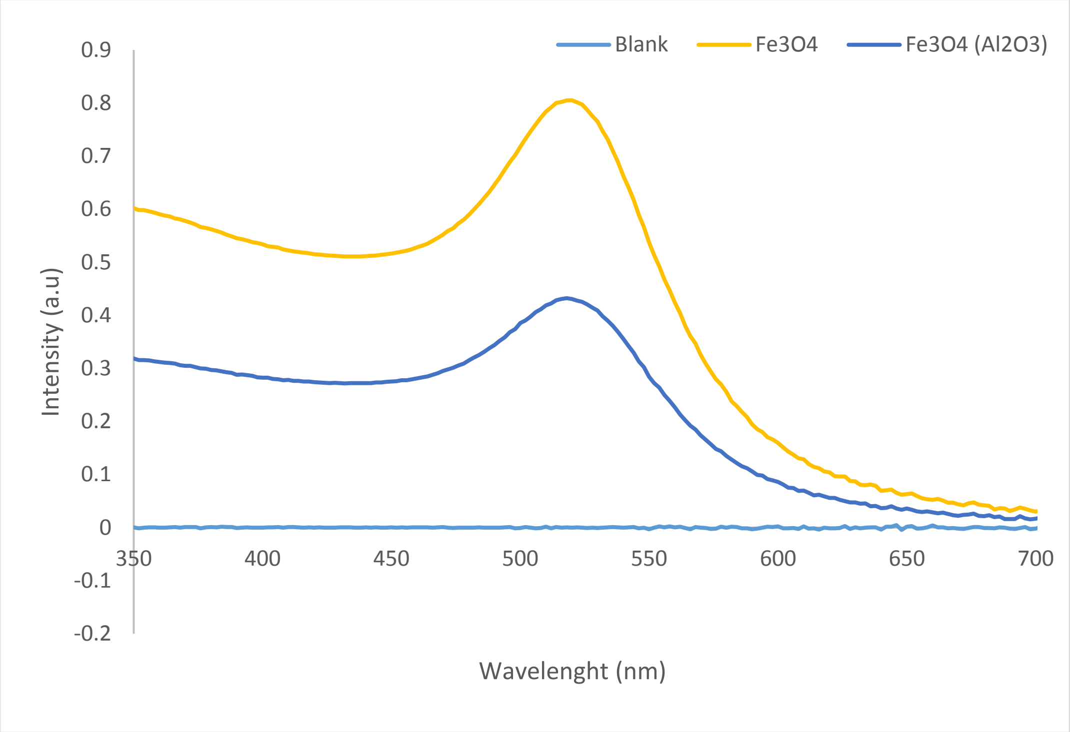


Figure 6.4: The UV- visible spectra for blank, Fe_3O_4 and $Fe_3O_4@Al_2O_3$ nanoparticles

6.3.1.3 X-ray Diffraction (XRD)

The XRD was also used for characterization which helped in the identification of the crystalline structures of the Fe_3O_4 and $Fe_3O_4@Al_2O_3$ nanoparticles. **Fig. 6.5** shows the X-ray diffraction patterns that were obtained from the Fe_3O_4 and $Fe_3O_4@Al_2O_3$ nanoparticles, respectively. It can be seen from **Fig. 6.5** that , strong diffraction peaks with 2ϴ values of 30.2°,35.5°, 43.5°, 53.8° and 57.3°, which corresponded to the crystal planes of (200), (311), (511), (422) and (440) of crystalline Fe_3O_4 nanoparticles, respectively [34]. However, for Fe_3O_4 and $Fe_3O_4@Al_2O_3$ also reported the strong diffraction peaks with 2ϴ at,30.2°,35.5°, 43.5°and 53.5°. Therefore, the results from the current study showed the spinel phase structure of magnetite and are in agreement with XRD standard for the iron oxide MNPs [34]. Additionally, the diffraction peaks of the $Fe_3O_4@Al_2O_3$ NPs in **Fig. 6.5** presented a series of additional peaks which are attributed to alumina as per literature [21, 35].

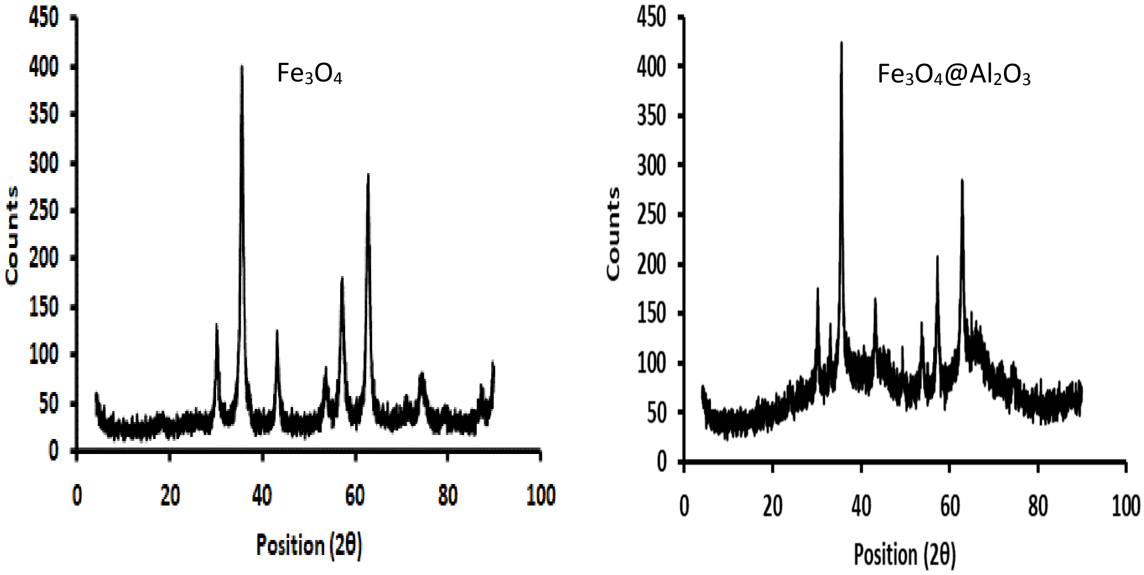


Figure 6.5: X-ray diffraction patterns obtained from Fe_3O_4 and $Fe_3O_4@Al_2O_3$ magnetic nanoparticles

6 .3.1.4 Fourier transform infrared spectroscopy (FT-IR)

The FTIR spectrum obtained from pure magnetite nanoparticles is presented in **Fig. 6.6**. The stretching vibration mode associated with the metal-oxygen Fe-O bonds in the crystalline lattice of Fe_3O_4 is responsible for the two peaks observed between 580 cm^{-1} and 630 cm^{-1} as presented by both the Fe_3O_4 and $Fe_3O_4@Al_2O_3$ spectra in **Fig. 6.6**. These peaks are distinctively pronounced in all spinel structures, but especially in ferrites [36]. A band at 1629 cm^{-1} and the broad band centred at 3435 cm^{-1} are related to the presence of hydroxyl groups and attributed to OH-bending and OH-stretching, respectively. Additionally, the high intensity band at around 580 cm^{-1} in $Fe_3O_4@Al_2O_3$ spectrum is Al-O stretching vibrations [37].

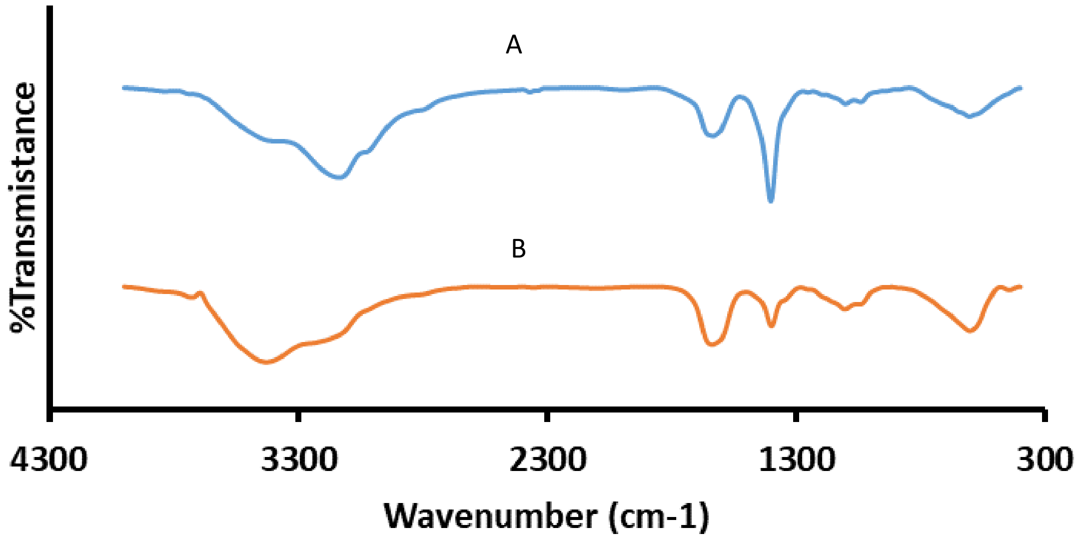
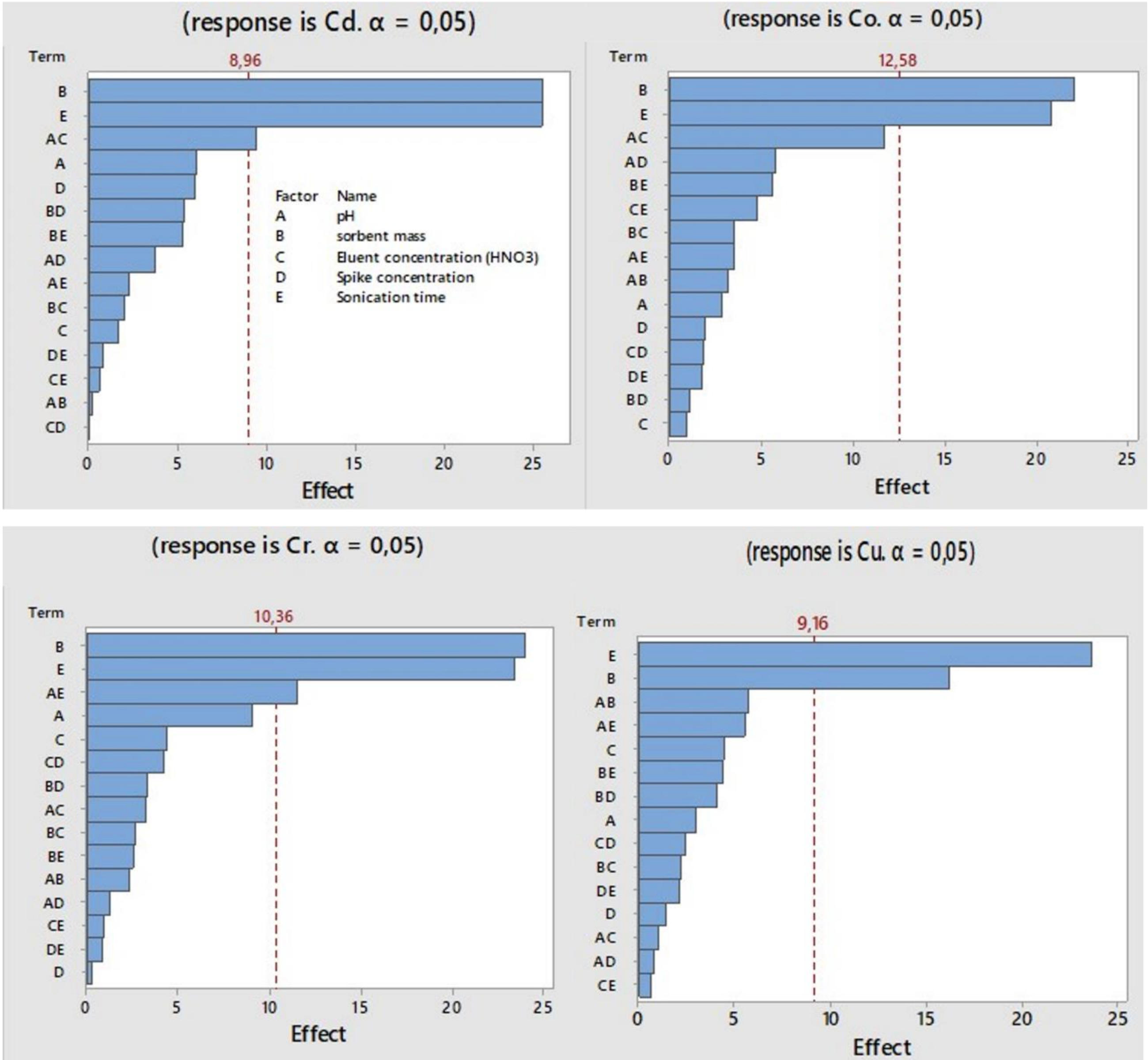


Figure 6.6: The FTIR spectrum for $Fe_3O_4@Al_2O_3$ (A) and Fe_3O_4 (B) nanoparticles

6.3.2 Multivariate optimization

6.3.2.1 The ½ fraction factorial design

The screening process of the most significance parameters in m-SPE were obtained by using the ½ fractional factorial design (FrFD). The factors that were statistically significant were further optimised using the central composite design (CCD). The experimental results from the ½ fractional factorial design are presented in **APPENDIX Table 3**. The results were examined by using the analysis of variance (ANOVA) at 95 % confidence level (p=0.05). The ANOVA results were then presented in form of Pareto charts for each metal as shown in **Fig. 6.7**. The results indicated that sonication time and sorbent mass ware statistically significant at 95% confidence level for the high recoveries of Cd, Co, Cr, Mn, Pb and Ti. However, with V, only sonication time was significant at 95% confidence level. Even though sorbent mass was not significant only for V, it was taken together with sonication time for further optimization since it was most significant with many elements it was most significant with many elements.


(response is Cd. α = 0,05)
Term
8,96
B
E
AC
A
D
BD
BE
AD
AE
BC
C
DE
CE
AB
CD
Factor
Name
A
pH
B
sorbent mass
C
Eluent concentration (HNO3)
D
Spike concentration
E
Sonication time
0
5
10
15
20
25
Effect
(response is Co. α = 0,05)
Term
12,58
B
E
AC
AD
BE
CE
BC
AE
AB
A
D
CD
DE
BD
C
0
5
10
15
20
25
Effect
(response is Cr. α = 0,05)
Term
10,36
B
E
AE
A
C
CD
BD
AC
BC
BE
AB
AD
CE
DE
D
0
5
10
15
20
25
Effect
(response is Cu. α = 0,05)
Term
9,16
E
B
AB
AE
C
BE
BD
A
CD
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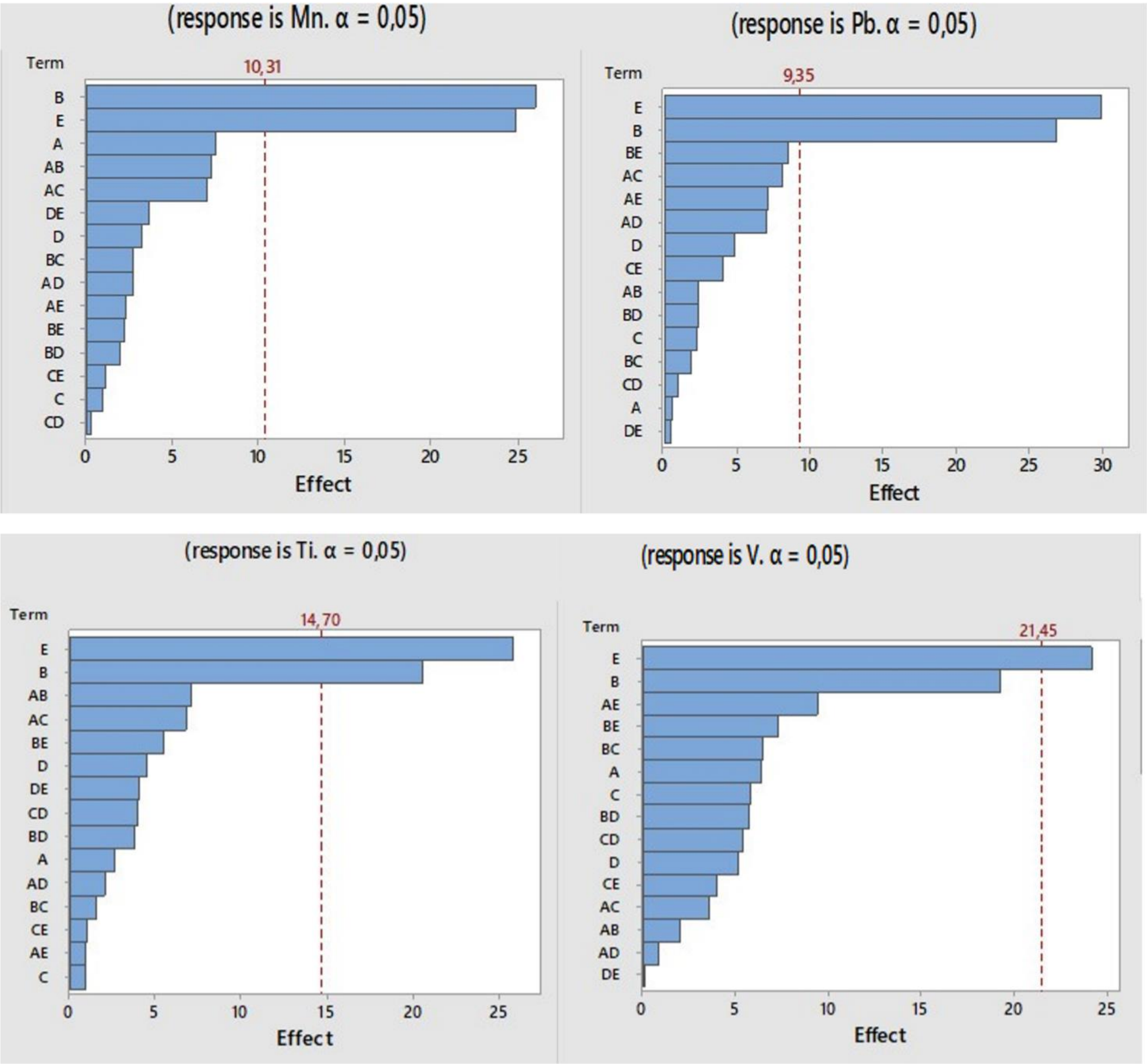


Figure 6.7: Pareto charts A-H for Cd, Co, Cr, Cu, Mn, Pb, Ti, and V from level ½ fractional factorial full design (2^{n-1}) at 95% confidence level for optimization of sorbent mass, sonication time, pH, spike concentration, eluent concentration (n=3).

6.3.2.2 Response surface methodology (RSM)

Response surface methodology (RSM) are chemometric tools that helps in establishing quadratic models. These models assist to determine the critical conditions of factors under study. Several RSM have been reported in literature which include BBD, CCD, three level factorial design and Doehlert matrix [21, 28, 40]. Sonication time and sorbent mass were further optimised using the central composite design. The parameters that were statistically insignificant, were kept at 6.5 pH, Spike concentration 20 µg/L and 1 M of HNO_3 eluent. The parameters, number of experiments, experimental conditions and results from the central composite design (CCD) are presented in **APPENDIX Table 4**. The CCD was chosen based on being mostly reported in literature and its most reliability [36]. The response surface plots (**Fig. 6.8 A-F**) were used to evaluate the effects of digestion time and digestion temperature on the analytical response. Based on the quadratic equations (**Eq. 6A-D**) and the surface plots, the most extraction conditions were chosen to be 40 mg (sorbent mass), 35 minutes sonication time, 6.5 pH, 20 µg/L spike concentration and 1 mol/L eluent concentration. The surface plots showed that increasing recoveries as sonication time is increased, however, Zn never showed good recoveries when compared with the other metals.

The optimum conditions were then used on the real samples (spiked and not spiked) and percentage recoveries were from 74-96 % with precision of for Zn, Pb, Mo, Mn, Cu, Cr, Co, Ti and Cd. The results for each analytes were confirmed by the quadratic model (**Eq. 6A- F**), where A and B represent digestion time and digestion temperature respectively.

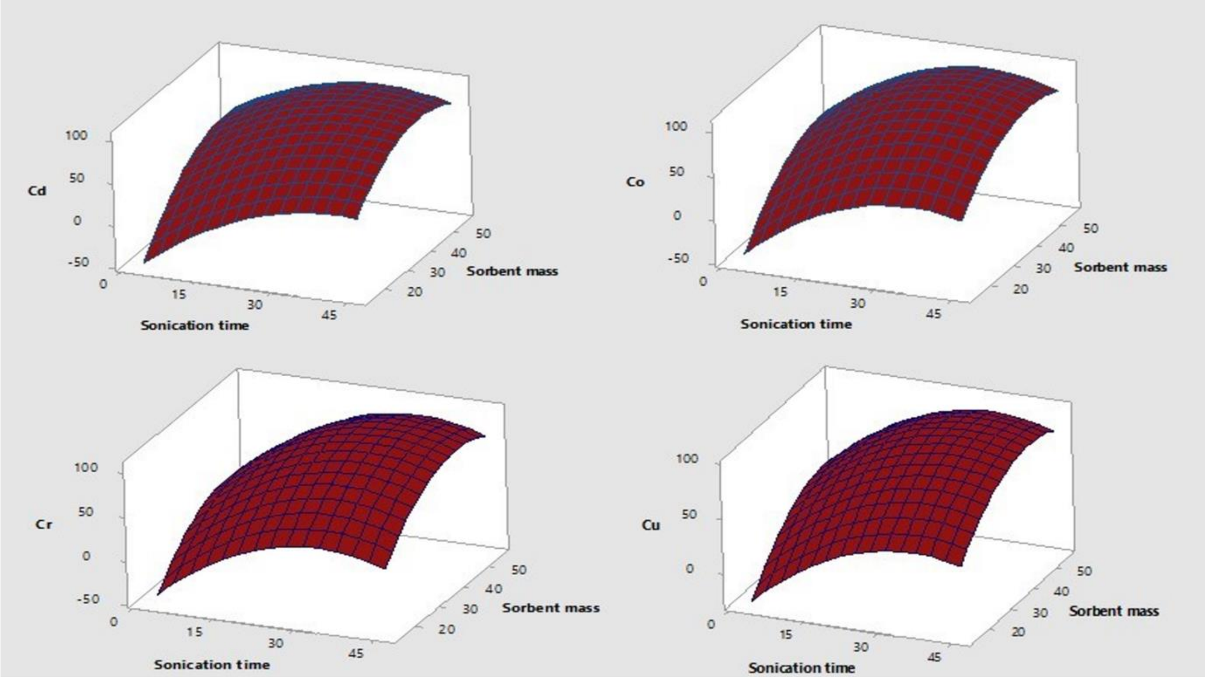
$$Cd = -147.8 + 5.368A + 7.08B - 0.0590A^2 - 0.0693B^2 - 0.0273AB \qquad Eq.6A$$

$$Mn = -134.3 + 5.038A + 6.526B - 0.0625A^2 - 0.0540B^2 + 0.0035AB \qquad Eq.6B$$

$$Mo = -89.5 + 3.85A + 4.99B - 0.0528A^2 - 0.0540B^2 + 0.0035AB \qquad Eq.6C$$

$$Zn = -63.6 + 2.80A + 4.18B - 0.0432A^2 - 0.0490B^2 + 0.0060AB \qquad Eq.6D$$

$$Ti = -102.7 + 3.96A + 5.61B - 0.0501A^2 - 0.0591B^2 - 0.0065AB \qquad Eq.6E$$



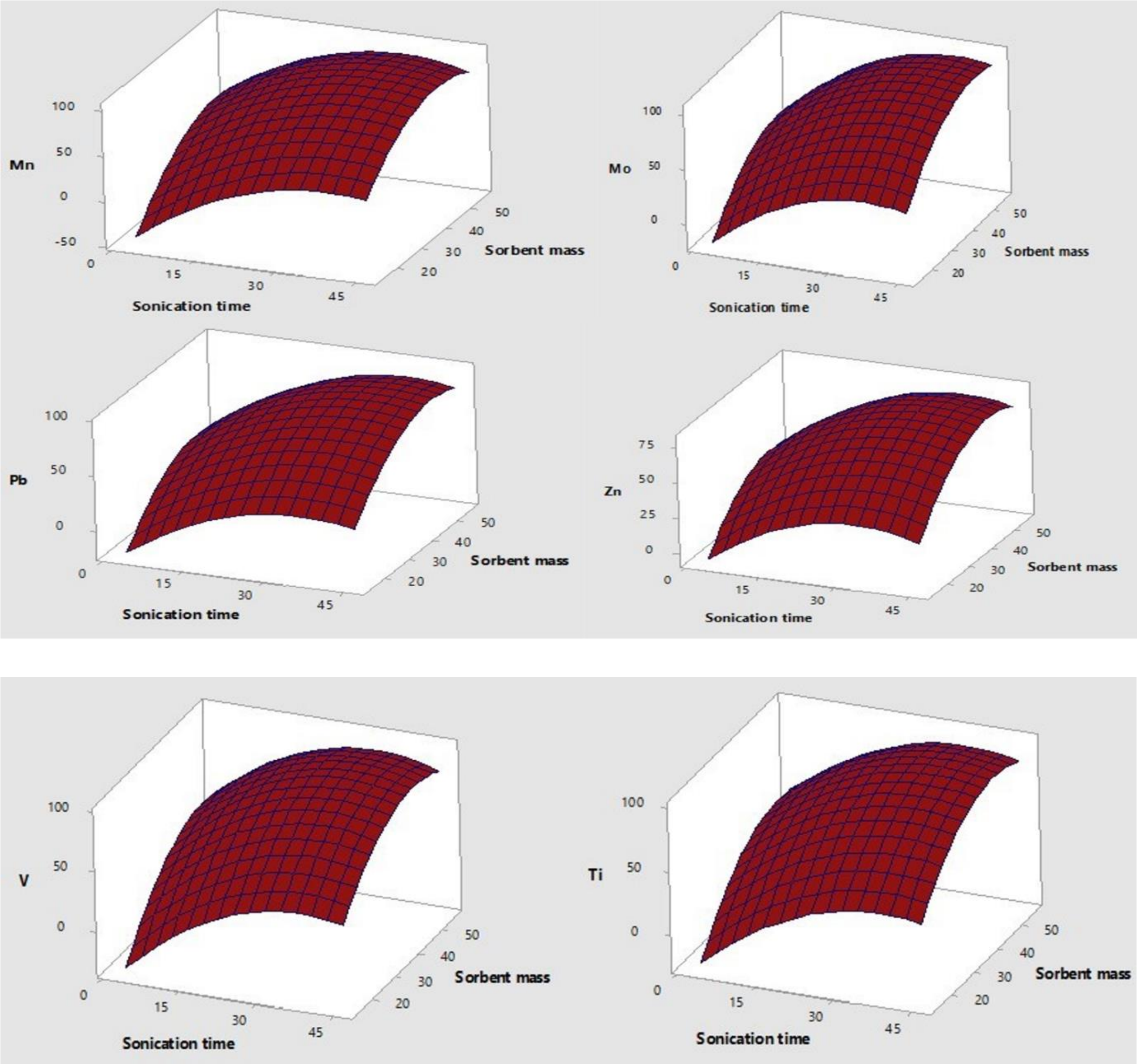


Figure 6.8: Response surfaces A-H for Cd, Co, Cr, Cu, Mn, Mo, Pb, Zn, V and Ti for sorbent mass and sonication obtained from central composite (n =3).

6.3.3 Analytical figures of merits

The optimum conditions of the newly developed m-SPE method were then used to determine analytical figures of merits which include limit of detection limits (LOD), limit of quantification (LOQ), sensitivity, accuracy, precision, and correlation coefficient, just to name the few. These analytical merits help in drawing a conclusive decision on whether the newly developed method is better than the literature reported methods [6]. This was achieved by preparing nine samples of crude oil from which one was not spiked and the other eight samples were spiked with 10, 20, 35, 50, 65, 80, 90 and 100µ g/L. The concentration of each sample was plotted against intensity. The plotted graphs were able to provide linearity information such as correlation coefficient (R^2) and method calibration gradient (which is equivalent to the sensitivity of each metal). The metal ion that showed high sensitivity was Mn (1.55 x 10^5 cps L mg^{-1}) and the least sensitive metal was V (4.84 x 10^3 cps L mg^{-1}). The R^2 ranged from 0.9961-0.9996 for all the metals **(see Table. 6.3)**. The gradient (slope) was then used to calculate LOD and LOQ. The LOD is referred to as the lowest concentration likely to be reliably distinguished from a blank sample and at which detection is feasible [41]. On the other hand, LOQ is referred to as the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy. The LOQ is equal to ten times the standard deviation of the blanks and all is divided by the method calibration (slope). The calculated LOD and LOQ were used to calculate the method detection limit and method quantification limit (**see Table 6.3**). Additionally, it is worth in noting that the LOD and LOQ provides the detection and quantification limits of the elements close to ideal conditions, where there are few other alloying elements. Since this happen in a very clean matrix, this LOD and LOQ are referred to as instrument detection and quantification limits, respectively. Therefore, the method detection limits and quantification limits were also calculated as these consider real-life matrices [37]. Additionally, the enrichment factor (EF) of each element (Co, Cr, Cu, Mn, Mo, Pb and Ni) was calculated. In the present work, the EF was calculated by the ratios between the slope of the calibration **(see Eq. 6.7)** curve of each analyte obtained with the organic standards after the preconcentration procedure and the slope of the respective calibration curve obtained with the organic standards without preconcentration. The enrichment factors were 30, 24, 11, 20, 26, 10 and 8 for Co, Cr, Cu, Mn, Mo, Pb and V, respectively. The differences obtained in the EF values may be related to the different affinities and retention process of each element with the $Fe_3O_4@Al_2O_3$ core shell magnetic nanoparticle. Additionally, the preconcentration factor was computed as per **Eq. 6.8**.

$$Enrichment\ factor = \frac{Cf}{Ci} \qquad Eq. 6.7$$

Cf = Slope after preconcentration of analyte

Ci = Slope before the preconcentration of analyte

$$Preconcentration\ factor = ER * \frac{Vi}{Vf} \qquad Eq. 6.8$$

Where ER is the enrichment recovery, Vi and Vf are the volumes of sample and eluent respectively [42]. The preconcentration factors were calculated to be 168, 166, 152, 165, 164, 150 and 150 for Co, Cr, Cu, Mn, Mo, Pb and V, respectively.

Table 6. 3: Analytical features of the m-SPE method for quantitative extraction of Co, Cr, Cu, Mn, Mo, Pb and V in fuel samples: m-SPE conditions; 40 mg (sorbent mass), 35 minutes sonication time, 6.5 pH, 20 µg/L spike concentration and 1M of HNO_3 eluent concentration replicates (n =3).

Metal	**SD of blank intensity (cps) (n=20)**	**Sensitivity (cps L mg^{-1})**	**Accuracy (%)**	**Precision (%)**	**LOD (µg/L)**	**LOQ (µg/L)**	**R^2**	**Enrichment factor**	**MDL (µg/g)**	**MQL (µg/g)**
Co	4.1	3.09 x 10^4	96	3.3	0.398	1.31	0.9961	30	0.498	1.660
Cr	2.6	1.69 x 10^4	95	4.8	0.460	1.52	0.9971	24	0.575	1.90
Cu	1.8	3.42 x10^4	87	2.5	0.158	0.53	0.9978	11	0.198	0.652
Mn	4.7	1.55 x10^5	93	2.0	0.091	0.30	0.9996	20	0.114	0.380
Mo	3.7	2.7 x10^4	94	1.8	0.411	1.36	0.9992	26	0.514	1.71
Pb	4.8	5.0 x10^4	86	0.9	0.288	0.959	0.9981	10	0.36	1.199
V	0.8	4.84x10^3	86	1.8	0.496	1.65	0.9993	8	0.62	2.046

6.3.4 Comparison of analytical figures of merit with literature reports

The analytical figures of merit were then compared with several reported studies on SPE methods and precisely in fuel matrices. Literature report from **Table 6.4** have indicated that this newly developed m-SPE method can be the most appropriate metal extracting method in the future based on its precision, sensitivity and high enrichment factor.

Table 6.4: Comparison of the figures of merits between newly developed m-SPE with other SPE report on fuel matrices

Sample	**element**	**MDL (µg/g)**	**R^2**	**EF**	**RSD (%)**	**REF.**
Crude oil	Hg	0.25	0.991	240	1.9	[16]
Ethanol fuel	Cu, Ni and Zn	1.3, 1.1 and 0.9	0.997	38,35 and 52	2.4-4.4	[7]
Fuel alcohol	Cd	1.7	0.998	32	2.4	[43]
Gasoline	Cu, Fe, Pb and Zn	3.1, 1.2, 2.3 and 2.6	0.991-0.996	5.4, 5.3, 6.7 and 6.1	5.8-9.7	[8]
Diesel	Cd	0.09	0.996	184	1.7	[27]
Gasoline	Cd, Cu, Fe, Pb and Zn	0.1, 0.1, 0.2,0.3 and 0.1	0.9965-0.9997	30	4.9-5.9	[44]
Crude oil, diesel, gasoline and kerosene	Co, Cr, Cu, Mn, Mo, Pb and V	0.498, 0.575, 0.198, 0.114, 0.514,0.36 and 0.62	0.9961-0.9996	30,24,11,20,26,10 and 8	0.8-4.8	This work

6.3.5 Application of m-SPE in real fuel samples

The optimum and validated m-SPE sample preparation method was applied in different samples which were crude oil, diesel, gasoline and kerosene. There were five different samples for crude oil which were labelled as A, B, C, D and E. However, for diesel, kerosene, and gasoline, the samples were labelled as A, B and C. The extraction of metals was conducted under optimum conditions. The aqueous extracts were taken for analysis of As, Co, Cr, Cu, Mn, Mo, Pb, Sb, Sn, Tb, Te and V using ICP-OES. The investigated metals and their concentration are reported in **Table 6.4**. The latter indicated that elements including As, Mo and Tb were at trace level with concentration ranges less than 1 µg/g. The concentration of the trace elements were 0.054-0.88, 0.08-0.66, and 0.01-0.14 µg/g for As, Tb, and Mn, respectively. It is worth noting that most samples for As reported concentrations that were less than 0.2 µg/g and the 0.88 µg/g was the outlier. The later might be due to lack of proper maintenance of the storage tanks. The other metals (Ba, Cd, Cr, Pb, Mo, Ti, V, Sb and Te) showed concentrations ranging from 0.59 to 8.99 µg/g. Therefore, there is an agent need to make sure that the storage and transportation tanks are well taken care of to minimise the chances of having contaminated fuel.

Table 6. 4: Concentration levels of metal ions expressed as µg/g in the real crude oil samples, diesel, gasoline and kerosene (A, B and C) after m-SPE and analysis by ICP-OES

Element	Crude oil samples (µg/g)					Diesel samples (µg/g)			Kerosene samples (µg/g)			Gasoline samples (µg/g)		
	A	B	C	D	E	A	B	C	A	B	C	A	B	C
As	0.117±0.005	0.203±0.03	0.091±0.001	0.095±0.001	0.161±0.001	0.208±0.0	010.187±0.01	0.112±0.01	0.123±0.02	0.094±0.01	0.88±0.01	0.113±0.01	0.074±0.003	0.054±0.002
Ba	2.1±0.15	2.09±0.04	4.00±0.08	3.07±0.2	1.44±0.06	6.9±0.2	6.1±0.8	6.4±0.2	7.0±0.4	5.6±0.1	5.88±0.7	8.43±0.2	1.02±0.05	7.6±0.8
Cd	5.1±0.08	5.0±0.07	6.3±0.02	7.1±0.2	3.1±0.08	0.8±0.02	4.1±0.6	0.98±0.08	5.0±0.1	6.2±0.2	5.1±0.4	5.1±0.3	0.59±0.01	3.4±0.1
Cr	6.06±0.2	8.12±0.6	8.99±0.7	4.8±0.1	3.7±0.1	5.9±0.1	2.1±0.06	1.9±0.04	1.2±0.02	2.3±0.1	1.8±0.05	2.3±0.1	1.2±0.08	1.1±0.1
Cu	2.05±0.07	2.98±0.08	0.78±0.09	0.95±0.05	0.84±0.004	0.69±0.03	0.39±0.01	0.4±0.01	0.45±0.01	0.66±0.01	0.68±0.02	0.75±0.01	0.84±0.05	0.52±0.03
Mn	0.14± 0.006	0.18±0.04	<DL	0.01±0.006	0.09±0.001	<DL	0.02±0.001	0.09±0.001	0.18±0.01	0.06±0.001	0.13±0.008	0.08±0.004	0.06±0.002	0.15±0.01
Mo	1.02±0.03	1.37±0.06	<DL	0.69±0.01	1.2±0.01	1.71±0.1	2.00±0.01	<DL	3.4±0.1	2.07±0.1	<DL	0.79±0.02	0.65±0.008	0.24±0.03
Ti	4.0±0.09	4.32±0.2	4.8±0.3	3.98±0.2	2.72±0.03	1.46±0.2	1.49±0.08	1.57±0.01	2.4±0.2	2.5±0.2	1.39±0.1	1.38±0.1	1.51±0.07	1.23±0.1
V	3.64±0.03	3.89±0.2	3.91±0.3	3.27±0.1	2.15±0.09	1.81±0.1	1.75±0.1	1.83±0.1	1.84±0.08	1.83±0.1	2.1±0.1	2.3±0.1	2.09±0.06	2.8±0.3
Pb	6.00±0.05	5.03±0.09	5.43±0.2	6.01±0.5	5.48±0.4	5.57±0.2	6.09±0.4	5.10±0.2	7.910±0.6	5.11±0.4	3.95±0.1	4.45±0.1	6.24±0.1	4.46±0.2
Sb	5.98±0.1	5.76±0.8	8.71±0.6	1.49±0.08	1.64±0.08	0.98±0.06	0.85±0.01	0.43±0.03	1.00±0.08	0.86±0.03	0.78±0.02	0.40±0.02	1.53±0.1	1.19±0.03
Sn	0.78±0.06	0.87±0.03	0.88±0.4	0.79±0.03	1.32±0.06	1.81±0.1	1.44±0.05	0.85±0.05	0.65±0.04	0.57±0.02	0.54±0.01	0.71±0.03	0.48±0.02	1.44±0.01
Tb	0.53±0.006	0.55±0.07	0.51±0.02	0.50±0.02	0.50±0.01	0.54±0.02	0.45±0.02	0.51±0.03	0.08±0.002	0.080.002	0.07±0.001	0.66±0.02	0.59±0.02	0.64±0.02
Zn	8.59±0.2	3.48±0.1	9.23±0.05	8.21±0.8	0.28±0.02	5.52±0.2	6.23±0.2	4.89±0.1	7.44±0.3	5.270.5	5.91±0.08	0.2±0.02	1.6±0.1	9.43±0.4
Te	3.05±0.6	1.82±0.3	3.05±0.08	3.50±0.1	4.20±0.08	2.20±0.1	3.82±0.4	3.45±0.8	0.85±0.05	0.98±0.01	0.75±0.02	0.1±0.03	1.44±0.1	2.12±0.1

6.4 Conclusion

The simple and rapid m-SPE method was successfully developed for the extraction of As, Ba, Cd, Cr, Cu, Mn, Mo, Ti, V, Pb, Sb, Sn, Tb, Te and Zn in fuel oils. The synthesised magnetic nanoparticles were characterized using SEM-EDX, TEM, UV-visible, FT-IR and XRD which all confirmed the presence of $Fe_3O_4@Al_2O_3$ nanoparticles. The m-SPE method showed good accuracy: 86-96% with the exception of Zn which reported 74%. The method also reported very good precision (≤ 4.8) and MDL (≤ 0.114-0.62 µg/g). It is worth noting that the method also reported good enrichment factors of 30, 24, 11, 20, 26, 10 and 8 for Co, Cr, Cu, Mn, Mo, Pb and V, respectively. The concentrations of the studied metals and metalloids were less than 10 µg/g, indicating that proper strategies of removing trace elements in crude oil and its derivatives still need to be done to ensure minimal exposure of these metals to living organisms.

APPENDICES

Table S1: The Full factorial design for the optimization of pH, eluent concentration, sorbent mass, spike concentration and sonication time for efficient extraction of metals and metalloidsusing m-SPE Replicates (n=3)

pH	Sorbent mass	Eluent M of HNO_3	Spike concentration	Sonication time	Cd	Co	Cr	Cu	Mn	Pb	Ti	V
6	10	0.1	10	30	78.0	76	76	81	72	78	77	83
9	10	0.1	10	5	54	58	48	49	50	48	45	50
6	50	0.1	10	5	72	70	68	67	58	66	64	70
9	50	0.1	10	30	99.8	105.9	82	88	110	108	108	81
6	10	1	10	5	54	60.3	46.9	50.5	42.5	46.0	54.0	50.5
9	10	1	10	30	74.0	68.0	66.0	68	68	76	79	73
6	50	1	10	30	101	92	116	95	97	103,7	99.4	117.4
9	50	1	10	5	68	78	80	79.7	81	87.5	81	87.9
6	10	0.1	50	5	38	42	48	52	43	34	49	51.1
9	10	0.1	50	30	66.7	74.7	67.3	73.4	72.3	75.0	77.6	74.9
6	50	0.1	50	30	97.1	96.4	101.4	86.9	81.9	99.5	84.1	85.9
9	50	0.1	50	35	78	81	73	69	81	76.4	81.0	73.0
6	10	1	50	30	80	90	85	93	72	91	82.6	89.8
9	10	1	50	5	30	43	48	53	40	38	43	43.0

6	50	1	50	5	81	85	76	70	69	78	69	70
9	50	1	50	30	82	80	81	92.8	92	82	85	83.9

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CHAPTER 7

GENERAL CONCLUSION AND RECOMMENDATIONS

7.1 GENERAL CONCLUSION

The purpose of this study was to develop greener methods for the determination of metals and metalloids (Al, As, Ba, Cd, Co, Cr, Cu, Mg, Na, Ni, Pb, Sb, Sn, Tb, Te, Ti and V) in crude oil, gasoline, diesel, and kerosene. These methods that were developed were microwave assisted hydrogen peroxide digestion (MA-HPD), ionic liquid assisted-extraction induced by emulsion breaking (ILA-EIEB) and magnetic solid phase extraction (m-SPE). These methods were developed to reduce or completely remove matrix effects of fuel oils prior to inductively coupled plasma-optical emission spectroscopic (ICP-OES) analysis of the investigated metal ions. The MA-HPD was used for the screening of the presence of metals in crude oil and crude oil derivatives (gasoline, diesel, and kerosene). The screening just gave a picture of which elements were there in the samples. Additionally, the extraction methods (ILA-EIEB and m-SPE) were developed for the preconcentration of trace elements, which were that were not detected by MA-HPD method.

The MA-HPD was used for the decomposition of crude oil and crude oil derivatives prior to ICP-OES analysis. This method proved to be cost effective, and environmentally friendly, since dilute hydrogen peroxide decomposes to water and oxygen at high temperatures of the microwave. The optimum parameters for digestion were 0.1 g sample mass, 5 mol/L of H_2O_2, digestion temperature of 245 °C and digestion time of 25 minutes. The method reported on very good recoveries which ranged from 104.8-117.8 % and the precision $\leq$ 4.1 %. The MA-HPD reported very good method detection limits which were 0.046, 0.030, 0.408 and 0.057 µg/g for Ba, Na, Ni and V respectively. There was a variation in the concentration of metals and metalloids between the crude oil samples and the crude oil derivatives. The concentration ranges for metals and metalloids (Al, Ba, Cd, Co, Cr, Cu, Mg, Na, Ni, Pb, Sb, Ti and V) ranged from 1.21-58.86 µg/g, 0.55-36.37 µg/g, 0.56-47.0 µg/g and 0.6-35.1 µg/g for crude-oil, diesel, kerosene, and gasoline respectively.

The ILA-EIEB proved to be very good as it improved the detection of metals that were in trace levels. The use of ILA-EIEB helped to eliminate the challenges that were associated with other liquid-liquid extraction methods which included the use of high volumes of carcinogenic solvents which in turn generate more hazardous waste and increase operational cost. Additionally, this method also solved problems that were previously reported by other researchers who have investigated the use of the traditional EIEB for metal extraction in oily matrices. One of the major challenges were the formation of very unstable emulsions, which in turn resulted to very low extraction efficiencies. However, this challenge was eliminated by the use of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) ionic liquid, which enhanced the emulsion stability, thereby increased strong interaction between target analyte and the aqueous phase. Additionally, this method used very small dilute volumes of reagents, which made it even much greener. This method reported very good percentage recoveries (80.1 -101%) with precision of ≤ 4.7 %. This method was successful applied in crude oil and its derivatives for the preconcentration of As, Ba, Co, Eu, Ge, Lu, Pb, Sb, Sn, Tb and Te prior to ICP-OES analysis.

The m-SPE method was also developed for the preconcentration of metal ions in fuel oils. The most attractive feature of m-SPE is the easy separation of the adsorbent from the bulk sample by using external magnet. Additionally, this environmentally friendly, since $Fe_3O_4@Al_2O_3$ was used as the magnetic adsorbent. Several characterization techniques (FT-IR, SEM-EDX, TEM, UV-visible, and XRD) confirmed the formation of the adsorbent. Thereafter, two-level fractional factorial design (FrFD) and the central composite design (CCD) were used for the optimization of the most influential parameters affecting the extraction and preconcentration of target analytes. Under optimum conditions, all the investigate metals (As, Ba, Cd, Cr, Cu, Mn, Mo, Ti, V, Pb, Sb, Sn, Tb and Te) reported extraction efficiencies that were above 80%, except for Zn, which reported 74%. This m-SPE method also reported very good precision: ≤ 4.8 and MDL: ≤ 0.114-0.62 µg/g. The proposed m-SPE method also reported preconcentration factor of 168, 166, 152, 165, 164, 150 and 150 for Co, Cr, Cu, Mn, Mo, Pb and V respectively. Additionally, the enrichment factors were 30, 24, 11, 20, 26, 10 and 8 for Co, Cr, Cu, Mn, Mo, Pb and V, respectively, which superior to literature reported methods. When comparing the m-SPE and ILA-EIEB in terms of sensitivity, cost effectiveness, and accuracy. There was no significance difference in terms of sensitivity between the two methods, while for accuracy, ILA-EIEB was favourable as it showed above 80% recoveries for all elements while m-SPE showed some short comings with Zn. However, m-SPE was more time consuming compared to ILA-EIEB.

7.2 Recommendations

The reported concentrations of the studied analytes showed that there is a need for developing methods that can further be used in the removal of metals and metalloids even at storage centres. The adsorption capacity and reusability of the $Fe_3O_4@Al_2O_3$ NPs still need to be considered for future studies. Other biodegradable nanocomposites can also be used as adsorbents for extraction of metal ions in oily matrices. Additionally, other greener preconcentarion methods like biodegradable magnetic solid phase extraction can also be investigated for the detection of metal ions in fuel oils using ICP-OES. Lastly, the developed sample preparation methods can also be applied for the determination of metal ions in other oily matrices like edible and lubricant oils.