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ELEMENTAL DETERMINATION OF LUBRICATING GREASE USING ICP-OES

ELEMENTAL DETERMINATION OF LUBRICATING GREASE USING ICP-OES

By

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Preface

This work was done in the Department of Chemistry, Durban University of Technology, ML Sultan Campus in Durban, KwaZulu Natal Province, South Africa

Declaration

I hereby certify that this research is the result of my own investigation, which has not already been accepted in substance for any degree, and is not being concurrently submitted for any other degree. Where use was made of the work of others, it has been duly acknowledged in the text.

....

Miss C. Marume

I hereby certify that the above statement is correct

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Professor G.G. Redhi

....

Mr S. Govender

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- And lastly to the Almighty for making it all possible.

Dedication

I would like to dedicate this thesis to my mother Mrs. Sencia Marume

ABSTRACT

The focus of most lubricating grease testing has been based on performance and appearance rather than determining the concentration of chemical components. The primary reason being lubricating grease is a difficult matrix to work with from the perspective of the analytical laboratory. The purpose of this study was to develop a simple, reproducible method for elemental determination in lubricating grease and to apply the developed method to work out a flushing procedure for the filling lines in a grease manufacturing plant.

The first part of the experimental work focused on developing a suitable and efficient sample preparation technique. Three techniques were explored: direct dilution, microwave assisted acid digestion and emulsification. Direct dilution involved shear mixing the lubricating grease with metal free base oil and diluting it with an organic solvent. Use of these solvents caused plasma destabilization or even plasma extinction and their use posed health risks for laboratory personnel. Microwave digestion involved mineralising the lubricating grease using an optimised microwave assisted acid digestion procedure. In the third sample preparation technique, microemulsions were formed by mixing the lubricating grease with a relatively small volume of a strong mineral acid mixture followed by the surfactant (triton X-100) at room temperature and pressure (RTP). This approach does not require the destruction of the organic matter or the use of large amounts of organic solvents. For all three techniques the sample was subsequently analysed for Al, B, Ba, Ca, Li, Na, S, Mo and Zn.

All analysis was performed using an Optima ICP-OES with previously optimised parameters. The direct dilution method gave the most inconsistent results with relative standard deviation (RSD) as high as 56% for calcium, 79% for boron and 66% for lithium. Microwave digestion and emulsification gave comparable results, with the calibration curves of oil emulsions not differing significantly from aqueous ones. For microwave assisted acid digestion the limits of detection ranged from 0.028 mg/L for sodium to 0.255 mg/L for boron. Correlation coefficient values (r^2) of all the elements were greater than 0.99. Likewise the limits of detection for emulsification ranged from 0.03 mg/L for aluminium to 0.37 mg/L for sulphur. The correlation coefficients for all the elements were greater than 0.99 and this indicates that the calibration curves were sufficient for analysing the digested grease samples.

Five quality assurance samples were analysed using both methods and in addition a t-test performed at the 99.9% confidence level and 4 degrees of freedom showed that the two sample preparation techniques gave similar results. Emulsification has several advantages over microwave digestion technique and superior analytical performance over direct sample dilution using solvents, and hence was chosen as the method of choice for routine analysis of lubricating grease.

The second part of the experimental work focused on developing a flushing procedure for filling lines in a lubricating grease plant. A flushing procedure is essential in order to minimise waste, which will in turn minimise production costs and avoids incurring disposal costs. In this series of experiments, the microwave digestion sample preparation technique was utilised for the subsequent determination of the flushing mass required in between product changes. The flushing procedure was implemented and monitored by the use of statistical quality control tools for a specified period of time, and as indicated by Shewart Control charts, the process was in statistical control.

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List of Abbreviations

AAS	Atomic Absorption Spectroscopy
AVG	Average
ASTM	American Society of Testing Material
CCD	Charge Coupled Device
CRM	Certified Reference Material
EP	Extreme Pressure
FM	Friction Modifiers
FTIR	Fourier Transform Infrared
GF-AAS	Graphite Furnace – Atomic Absorption Spectroscopy
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
IEC	International Engineering Consortium
IRZ	Initial Radiation Zone
ISO	International Organisation for Standardisation
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of Detection
LOQ	Limit of Quantitation
NAZ	Normal Analytical Zone
NIST	National Institute of Standards and Technology
NLGI	National Lubricating Grease Institute
O/W	Oil-in-water-microemulsion
PTFE	Polytetrafluoroethylene
RF	Radio Frequency
RSD	Relative Standard Deviation
RTP	Room Temperature and Pressure
W/O	Water-in-oil-microemulsion
ZDTP	Zinc Dialkyldithiophosphate

Publication

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CHAPTER 1

INTRODUCTION

1.1 Grease Definition

According to the American Society for Testing and Materials (ASTM) grease is a lubricating oil in which a thickening agent together with other ingredients that impart special properties have been dispersed (Mortier, *et al*., 1997). However rheologically, grease is a lubricant which under certain loads and within its range of temperature application behaves like a solid body that undergoes plastic strain and starts to flow like a fluid, if the load reaches the critical point. It regains the solid-body properties on removal of the stress (Sinistyn, 1974). It is this multi-phase nature of grease that makes it a difficult sample to handle and to analyse (Mortier, *et al*., 1997).

1.2 Grease Composition

Grease is composed of approximately 90% base fluid and a thickener system which can be organic or inorganic. Organic thickeners are as a result of a saponification reaction between a suitable alkali metal and high molecular weight carboxylic acids or fats (Rudnick, 2006). In-situ neutralisation or in-situ saponification is when the neutralisation or saponification reactions occur in the base oil used in formulating the lubricating grease, with carboxylic acids or fats respectively as the co-reactants (Hutchings, *et al*., 2002). Base oils can be divided into two major groups, mineral oils and synthetic oils.

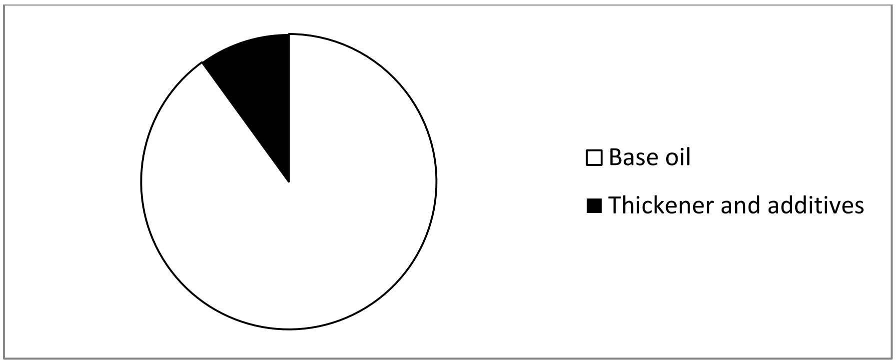


Fig 1.1 Lubricating grease composition

1.2.1 Base Oils

1.2.1.1 Mineral Oil

Mineral oil is an indefinable mixture of hundreds and thousands of different hydrocarbons depending on the specific crude oil involved as well as the method and degree of refining (Mortier, *et al*., 1997).

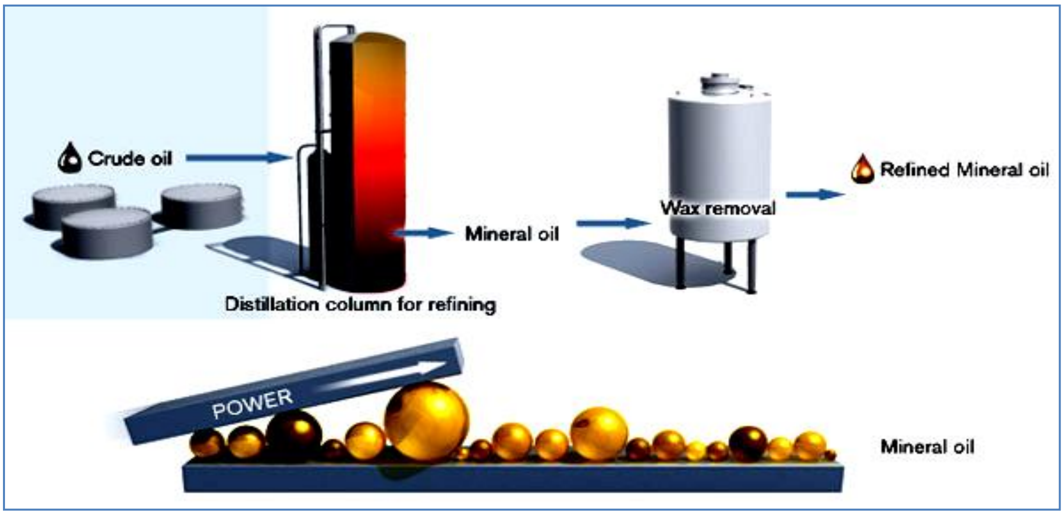


Fig 1.2 Schematic flow chart for mineral oil refining

Aromatic and or naphthenic oils were used predominantly in the past because of their high degree of polarity. However, these oils can contain considerable amounts of polycyclic aromatic hydrocarbons which are possible carcinogens. Paraffinic oils are preferred as they have been shown to meet national and international health and environmental stipulations. The oil component must meet specific requirements such as viscosity, evaporation loss, oxidation stability, response to inhibitors, etc., but perhaps the most important property of oil in grease manufacture is its solubility capability (Mortier, *et al*., 1997).

1.2.1.2 Synthetic Oils

Synthetic fluids, in contrast to mineral oils are well defined chemical substances with given physical and chemical properties, and their only disadvantage presently is the high cost of production. In some instances synthetic hydrocarbons such as alkylated aromatics esters, perfluoropolyethers, polyalphaolefins, polyglycols silicone oils, etc., are used instead of mineral oils (Rudnick, 2006). In addition to a wider temperature range synthetic fluids provide other advantages such as chemical resistance and plastic compatibility, electrical properties, the lubrication of non-metallic surfaces, environmental acceptability, and biodegradability. The molecular uniformity of synthetic oils makes them more consistent, more predictable and more robust than petroleum products (Rudnick, 2006).

1.3 Additives and Thickeners

1.3.1 Thickeners

Different thickener systems are used to provide a suitable consistency to the finished product. The type and amount of thickener is often used to classify lubricating greases. In the great majority of cases different metal soaps are used to provide a network of fibres which can act as a sponge (Gow, 2004). Most lubricating greases contain lithium-12-hydroxy stearate in mineral oil, as indicated in Fig 1.3 overleaf.

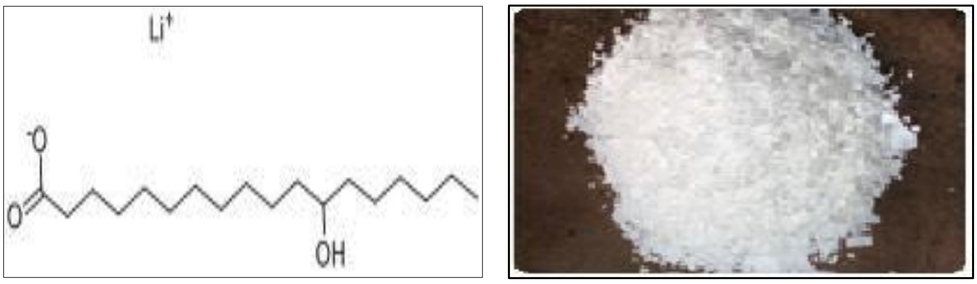


Fig1.3 Chemical formula and photograph showing Lithium-12-hydroxy stearate

Other metal cations are also used with the most common being, calcium, aluminium, sodium and barium.

(a) (b) (c)

Fig 1.4 (a) Calcium soap grease (b) Clay thickener grease (c) Lithium soap grease

12-hydroxy-stearate in its refined fatty acid form or as a triglyceride (hydrogenated castor oil) is the predominantly used anion. Tallow, lard, stearic acid, oleic acid and many other fatty acids or fats are used either as the major anion or as the modifiers for the desired soap structure (Hamnelid, 2000). Different types of clays (bentonite and hectorite), silica gel, polytetrafluoroethylene (PTFE) and graphite are examples of inorganic thickeners. Polyurea and polyurea complexes are also used as thickeners, these perform excellently at high temperatures, however the toxicity of the raw materials limits their manufacture.

In complex greases different metal soaps and salts are co-crystallized into the same fibre structure. Complex greases offer the advantage of higher melting point (Mortier, *et al*., 1997).

1.3.2 Additives

Lubricating grease contains several different additives such as anti-oxidants, corrosion inhibitors, anti-wear, friction modifiers and extreme pressure additives. All these additives allow grease to work under different conditions thereby improving its performance.

1.3.2.1 Anti-oxidants

Oxidation of lubricating grease often results in the build-up of acidic oxidation products accompanied by darkening in the colour of the lubricant. These products have a negative effect on the thickener system, often leading to oil bleeding, leakage and causing softening. Oxidation of grease can occur during its use or in storage. Lubricating grease is a poor conductor of heat, this allows oxidation to begin at a hot point and gradually spread through the grease causing carbonization and progressive hardening or crust formation (Mortier, *et al*., 1997). Mineral oil contains a small amount of ant-oxidants but these are insufficient to significantly hinder the oxidation process hence the use of antioxidants are frequently added to neutralise the acidic products of oxidation (Rudnick, 2006).

1.3.2.2 Corrosion Inhibitors

Corrosion inhibitor is defined (ISO 8044) as a substance which when present at a suitable concentration, lowers the corrosion rate without significantly altering the concentration of any other corrosive agent. These additives function by forming a physical hydrophobic barrier composed of chemisorbed surfactant molecules which prevent water and oxygen from reaching the metal surface (Mortier, *et al*., 1997).

1.3.2.3 Anti-wear and Extreme Pressure (EP) Additives

These are substances which react with the sliding surfaces under severe conditions in the contact zone to give compounds with low shear strength, thus forming a lubricating film at precisely the location where it is needed. Additives of this type usually contain sulphur, phosphorous or less commonly chlorine, and function by adsorbing on the metal surface and then reacting in the contact zone to form local sulphide, phosphide or chloride films which are easily sheared. The most widely used EP additives are zinc diorthophosphate, tricresyl phosphate and dibenzyl disulphide (Mortier, *et al*., 1997).

1.3.2.4 Friction Modifiers (FM)

These are generally long slender molecules which consist of a polar head and a hydrocarbon chain of ten or more carbon atoms. When dissolved in oil the polar head is attracted to the metal surface whilst the hydrocarbon chain remains solubilised in the oil. This orientation of the friction modifier between the metal surface and the oil enables it to reduce friction between two surfaces. Dyes are also added to improve on the appearance of the grease (Mortier*, et al*., 1997)

1.4 Physical Properties of Grease

Different applications of lubricating grease require grease with specific rheological and physical properties. These are determined by standard methods to avoid ambiguity and promote consistency within grease trade.

1.4.1 Grease Consistency

Consistency is a measure of the softness or stiffness of the grease. It varies with temperature and depends principally on the amount of thickener used. It is measured by allowing a cone of specified size and weight (penetrometer) to sink into the grease under its own weight for 5 seconds; the depth of the penetration of the cone is then measured. The National Lubricating Grease Institute (NLGI) consistency number sometimes called "NLGI grade" gives the relative hardness of lubricating grease as outlined by the standard classification developed by the NLGI. This system specifies nine grades ranging from 000, the softest, through 00, 0, 1, 2, 3, 4, 5 and 6 the stiffest, the greater the penetration the softer the grease and the lower the NLGI grade (ASTM D217, 2007).

1.4.2 Mechanical Stability

Mechanical stability is the ability of grease to withstand changes in consistency during conditions of use. Most grease tends to soften slightly when heavily worked and then gradually regain their original consistency once working has ceased. Mechanical stability is assessed by measuring the consistency of grease before and after it has been worked for a prolonged period (Exxon Mobil Corporation, 2009).

1.4.3 Dropping Point

When soap based grease is heated it gradually softens until, it reaches a critical temperature at which its structure breaks down and the grease liquifies. This temperature is known as the dropping point (Mortier, *et al*., 1997). Some non-soap based greases such as clay or polyurea are not affected in the same way as soap based greases, as their thickeners do not melt down when the grease is heated. The dropping point of grease is measured by heating the sample in a cup clipped to the end of a thermometer. The temperature is noted when the first drop of grease falls out of a hole in the bottom of the cup (Hamnelid, 2000). When grease is cooled, it gradually hardens and eventually a point is reached at which the grease is too hard to act as an effective lubricant.

1.4.4 Oxidation Stability

After exposure to air either in the container, or after the container has been opened the base oil in grease will oxidise in exactly the same way as the lubricating oil of a similar type. Thickeners can also be oxidised although they are less susceptible to oxidation than base oil. Some indication of oxidation stability can be obtained by heating grease samples in an atmosphere of oxygen in a pressurised vessel. At the end of a specified period of time, the amount oxygen that has been absorbed is determined (Mortier, *et al*., 2009).

1.4.5 Corrosion Protection

Like other lubricants, greases are expected to provide protection against corrosion as well as to provide lubrication. In some lubricants this is an inherent property, whilst for others, additives which possess this particular property have to be added (Rudnick, 2006). Tests for the degree of corrosion protection given by grease, involve exposing a lubricated bearing to conditions likely to promote corrosion. After the test the bearing surfaces are visually examined for signs of corrosion (ASTM D5969, 2008).

1.4.6 Oil Separation

Under certain circumstances the base oil in grease may separate from the thickener. Some degree of separation is essential otherwise the grease would not be able to provide adequate lubrication. However excessive oil separation in grease lubrication systems may cause problems (ASTM D1742, 2006). For example when grease is pumped through a pipe under pressure the base oil may be separated from the thickener as if it were filtered. The oil may then leak from the bearings it is supposed to lubricate while the soap remains behind blocking the pipe. Oil separation is tested by placing a sample of grease on a fine wire mesh suspended in a beaker, pressure is then applied to the grease which may also be heated and after a specified time period the oil collected in the beaker can then be determined (ASTM D1742, 2006).

1.4.7 Wear and Extreme Pressure Protection

When grease lubricated mechanisms are subjected to high pressures it may be difficult to efficiently lubricate the bearing surfaces. It is then necessary to include anti-wear or extreme pressure additives in the grease to increase its load carrying capacity and prevent metal to metal contact (Booser, 1997). These additives react with the metal surface at high temperature to form a thin film that prevents direct contact between the sliding parts and thus reduces friction. The Four Ball Weld Load apparatus shown in Fig 1.5 is used to measure the ability of the grease to lubricate under extreme pressure. In this test 3 steel ball bearings are clamped together and the fourth ball rotates at a set speed, under specified load.

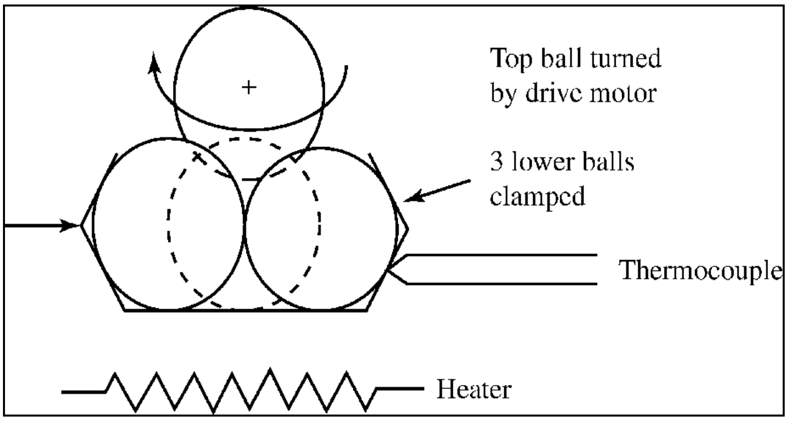


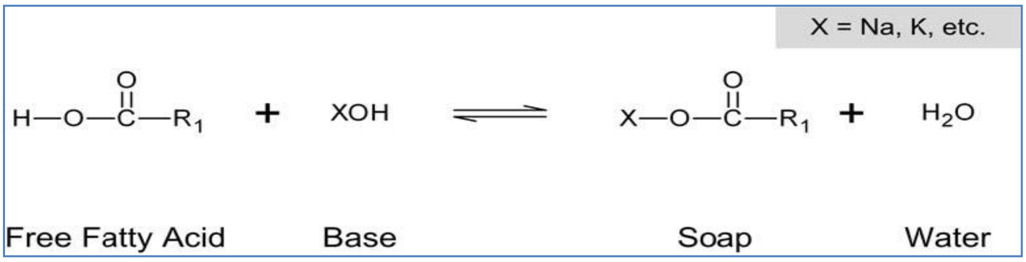
Fig 1.5 Schematic of a Four-Ball Test machine

The grease is used to lubricate the balls. A series of 10 second runs are made at increasingly higher loads until welding of the 4 balls occurs. This load is known as the weld point. The higher the weld points the better the grease's ability to withstand high pressures (ASTM D2596, 2008).

The Timken OK Load is another test used to determine the extreme pressure properties of grease. In this test, a ring rotates against a steel block, lubricated by the grease. The test is run for ten minutes at successively higher loads until scoring occurs. The Timken OK load is the heaviest load that the grease can withstand before the block is scored. Timken and the four ball test are useful in studying the load carrying capacities of grease and for comparing different greases (ASTM D2509, 2008).

1.5 Method of Manufacturing Lubricating Grease

The production of grease on a large scale involves a complicated saponification process i.e. the reaction of a fatty acid with a metal hydroxide.



$$\mathrm{H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R_1} + \mathrm{XOH} \rightleftharpoons \mathrm{X{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R_1} + \mathrm{H_2O}$$

Fig 1.6 Saponification process

The saponification process shown in Fig 1.6 above is carried out as either a batch process in kettles or contactors or as a continuous process in small reactors (Rudnick, 2006). Most thickener systems are produced by the reaction of metal hydroxides and fatty acids in the presence of a portion of the base oil. The reactants are heated to the reaction temperature, and temperature is held constant for a specified period, after which temperature is often increased further to dehydrate and melt the soap.

Cooling is carried out with continuous stirring and the soap crystallizes into its characteristic fibre structure. Regardless of how carefully the cooling step is carried out, the resulting mass is often lumpy and must be homogenised. Additives are then introduced, the consistency adjusted and the whole mixture homogenized. The grease is then passed through a dearation unit, filters and finally goes for packaging (Rudnick, 2006). Fig 1.7 is a schematic diagram for the manufacture of lubricating grease

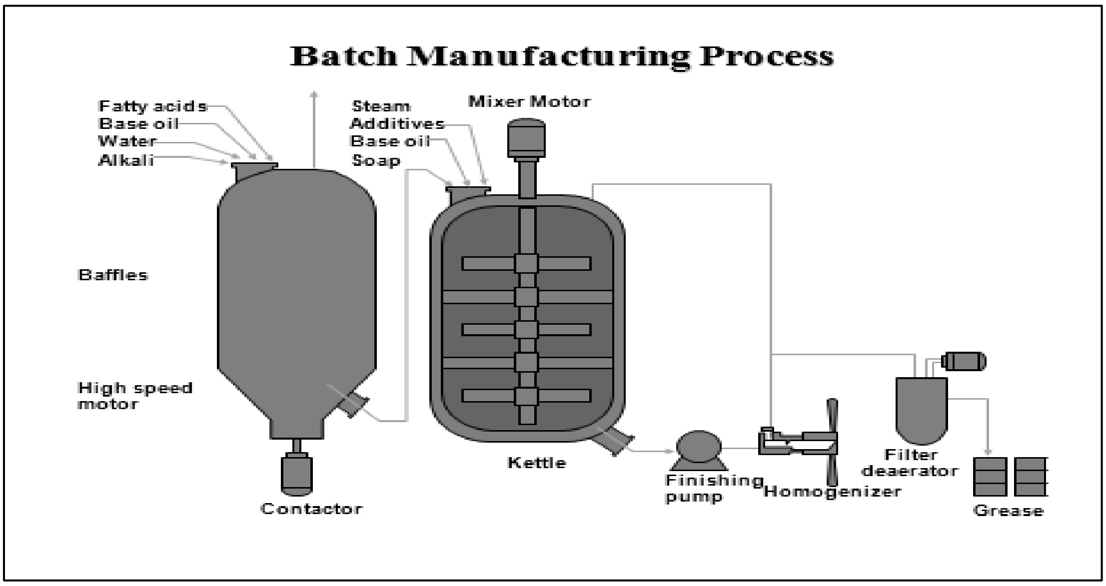


Fig 1.7 Manufacture of lubricating grease

The choice of dispensing equipment for lubricating grease is influenced by grease consistency and its oil separation tendencies. In manufacturing lines with a high product throughput, greases with a low consistency (NLGI grade 2 or lower) can be piped under pressure from storage tanks to packaging points. With greases of NLGI grade 3 or greater, long piping lines to packaging points are impractical because of the potential pressure build-up in the lines (Rudnick, 2006). Continuous grease manufacture requires that all the raw materials of the grease be in a liquid form hence batch processing is increasingly becoming the method of grease manufacture (Rudnick, 2006).

1.6 Advantages of Lubricating Grease over Lubricating Oil

Advantages of grease over lubricating oil rely on its capabilities as a lubricant, as a sealant i.e. protecting surfaces from contamination, as a matrix i.e. providing a carrier for various additives, and as a corrosion inhibitor i.e. a matrix for anti-corrosion additives. Lubricating grease also has several advantages which include longer re-lubrication and service intervals, reduced wear, and lower energy consumption and most important is the reduction in maintenance costs. Additionally due to flexibility in formulations, the range of conditions under which grease can perform optimally can be made broader (Gow, 2004). These benefits can be best exploited by selecting the grease to fit the machine components to be lubricated, the operating temperature and the surrounding environment (Gow, 2004).

1.7 Grease Incompatibility

The fourth edition of The National Lubricating Grease Institute Lubricating grease guide defines grease incompatibility as follows, “When greases made from different thickeners are mixed, the mixture may be poorer in service performance or physical properties than either of the component products”. The resulting reduction in performance is called incompatibility and results in reduced wear resistance, change in consistency commonly softening and a reduction in shear stability. Compatible mixtures do not exhibit any of these changes (Chevron USA Inc., 2012).

Grease consist of thickener, base oil and additives hence incompatibility can also arise from other interactions between other components of grease besides thickeners i.e. thickener of one grease is incompatible with the additives present in another formulation (Chevron USA Inc., 2012). If the mixture exhibits properties of an incompatible mixture i.e. reduced heat resistance, reduced shear stability or is markedly softer than the original grease, the mixture must then be deemed to be incompatible.

Various factors affect grease compatibility making it a complex subject, consider for example mixing fresh grease with an oxidised portion of the same grease, the mixture could result in immediate progressive changes. In contrast, mixing lubricating greases with different thickener systems may result in hardening, very soft or low melting mixtures which do not provide sufficient lubrication and may lead to early failures. Other parameters e.g. temperature, contaminants and time all increase the unpredictability associated with determining the compatibility of grease (Chevron USA Inc., 2012). In some instances intermixing of grease is undesirable, for example, sodium stearate thickened greases are often employed as lubricants in food machinery applications, on the other hand the same sodium stearate thickeners are not approved components for greases that may come into direct contact with food hence their intermixing during manufacture can have adverse effects.

ASTM D6185-97, 2008 is a standard test method for determining if two lubricating greases are compatible. This method can be used to speculate technical problems that may arise upon the change from one grease to another (ASTM D6185-97, 2008).

Two different tests are carried out to determine if greases are compatible. In the first test method a 50/50 mixture of the two greases is analysed at a worked penetration of 60 strokes to see if the mixture does not change in consistency. If there is no marked change in consistency a second and more demanding roll stability test is run. This test involves running a cylindrical roller at 165 rpm. The worked penetrations of the samples are measured before and after the roll test. The compatibility is determined by evaluating each of the greases individually as well as for the mixtures at (25% / 75%), (50% / 50%) and (75% / 25%) of the two greases of interest. The penetrations are measured and the results are plotted to illustrate the blending and shearing effects on the grease mixtures. The grease compatibility is determined by comparing the measured worked penetration results after the test to the theoretical calculated results expected for the mixture (ASTM D6185-97, 2008).

1.8 Trends in Lubricating Grease Manufacturing

Grease manufacturing methods and equipment have evolved over the years to accommodate the dynamic grease market. Lubricating grease has to meet strict specifications stipulated by regulating bodies and accommodate advancements in mechanical engineering. In addition industrial machinery and components are increasingly requiring specialty greases, this gives pressure to the grease technologist to formulate products that are efficient whilst conforming to the stringent specifications (Rudnick, 2006). Formulators are intermixing thickener systems and various grease additives in order to achieve the quality and performance requirements. Environmental legislation and consumer trends awareness are also influencing the design and application of grease. The current trend is toward eco-friendly grease, biodegradability, low toxicity and absence of sheen on the water surface in the event of a release. Lithium complex greases are becoming more popular on the industrial lubricant market (Rudnick, 2006).

1.9 Project Justification

Lubricating grease is often a low priced product and those in the grease making industry highly prioritise cost saving measures in order to make its manufacture profitable. Grease Manufacturing companies are under increased pressure to improve productivity whilst minimising the cost of operations. Manufacturing budgets are limited while output targets are increased, therefore equipment reliability in processes, equipment quality testing and capital preservation are critical to the success of any grease manufacturing process (Mortier, *et al*., 2009).

Blendcor (Pty) Limited manufactures a wide variety of grease products from different family groups i.e. lithium and calcium simplex greases, clay based greases, lithium complex greases, etc. The company currently has only four autoclaves and this is so because these are very expensive to purchase and install. The manufacture of all grease products is done using these four autoclaves and this poses a cross contamination problem especially when switching between different grease products. Failure to meet the physical test specification is evidence of a contaminated product and considerable man hours are lost in attempting to rework a product. This also results in a loss to the company and sets it behind in the production plan.

An elemental determination method is essential as it can help to determine the degree of contamination in a product and also provide guidance as to how the contaminated product can be reworked, down-graded or even be written off as useless. Consider a Lithium simplex product A being the current batch and a Lithium complex product B the previous batch.

To determine the degree of contamination of product A with product B the concentration of boron in the current batch can be determined since product A does not contain any boron and hence its presence indicates contamination from product B. In order to minimise cross contamination both the reaction vessel and the filling lines have to be flushed using the current batch and hence considerable quantities of flushing waste is generated, which not only causes product loss, but also substantial disposal cost for these flushings is incurred.

Blendcor (Pty) Limited is committed to conforming to lubricant manufacture and supply standards, and thus implements the ISO9001/TS16949 quality management system. Lean manufacturing technique requires that all the wastes are identified and eliminated from the system. Anything that does not add value to the product is defined as waste. This can be waste of inventory, time, materials, equipment, plant space, labour and capital. A well optimised and validated flushing procedure is essential to minimise unnecessary product loss. To achieve this, a quantitative method is necessary to determine how much flushing is required to ensure that the current product batch is free from contamination by the previous batch.

Disposal of lubricating grease waste is an environmental concern as it contains trace amounts of sulphur and nitrogen, which depending on their form can be harmful to humans, wildlife and vegetation. The grease can also react with the environment to produce secondary poisonous chemicals. In addition large areas of soil may be contaminated making the soil economically unviable as well as hazardous to the health of organisms living in and around them.

In addition to determining the amount of contamination, a method for the elemental analysis is crucial for the quality characterisation of the product, thus minimising the risk of a contaminated or unsatisfactory product reaching the customer.

1.10. Aims and Objectives of this Research

- To develop and validate a method for the elemental determination of specific elements in lubricating grease
- To develop an efficient flushing procedure

CHAPTER 2

SAMPLE PREPARATION TECHNIQUES AND INSTRUMENTATION

2.0 Introduction

Several analytical techniques are extensively used for the elemental determination in petroleum related materials (Nardkarni, 2005). The bulk of these techniques have been well documented in literature and are fully understood. Before selecting a specific analytical technique, there are several factors that the analyst has to consider and these include matrix interferences, ease of operation, sample pre-treatment requirements, cost, linear dynamic range, sensitivity of the technique, precision and speed of analysis (Nardkarni, 2005). Significant developments in analytical instrumentation have seen improvements in the selectivity and sensitivity of analytical determinations. The choice of technique for the analysis of real samples should be based on the analytes to be determined, the matrix and the equipment available (Khuhawar, 2012). Many modern analytical instruments were developed to improve elemental determination in the last few years, nonetheless sample preparation remains a challenge because it is cumbersome, labour-intensive and time-consuming (Hwang, 2005).

2.1 Comparison of Elemental Techniques

2.1.1 Atomic Spectroscopy

Flame absorption spectroscopy is the most common form of atomic absorption spectroscopy (AAS). In this technique a solution of the analyte is passed through a flame in order to atomize the analyte. Simultaneously light from a hollow cathode lamp of the same analyte is passed through the flame. Ground state atoms can absorb radiant energy of their own specific resonance wavelength, which essentially is the wavelength of the radiation that the excited atoms would emit. Consequently if light of the resonance wavelength is passed through a flame containing ground state atoms a portion of the light will be absorbed and the extent of the absorption is dependant on the number of ground state atoms present in the flame. Using different oxidant and fuel combinations result in variation in the flame temperature. Atomic absorption spectroscopy is a simple technique that employs relatively cheap and easy to use equipment. The technique gives a high sample throughput and minimal matrix and other interference effects are encountered (Beaty, *et al*., 1993). Atomic absorption spectroscopy is a sequential technique and is suitable for small suites of elements. Some elements such as sodium, calcium, potassium and lithium ionise rather easily thereby reducing atomisation complicating the measurement technique.

2.1.2 Graphite Furnace Atomic Spectroscopy

Graphite furnace atomic absorption spectroscopy (GF-AAS) is fundamentally similar to flame absorption spectroscopy except that instead of a flame GF-AAS uses a small electrically heated graphite cuvette or tube which is heated to maximum temperature of 3000 ºC to achieve a cloud of atoms. Longer residence time in the tube and higher atom density lowers the AAS detection limits by a factor of up to 1000 times compared to flame AAS (Andrade-Garda, 2009). Refractory element performance is however restricted by the use of cuvettes and the temperature limitation.

Additionally graphite furnace AAS has slower analysis time, no screening ability and a limited dynamic range. The technique is applicable to only fifty elements fewer than can be determined by inductively coupled plasma technique (Andrade-Garda, 2009). It is difficult to determine most elements by Graphite Furnace – Atomic Absorption Spectrometry. Volatilisation interferences are commonly encountered in GF-AAS and ways for their minimisation somewhat complex. In addition with GF-AAS, the single element technique is usually slow. Multi-element determination with GF-AAS has been made possible in recent years, however, achieving a set of standard operating parameters poses some challenges (Andrade-Garda, 2009).

2.1.3 X-Ray Fluorescence Spectroscopy

X-Ray fluorescence spectroscopic technique is sometimes used to quantify elemental concentrations in grease samples. However, it suffers from the major drawback that it is unable to quantify important lubricating grease components lithium and boron (Fox, 2005). In the case of lubricating grease it is a challenge to reproducibly fill sample cups making X-Ray fluorescence spectroscopy an inconsistent technique for lubricating grease analysis (Bühler*, et al*., 2008).

2.1.4 Inductively Coupled Plasma Atomic Emission Spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is based upon the spontaneous emission of photons from atoms and ions that have been excited in a RF discharge (Hou., *et al*, 2000). The detection limits with ICP-AES are from 1-50 times better than with flame AAS for the vast majority of elements and generally lay in the range 10^{-1}-10^{-4} mg/L (Beaty, *et al*., 1993). Formation of refractory carbides that resist dissociation to free atoms restricts the determination of some elements by flame atomic absorption spectroscopy.

This problem is subdued by the inert argon environment and much higher temperature in the plasma (Hou., *et al*, 2000). Alkali metals are almost completely ionised in the ICP, the resulting ions have very stable electronic configurations and do not produce intense emission spectra at ICP temperatures, as a result AAS exhibits better detection limits than ICP for alkali metals (Hou, *et al*., 2000).

ICP has several advantages over other spectroscopic techniques and hence has achieved tremendous popularity in the petroleum related field (Fox, 2005). It has a linear dynamic range of over five orders of magnitude for many elements. This is particularly advantageous since it permits one to measure per cent levels to trace levels of different elements in a sample simultaneously without dilution. Because of the high temperature of the plasma, refractory elements can be easily determined. Alkali metals however give poor sensitivity. Again because of the high temperature, chemical or matrix interferences common in flame AAS are not encountered in ICP-AES (Andrade-Garda, 2009).

ICP-AES has a broader linearity range up to concentrations of (10^4 – 10^5) times the limit of detection, compared to AAS which exhibits linear absorbance response of only (10^2 – 10^3) times this limit. ICP is less prone to volatilisation interferences (Hou, *et al.,* 2000). In flame AAS introduction of one or more chemical additives is essential to minimise ionisation and volatilisation interferences. Ion exchange and solvent extraction may be required to remove interferences caused by major constituents. This decreases the speed of the analysis and increases its complexity. While such interferences are not completely absent in ICP their magnitude is way less than flame AAS (Laszlo, *et al*., 2003).

2.2 Sample Preparation

After sampling, the sample preparation procedure is the next step which affects the final results obtained. Ideally this step should have the least sample handling as this might introduce contaminants, and should at all cost avoid sample loss as this will render the whole quantitation process pointless. Physical and chemical properties of petroleum and petroleum products are used to establish standard prices, volumes and compliance with regulatory and commercial specifications making representative samples for determination of these properties crucial (ASTM D4057, 2011). Sample preparation for a method that is used on a routine basis should be easy, precise and short. The sample preparation step puts the sample in a state that is compatible with the method of measurement. Desirable features of this step are:

- complete dissolution with no insoluble residue
- reasonably quick
- final solution should contain metals as cations and non-metals as anions
- there should be no interfering species from the reagents
- contamination from the vessels and atmosphere should be minimal
- there should be negligible losses through volatility or adsorption onto the walls of the vessel.
- vessels should also be inert to attack by reagents and sample
- the procedure should be safe.

2.3 Different Sample Preparation Techniques and their Limitations

The determination of metal elements in lubricants is employed in quantifying various lubricant additives in finished oils, screening for toxic elements in used oils and in the preventive maintenance oil-wetted mechanisms. All the oil samples require some form of sample pre-treatment before being introduced into the instrument for analysis (Pouzar, *et al*., 2001). A number of different techniques exist for the preparation of oils such as direct dilution, micro emulsification, microwave digestion and sulphated ashing. These techniques have also been applied to lubricating grease samples in order to determine the most suitable preparation that would give the best possible analytical data.

2.3.1 Direct Dilution

The most commonly used organic solvents for diluting lubricating oil samples for the determination of wear metals in the oil are m-xylene, cyclohexanone and 4-methyl-pentan-2-one (McKenzie, 1981). Kreuning, *et al*., 1987 presented a study on the organic solvent load of ICPs as a function of inner gas flow rates and liquid uptake rate. The study showed that, the relative contribution of the aerosol to the total amount of the solvent that exits the spray chamber increases with decreasing evaporation factor and that solvent plasma load is determined by the saturation vapour of the applied solvent (Kreuning, *et al*., 1987).The effect of sample viscosity on the analytical response has also been studied (Brown, 1983). In this study, to xylene solution containing a constant amount of manganese, varying amounts of neutral base oil were added. The solution was aspirated freely and peristatically pumped through the nebuliser. A reduction in the apparent concentration of manganese was noted implying transport interference. Aerosol mist formation is affected by the presence of large amounts of base oil, resulting in a reduction in the amount of analyte reaching the plasma (Brown, 1983).

When introducing organic solvents into the ICP the first priority is to achieve a stable plasma with constant and reproducible sample introduction. Sample characteristics like high volatility or the ability to dissolve the pump tubing pose typical challenges to be overcome at this stage. After the selection of a suitable nebulizer and spray-chamber, suitable excitation conditions in the plasma should be chosen. The plasma must be stable under varying sample composition, while achieving the necessary analytical figures of merit (detection power or stability over time). Very often, a compromise has to be found, e.g. via a simple optimisation of plasma power or plasma gas flows, resulting in a plasma that is little or unaffected by matrix effects

2.3.2 Microemulsion

The unique properties of microemulsions namely large interfacial area, their ability to solubilise otherwise immiscible liquids, ultra-low interfacial tension and thermodynamic stability have seen them attaining increasing significance in both industry as well as in research and development. Microemulsions have found numerous uses and applications (Paul, *et al*., 2001).The difference between normal emulsion and microemulsion is their stability and particle size. Normal emulsions are “kinetically stable” whereas microemulsions are “thermodynamically stable” (Paul, *et al*., 2001). Internal contents of the microemulsion droplets are known to exchange typically on the millisecond time scale (Fletcher, *et al*., 1987). In the case of the collisions being adequately violent, the surfactant film may collapse thereby allowing droplet exchange i.e. the droplets are kinetically unstable. The presence of the surfactant lowers the energy required to increase the surface area so that spontaneous dispersion of oil or water droplets occurs and the system is thermodynamically stable (Vicentini, *et al*., 2011).

Temperature, pressure and the addition of salt or other additives can influence the stability of the microemulsion. Controlled addition of lower alkanols to milky emulsions gives transparent solutions called microemulsions. These comprise of in nanometer or colloidal dispersions of either oil-in-water (o/w) or water-in-oil (w/o) (Hunter, *et al*., 2007).

The lower alkanols are called co-surfactants they lower the interfacial tension between oil and water sufficiently enough to allow for an almost spontaneous formation of microheterogeneous systems. The overall composition of the microemulsion is specific to each system and determines the miscibility of oil, water and amphiphile (surfactant and co-surfactant) (Hunter, *et al*, 2007). Ternary and quaternary phase diagrams are used to describe the phase manifestations and are important in the study of microemulsions (Paul, *et al*, 2001). Applications of microemulsions have been extended to the field of analytical techniques. They are able to improve analytical spectroscopic techniques by functioning as intensity amplification agents, spectral shift reagents, solubilized media, etc. (Paul, *et al*, 2001).

In an emulsion the oil is incorporated in an aqueous phase, and can be directly introduced into the plasma. Application of emulsions for spectroscopic analysis does not require the use of large volumes of organic solvents or the destruction of the organic matrix by mineral acids and high temperatures. When an oil sample is uniformly dispersed in an aqueous phase, it behaves similarly to an aqueous solution, thus enabling the use of inorganic water soluble standards for calibration. Use of this sample preparation technique therefore minimises the time and cost of the analysis (Hunter, *et al*, 2007). In order to employ microemulsification as a sample preparation technique, the emulsions formed must be stable for the whole period of the analysis.

2.3.3 Microwave Digestion

Optimisation of microwave digestion parameters i.e. the most efficient reagent combinations, power settings and also mechanisms of how microwaves interact with the sample have been extensively investigated and acceptance of this technique is based on successful procedures on different sample types (Kuss, 1992). Reduction of processing time and improved analyte recoveries during microwave processing is as a result of energy transfer occurring at a molecular level throughout the sample (Das *et al*., 2008). This technique has been applied successfully to both organic and inorganic determinations for various sample matrices. Other advantages of microwave digestion are ease of automation and reduction in background contamination (Wong*, et al*.,1997). Microwave assisted digestion is generally more cost effective in the long run compared to sample ashing in the furnace, as it minimizes labour costs (Smith, *et al*., 1996)

There are several factors that determine the efficiency of a microwave digestion procedure, these include: pressure and temperature settings, sample mass, output power, extraction time and the acids used. Among these parameters, the choice of acids is important. Various concentrated acids such as hydrochloric acid, sulphuric acid, nitric acid or a mixture of these acids have been employed to destroy the matrix. This is carried out in inert, non-microwave absorbing vessels usually made of PTFE (polytetrafluoroethylene) (Wong, *et al*., 2007).

2.3.4 Sulphated Ashing

Sulfated ash sample preparation technique is used in the determination of ash forming metallic constituents in lubricating oils and additives. This method provides predictable and chemically understood salts when additives containing calcium, barium, phosphorous and zinc are ashed (Nadkarni, 1995). It involves treatment of the sample after charring using an open flame, with sulphuric acid (the char is wetted using the minimum amount of sulphuric acid and brought to dryness) and then placing in a muffle furnace. The main disadvantages of this method are loss of analytes by volatilisation, contamination of the sample by airborne dust since the sample is left open to the atmosphere and irreversible sorption of analyte onto the walls of the vessel (Mitra, 2003).

2.4 Method development

Having defined the problem and investigated the literature for possible approaches the route to be followed in the laboratory can then be determined. Cost benefit analysis may dictate which method will give the desired accuracy and reproducibility with the minimum expenditure of time and effort. Consideration in costs includes the type of reagents selected, the quantities used, the required instrumentation, and glassware dimensions.

2.4.1 Instrument Optimisation

Optimization may be defined as the process whereby many analytical characteristics of a method e.g. critical specifications (for equipment and materials), critical control points (e.g. test conditions such as dilutions, integration time, sample flow rates), ranges of the critical control points, and the process control or quality control needed at each critical control point is determined. Limits on controls are established and statistical control of the process confirmed (Wiegers, 2003).

The selection of a spectral line for the determination of an element by inductively coupled plasma-atomic emission spectroscopy is not merely choosing the most intense emission line of that element from tables of spectral lines as other factors must be considered, i.e. chances of overlap of the analytical line with some other spectral feature from the other elements in the sample or from the plasma source (Tognoni, *et al*., 2009). The primary factors in the optimisation procedure include nebuliser gas flow the power of the plasma, plasma gas and the viewing height. Other parameters such as sample uptake rate and auxiliary gas flows all play a secondary role (Tognoni*, et al*, 2009). When optimising an analytical method, it is best to eliminate possible hindrances rather than making amends for them for instance the possible problems arising from spectral interference can be eliminated through the selection of an appropriate wavelength. The primary wavelength of an element is usually the first wavelength selected to provide maximum sensitivity. However if spectral interference is found on the primary wavelength, an alternative interference-free wavelength for that particular element is used (Tognoni, *et al*., 2009).

After establishing that the selected wavelengths are free from spectral interferences, the next step is the optimisation of the plasma operating conditions. The intensity of the wavelengths is markedly increased with an increase in the power settings, this is because the subsequent higher energy in the plasma will enable high energy transitions (Manning, 1997). An increase in the residence time of the analyte in the plasma is achieved by lowering the nebuliser pressure, this gives the analyte a longer time to acquire the energy for the high energy transitions (Manning, 1997). An increase in sample uptake results in an increase in the signal intensity and also increases the possibility of thermal quenching. Along with the above benefits there is also an increase in noise levels due to the thermal quenching and increased sample consumption. If a lower sample uptake rate is required a smaller internal diameter pump is recommended instead of reducing the pump rate (Tolodi, *et al*., 2007).

An increase in integration time results in an improvement in both the precision of the analysis, on replicate determinations, and accuracy for trace level analysis (Manning, 1997). The precision and intensity of the analyses is dependent on the efficiency of the nebuliser. Intensity is proportional to the amount of sample that reaches the plasma, and precision has to do with the ability of the nebuliser to generate a consistent, fine aerosol. An increase in the sample viscosity which comes about as a result of increased levels of acids such as H_2SO_4 or increased amounts of dissolved solids lowers the nebulisation efficiency which in turn reduces the amount of sample reaching the plasma (Tolodi, *et al*., 2007).

2.5 Method Validation

For any measurement system to be considered reliable, it should employ a validated test method. Validation is the provision of objective evidence that a test method is fit for its intended use (Wiegers, 2003). International and national standard bodies i.e. ISO/IEC 17025/SABS require that laboratory-developed test methods or methods adopted by a laboratory be validated before being employed. Additionally method validation should be a planned activity that is carried out by qualified technicians with sufficient resources (Wiegers, 2003). A test method should be carefully selected and optimised in the preliminary validation stages and a project management system put in place for the entire period of method validation. The following conditions should be met before a test method is rendered valid: (Eurachem Guide, 2008)

- If the critical control points of the test method are known it follows that the quality and process control necessary for the method is known.
- The method should be in statistical control.
- The method should employ standard reference materials and measurements.
- Data supporting the performance of the method should be provided.
- Measurement variables should be known the testing procedure and for the method validation.
- A trial involving all the concerned users and departments should be done.
- A document containing a concise description of the test process should be created.
- All end users of the method should be given a chance to contribute to the method selection, development and final validation.
- All records created during the process should be secure and can be recreated.

- Test process has to be approved by qualified personnel.
- Proficiency criteria are in place and proficiency testing is available (Freeman, 2009).
- All the validation work should be carried out in an environment governed by a quality management system.

When should methods be validated?

Method validation is carried out when there is need to demonstrate that, a method’s performance parameters are fit for a specific analytical problem for example when an established test method is modified to include technical and technological advances or to extend to a new problem. Additionally a test method should be validated if it is being used in a different laboratory or with different instrumentation or when there is evidence that it is changing with time. Method validation can also be used in instances when there is need to prove the similarity of two test methods i.e. a new method and a standard method (Eurachem Guide, 1998).

When method development and validation is carried out in a quality management environment the integrity of the test method and results is enhanced the overall well-being of the laboratory improved as work is done efficiently, effectively, consistently and dependably. Other advantages offered by the validation process include reduction in waste, client satisfaction, work is done timeously and the laboratory is in a better position to defend the credibility of its data and opinions (Freeman, 2009).

The adoption of a quality management system that promotes method development and validation is of great benefit to the laboratory. Method development and validation cost money to the company but the expense incurred to the company is even greater when it loses proprietary rights or is involved in lawsuit cases with clients or even more damaging, the irrecoverable loss of credibility. If the test method is not valid, no amount of control can improve the quality of the output/product (Wiegers, 2003). This therefore implies that a test result is meaningless no matter how carefully produced, if there is no data to verify the performance characteristics of the test method employed.

Use of validated methods has also become a requirement by trade and regulatory bodies and a relevant factor regarding laboratory accreditation and in the creation of laboratory systems and networks. The requirement for and interest in measurement uncertainty has increased the importance of the quality assurance of method validation. Laboratories are now required to show proficiency in their method development and evaluation process even if only wish to be accredited for routine testing. Procedures for determining the validity and official status of a method will be more open to scrutiny, as will attendant records and data (Freeman, 2009).

The validation of an analytical method can be done by comparison with an existing fully validated method. The existing method acts as a reference method against which a new method is evaluated (Piet van Zoonen, 1999). It should be noted that the validated methods should be checked and quality assurance techniques be put in place to ensure the accuracy of results to be used to validate a new method.

A method can also be validated using certified reference material (CRM), this is material or substances of whose property value are adequately uniform and well established to be employed for calibration of an apparatus, the evaluation of a measurement method, or assessing values for materials (Freiser, *et al*., 1978). CRMs provide traceability to an accurate realization of the unit in which its properties are stated (Ndlovu, 2005). A method is said to be validated by using reference material if it can provide statistically accurate and validated results when reference material are analysed using that method. Note that to be statistically accurate and validated, a method will have to be checked against well-defined statistical criteria (Ndlovu, 2005).

2.6 ICP Principle

After selecting the elements to be determined by ICP-OES, solutions of the samples are prepared using established sample preparation techniques e.g. direct dilution acid digestion and microwave assisted dissolution. The analysis of the sample solutions follows these steps:

- A range of concentrations for each element is selected based on the expected concentration of that particular analyte in the sample.
- Solutions containing known concentrations of the analyte are then prepared and introduced into the plasma.
- The intensities of the selected emission lines are recorded and calibration graphs are plotted.
- The sample solutions are then analysed and the concentrations of the elements in each sample solution are determined from the calibration graphs.
- The concentrations in the original sample are then calculated from the measured concentrations of the elements in the sample and the known dilution factor.

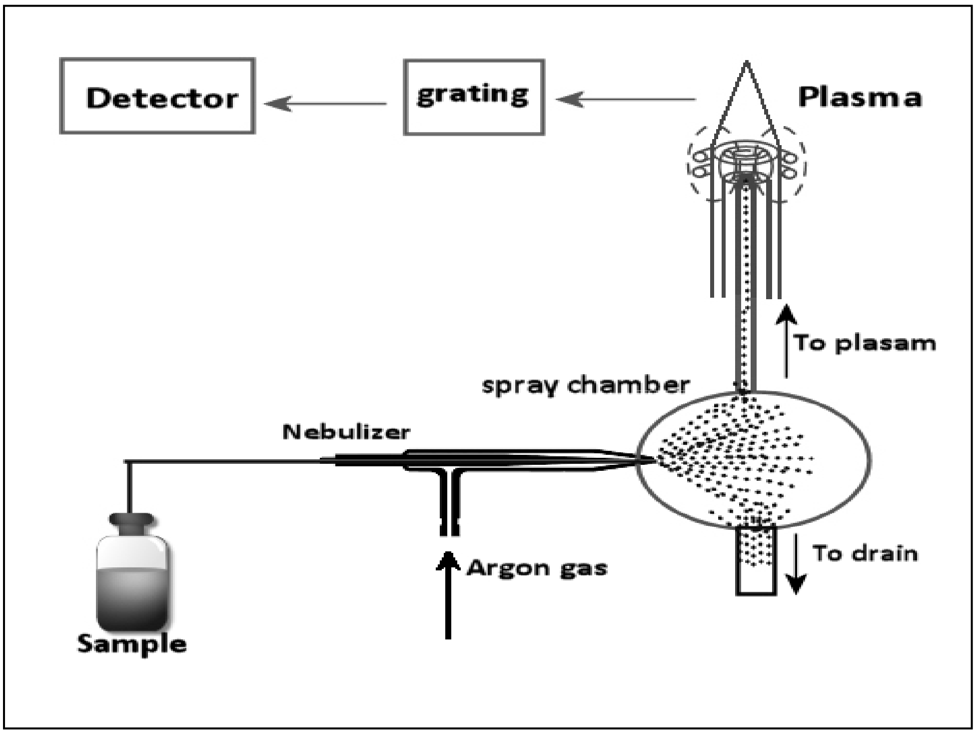


Fig 2.1 Diagram of sample introduction to ICP-OES

2.6.1 Sample Introduction

All three states (solid, liquid and gas) have been successfully introduced into the ICP. The ICP is compatible with both aqueous and nonaqueous solvents, however, most applications involve the analysis of cations in aqueous solution (Manning, 1997). Samples are introduced into the plasma as an aerosol this is due to the fact that direct injection of liquids into the plasma may lead to improperly desolvated atoms, making excitation and emission less efficient or can extinguish the plasma (Manning, 1997).

2.6.2 Pumps

Peristaltic pumps are the most frequently used in ICP-OES applications. They use a series of rollers to push the sample solution by peristalsis. The pump only comes into contact with the tubing that transports sample solution from its reservoir to the nebuliser and not the solution itself. As a result the possibility of sample contamination that occurs with other types of pumps is ruled out. The tubing used with the pump should be capable of withstanding weakly acidified aqueous solutions and a special type of tubing is employed for strongly acidic solutions (Manning, 1997).

2.6.3 Nebulisation

A small portion of the sample solution is converted to an aerosol which finally reaches the plasma. Large droplets of the sample is separated in the spray chamber and drained to waste (Ebdon, *et al*., 2007). Surface tension of the solution, flow rate, viscosity and the design of the nebuliser all affect the efficiency of the nebuliser in converting sample solution into usable aerosol. High levels of dissolved solids may increase the viscosity of the sample solution and reduce the efficiency of nebulisation, which in turn lowers the number of atoms and ions formed in the plasma. In contrast, organic solvents have lower viscosities than aqueous solutions and show enhanced efficiency of nebulisation (Ebdon*, et al*., 2007). The most widely used nebuliser is the pneumatic nebuliser. It works by drawing the sample solution through a capillary by the flow of nebulising gas (Bernouli effect). The aerosol generated in the spray chamber is separated by size, with smaller drops being carried to the plasma and the larger ones to the drain (Manning, 1997).

2.6.4 Spray Chambers

The aerosol formed in the nebuliser is transported to the torch for injection into the plasma. A spray chamber is placed between the torch and the nebuliser, its main function is to prevent large droplets of sample from reaching the torch and also to smooth out pulses that occur during nebulisation often due to the pumping of the solution (Todoli, *et al*., 2006). In general spray chambers are designed to allow droplets with diameters of up to about 10 µm or smaller to pass to the plasma. With typical nebulisers this droplet range constitutes about 1-5% of the sample that is introduced to the nebuliser. The remaining 95-99% of the sample is drained into a waste container (Todoli, *et al*., 2006).

2.6.5 Plasma

ICP-OES utilises plasma as the atomisation and excitation source. A plasma is an electrically neutral, highly ionised gas that consists of ions, electrons and atoms. Examples of naturally occurring plasmas are the sun, lightning and the aurora borealis. The energy that maintains the analytical plasma is derived from an electric or magnetic field. At altitudes of approximately 100km the atmosphere no longer remains non-conducting due to ionisation and formation of plasma by solar radiation.

As one goes further into the near-space altitudes the earth’s magnetic field interacts with the charged particles streaming from the sun. These particles are diverted and often become trapped by the earth’s magnetic field. The trapped particles are most dense at the poles and account for the aurora borealis (Fridman. 2008).Analytical plasmas use pure argon or helium which prevents combustion (Manning, 1997). Plasmas are characterised by their temperature as well as their electron and ion densities. Analytical plasmas typically range in temperature from 600 to 8000 K. As a comparison the temperature of the sun’s interior is millions of degrees, while its surface temperature is approximately 10000 K (Manning, 1997).

The high-frequency field of the induction coil accelerates positive argon ions and electrons. However, due to their small mass electrons are accelerated to higher velocities than ions. The energy transfer into the plasma is therefore largely due to processes involving electrons (Ebdon, *et al*., 2007). Energy is imparted to the electrons when a spark is passed through argon in the presence of a radiofrequency field of the induction coil. If the electrons gain sufficient energy they undergo inelastic collisions with the argon atoms. These atoms are raised to higher electronic energy states and subsequently lose the added energy by emission of light at discrete wavelengths.

When an electron collides with an argon atom with sufficient energy to ionise the argon an electron is released which is then available to participate in the transfer of energy from the coil to the gas (Ebdon, *et al*., 2007). Steady state plasma is produced when the rate at which electrons are released by ionizing collisions equals the rate at which they are lost by recombination. Ion electron recombination emits light, producing a continuous spectrum corresponding to the distribution of ion kinetic energies in the plasma.

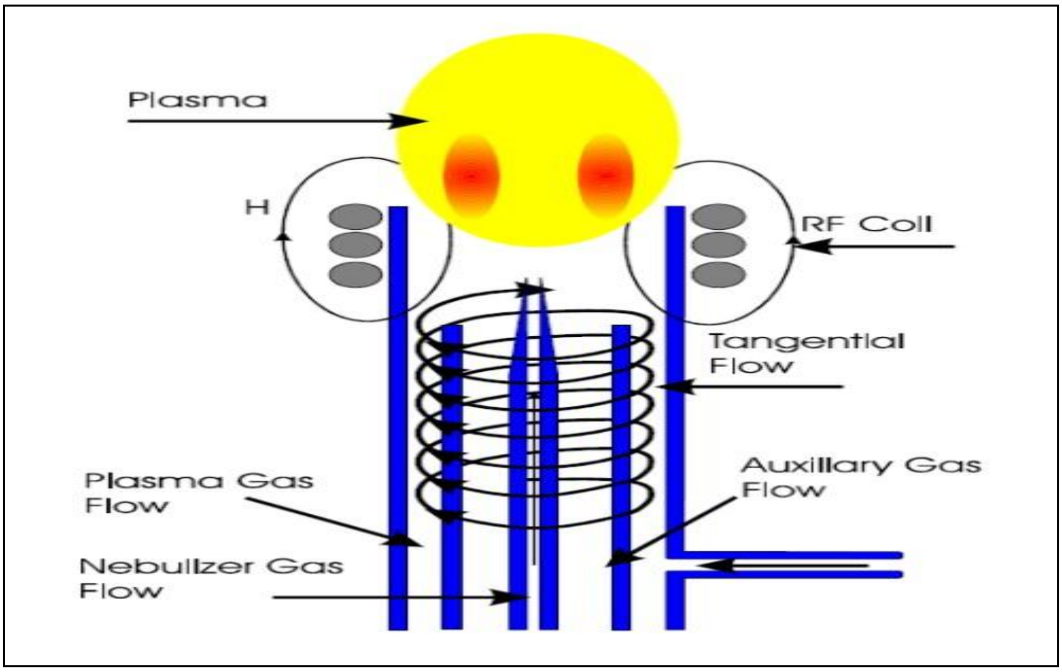


Fig 2.2 Schematic diagram of an ICP-OES torch (Manning, 2007)

The ICP discharge appears as a very intense, brilliant white, teardrop shaped discharge. The plasma is divided into four main zones, the preheating zone (PHZ) this is where atomisation of the gaseous molecules occurs, the induction zone is the region in which energy transfer from the load to the plasma occurs, the initial radiation zone (IRZ) and the normal analytical zone (NAZ) is where most of the excitation and ionisation processes take place and alalyte emission is measured from the normal analytical zone (Manning, 1997).

2.6.6 Plasma Torch

The most common ICP torch in use today has evolved over decades of development. The circular quartz tube (12-80 mm) outer diameter has three separate gas inlets. The only gas routinely used is argon which enters the plasma through the outer channel with a tangential flow pattern at a rate of 8-

20 $Lmin^{-1}$. The auxiliary gas which travels up the centre channel also has tangential flow (0.5-3 $Lmin^{-1}$) pattern. The nebuliser gas has a laminar flow pattern (0.1-1.0 $Lmin^{-1}$) and injects the sample into the plasma. The analytical zone is approximately 1cm above the coils and offers the best optical viewing area for maximum sensitivity (Hill, 2007).

At present the most popular torches are of the demountable type, which enables the torch to be dissembled so that the tubes can be modified or replaced without removing the entire torch. This results in a reduction of costs of replacing the torch and the ability to use a variety of injector tubes (Manning, 1997). Such injectors include corrosion resistant ceramic injectors, narrow bore injectors for the analyses involving organic solvents and wide-bore injectors for introducing samples with high dissolved solids contents.

The plasma temperature in the analytical zone ranges from 5000-8000 K (the temperature varies with power, flow rate, etc.). The high temperature assures that most samples are completely atomised although some molecular species (e.g. N_2, N_2^+, OH^-, etc.) do exist and can be readily measured in the plasma. The plasma emits a continuum of background radiation that extends from the visible into the ultraviolet region. The radiation originates from electrons, Ar and Ar^+, as well as various atomic and molecular species in the matrix. Although sample blanks can help to offset the unwanted flux of background photons, there is a certain level of instability in the continuum background and this instability plays a role in limiting the sensitivity of ICP-OES (Manning, 1997).

2.6.7 Drains

While it is a seemingly simple part of a sample introduction system, the drain that carries excess sample from the spray chamber to a waste container can have an impact on the performance of the ICP instrument. Besides carrying away excess sample, the drain systems provides the backpressure necessary to force the aerosol carrying nebuliser gas through the torch injector tube and into the plasma discharge (Manning, 1997). If the drain system does not drain evenly or if it allows bubbles to pass through it, the injection of the sample into the plasma may be disrupted and noisy emission signals can result. Drains for ICP-OES come in many forms – loops, blocks, u-tubes or even tubing connected to the peristaltic pump (Hill, 2007).

2.6.8 Analyte Emission in the ICP

After nebulisation the aerosol droplets must evaporate to form very small particles of dry solute. These must next be vaporised and the resulting molecules dissociated into free atoms. Further energy transfer to the atoms is required to raise their electrons to the excited energy states which then emit the characteristic line spectra (Hill, 2007). Atoms may also gain enough energy to ionise and the resulting ions in turn may be raised to excited electronic states and produce characteristic line spectra. Spectral lines from singly charged ions are prominent in the ICP spectra of many elements. Both ionic and atomic spectra are useful analytically (Hill, 2007).

CHAPTER 3

LITERATURE REVIEW

3.0 Introduction

Basic research into the principles of grease lubrication is somewhat scarce in the academic community, this could be attributed to lack of funding (Mortier, *et al*., 2009). Most research takes place under the patronage of oil companies and their personnel who are predominantly chemists. Whilst grease manufacture is unequivocally based on chemistry, the study of grease in practical situations, in which grease acts as a mechanical barrier between two moving surfaces serving to keep them apart, leads invariably into the realm of physics (Mortier, *et al*., 2009). The American Society of Testing and Materials (ASTM) together with its Japanese and European counterparts have standardised a large number of tests used to characterise a physical or specific property of grease. Some of these tests may be classified as those that are suitable for assessing batch to batch variability and those that measure characteristics particular to the composition of the lubricating grease (Rudnick, 2005). The focus of most standardised grease testing has been based on performance and appearance rather than determining the concentration of chemical components. In part this is likely due to the relative volume of grease demand when compared to other lubricants but the primary reason may be that grease is a rather difficult matrix with which to work from the perspective of the analytical laboratory (Nadkarni, 2005).

Morden analytical laboratory equipment with accompanying computer software can provide detailed knowledge on the constituents and function of lubricant formulations. Spectroscopic methods such as Fourier Transform Infrared (FTIR) spectroscopy can identify molecular signatures for base oil species, additives and various gellants (Rudnick, 2005). Thermal methods of analysis, viz. differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), derivative TG (DTG), dilatometry (DT) and penetrometry (TMA) are also used for the investigation of petroleum products including lubricating grease (Wesolowski, 2001).

Despite the complexity of lubricating grease there are well over a dozen elements of interest to the lubricating grease supplier in the form of additives, contaminants and wear metals. Determining their concentration can be an important aspect of grease manufacture. The metal content can also indicate the amount of thickeners in the grease and this can assist in the process of trouble shooting for technical problems with new and used grease (Nadkarni, 2005). A list of elements found in lubricating grease together with their potential sources is given in Table 3.1 overleaf.

Table 3.1: Elements in lubricating grease and their potential sources (Nadkarni, 2005)

Element	**Potential Source**
Aluminium	Clay/ other thickener
Antimony	Extreme pressure additives
Boron	Complexing additive for thickener
Barium	Rust inhibitor
Bismuth	Extreme pressure additive
Cadmium	Wear metal contaminant
Calcium	Thickener and Extreme pressure additive
Chromium	Wear metal contaminant
Iron	Wear metal contaminant
Lead	Extreme pressure additive
Lithium	Thickener
Magnesium	Clay thickener
Manganese	Clay thickener (minor element)
Molybdenum	Extreme pressure additive
Phosphorus	Additives such as zinc dialkyldithiophosphate
Sulphur	Additives such as zinc dialkyldithiophosphate
Silicon	Contaminant clay thickener
Tin	Contaminant
Zinc	Additives

Despite advances in endeavours to diminish sample pre-treatment for instance (electrothermal vaporization, laser ablation solid sampling, etc.), most procedures based on atomic spectrometric techniques still require some sample pre-treatment. Viscous complex oil-based organic materials give rise to major problems when analysing them by spectroscopic methods as they are difficult to introduce directly into the atomizers and selection of proper calibration standards is also a major challenge.

As a result, proper preparation of oil samples is important in order to make them compatible with the employed instrumentation and allow efficient and easy calibration procedures to be employed (Aucelio, et *al*., 2007).

Commonly, metallo-organic compounds dissolved in purified oil have been employed as standards, aimed at compensating for matrix effects and to permit the use of direct and simple external calibration. However, organic standards are expensive and may lead to inaccurate results due to fluctuations in concentration of the final organic analytical solutions which is brought about by the evaporation of organic solvent and deposition of analyte on the walls of the storage container (Silva, *et al*., 1993). Thus, several different methods which focus on matrix simplification have been used, including sample dilution with appropriate organic solvents, conversion of the sample into oil-in water emulsions and micro-emulsions, extraction methods to separate the analyte from the sample matrix, acid dissolution and acid digestion of the sample. Extraction and acid dissolution methods are time consuming and have appreciable risk of analyte loss as volatile species and sample contamination (Aucelio, *et al*., 2007).

3.1 Sample Preparation Techniques

3.1.1 Direct Dilution of Sample

One of the best ways to handle an organic matrix is simply to dissolve a portion of the sample in a suitable solvent and aspirate the solvent directly into the flame or plasma (Hwang, *et al*., 2005). Metal determination in organic samples can be achieved by dissolving sample in non-aqueous solvents, this minimises both cross contamination and sample preparation time.

Nonetheless use of these organic solvents gives rise to other difficulties due to their wide range of viscosities, densities, flammability and the increased caution necessary for their safe disposal. Additionally direct aspiration of an organic liquid typically calls for the use of specialised techniques or equipment i.e. use of desolvation devices or use of oxygen to stabilise the plasma. Introduction of oxygen into the plasma prevents carbon build up inside the torch and on the cooled cone, it also reduces molecular band emissions. However the efficiency of these procedures is predominantly poor due to high detector noise levels. Introduction of oxygen also produces polyatomic interferences for some elements in inductively coupled plasma mass spectroscopy (Wang, 2003).

Gow, *et al*., (2009) dissolved a lubricating grease sample in a mixture of kerosene and toluene, and the solution was aspirated into the ICP torch, a high solids nebuliser on the ICP was used, and added an internal standard to correct for matrix effects. The sample was diluted with kerosene/toluene at a ratio greater than 5:1 to avoid aspiration problems. The greater the dilution ratio the more closely the sample viscosity behaves like the solvent and the less the need for an internal standard, however for this method an internal standard was used to compensate for the differences in viscosity between the samples and standards (Gow, *et al*., 2009). This method however does not give total metals when there are particulates in the sample, if the sample contains metal particles this material will end up at the bottom of the sample container after dilution and hence the analysis will not represent “total” metals (Poppiti, 2009).Additionally, some organic compounds are insoluble in the more common organic solvents that are suitable for atomic spectrometric determination.

In some instances, a right solvent mixture, consisting of solvents with different polarities, may be an ideal choice (Duyck, *et al.,* 2007). The use of direct dilution sample preparation technique is restricted by several factors which include: unavailability of organometallic standards, the instability of the sample (after dilution), calibration problems as well as difficulty in determining solutions at the part per billion levels. However, it remains faster and less susceptible to sample loss and contamination (Duyck, *et al*., 2007).

The American Society of Testing and Materials methods D5185 and D4951 are probably two of the most popular methods for determining metal content in lubricating oils. However these methods are not useful when it comes to lubricating grease particularly because the solvents used in these methods are not capable of dissolving lubricating grease (ASTM, D7303, 2010). D5185 covers the determination of 22 elements in base oils and in used lubricating oils, it provides rapid analysis of used oils for evidence of wear. Analysis times are approximately a few minutes for each sample and detection limits for most elements are in the low parts per million range. In addition this test method includes several metals in refined base oils and virgin oil. Kerosene, ortho-xylene and mixed xylenes were successfully employed as dilution solvents (ASTM, D5185, 2005). Test method D4951 covers eight elements only but provides more accurate results than test method D5185, which is intended for the detection of metals used in lubricating oils and base oils (ASTM, D4951, 2009).

(Brown, 1982) determined twenty-one elements in new and used oils using 1:10 xylene dilution. The solution viscosity was found to cause large errors which were significantly diminished by the addition of neutral base oil to the standards. The analysis of constituent elements in lubricating oil additives was found to have an accuracy of 2 to 5% at the 95% confidence level. Combined with appropriate sampling and sample preparation techniques, the final precision for the analysis of wear metals is 5 to 10% and 2 to 5% for additive elements in used lubricating oils at the 95% confidence level.

3.1.2 Microwave Assisted Acid Digestion of Sample

The use of microwave assisted acid dissolution in closed vessels improves the efficiency of the sample mineralization. The main disadvantage with this approach is that it limits the amount of sample that can treated and also reduces sample throughput (Aucelio, *et al*., 2007).

Open vessel digestion using focused microwave devices allows the use of relatively larger sample masses as a result this technique is still occasionally used (Costa, *et al*., 2005). In both cases, risk of contamination from airborne particulates is reduced, but difficulties may still be encountered due to large quantities of mineralizing acids employed and also trace contamination from the digestion vessels (Munoz, *et al*., 2005).

Munoz, *et al*., (2005) used derivative potentiometric stripping analysis (DPSA) for the simultaneous determination of lead and copper in lubricating oils of vehicular engines. In this work lubricating oil samples were completely digested in a focused microwave-assisted oven using a powerful oxidant mixture containing sulphuric acid, hydrogen peroxide and nitric acid. The optimized heating program to digest about 1 mL of lubricating oil took 45 minutes. Residual carbon for all the samples was found to be less than 0.3%. Lead and copper were also analysed by graphite furnace atomic absorption spectrometry (GFAAS), and the results obtained were in good agreement with those obtained by electrochemical measurements. Recoveries of 93–103% and 94–109%, for lead and copper respectively, were obtained for used and new lubricating oil samples (Munoz, *et al*., 2005).

In another research factorial design approach was employed for the optimisation of the microwave assisted digestion of lubricating oil. The effects of the main parameters for the digestion i.e. concentrated acid volumes, digestion time, microwave radiation applied power and sample amount on the digestion efficiency were investigated. All the digestates were analysed for acidity and residual carbon content after microwave assisted digestion. The digestates were then analysed for copper, calcium, phosphorous, sulphur, magnesium and zinc. The accuracy of the method was checked using reference standard, NIST SRM 1848, lubricating oil additive package. Results obtained from certified reference material and all the values determined using the proposed method was in agreement at the 95% confidence level. The microwave applied power, digestion time, sample mass and the interaction between these variables were significant according to p-values when the analysis of variance (ANOVA) was used (Costa, *et al*., 2005).

Sanz-Segundo, *et al*., (1999) investigated the difficulties relating to the optimisation of a microwave assisted acid digestion of lubricating oils in the analysis of wear metals. The advantage of this sample treatment technique lies in the fact that it allows for the analysis of total metal content with enough sensitivity by flame atomic absorption spectrometry (FAAS). A four stage microwave digestion program employing hydrogen peroxide and nitric acid was used to determine lead, chromium copper and iron by flame atomic absorption spectrometry as a representative of engine wear. The detection limits were found to be 0.05 mg/g for lead and copper and 0.1 mg/g for chromium and iron. A comparison with other procedures was also investigated for spiked samples. Used lubricating oil samples supplied by an oil blending company were analysed to demonstrate the accuracy and efficiency of the proposed method (Sanz-Segundo, *et al*., 1999).

Bellido-Milla, *et al*., (2002) proposed a precise, sensitive and rapid method for wear metal determination by flame absorption spectroscopy. The proposed method is based on partial wet digestion in closed vessels assisted by microwaves and it permits the use of inorganic standards. The calibration curve, limits of detection stability and repeatability were established. The proposed procedure was used to analyse six samples with differing levels of wear for copper, lead, chromium and iron by flame absorption spectroscopy. The analysis of variance for both iron and copper applied to all the samples confirms the necessity of acid attack and the importance of HCl for the digestion. This work recommends the use of acids when analysing oils for several wear metals (Bellido-Milla, *et al.*, 2002).

3.1.3 Emulsification of Sample

Emulsification is another alternative sample preparation technique that can be used on lubricating oils. In this approach the organic matter is not destructed by acids and the use of large volumes of organic solvents is avoided. Emulsions lessen the organic content of samples (Lord, 1991) and, when the oil is uniformly dispersed in the water phase, the sample behaves in the same way as an aqueous solution (Sanz-Medel, *et al*., 1999). Addition of acid to the emulsion transforms the analyte species to a homogenous chemical form this minimises adsorption losses and makes the procedure independent of the type of metal wear source (Souza, *et al*., 1999). Like other sample preparation techniques emulsification results in an increase in the detection limits due to sample dilution (Aucelio, *et al*., 2007).

Goncalves, *et al*., (1998) presented an efficient method for the analysis of metals in used lubricating oils, by atomic absorption spectrometry. In this procedure oil samples were acidified using a predetermined acid mixture and then emulsified in water by the inclusion of 6% m/m ethoxy nonylphenol, a surfactant. Emulsion properties i.e. amount of surfactant, oil, surfactant content and acid were optimized to obtain the best AAS signal. Emulsified and aqueous standard solutions gave similar calibration curves when a peristaltic pump was used to introduce solutions into the flame. At the 95% confidence level the emulsification sample preparation technique was comparable to traditional ashing procedures when a standard reference oil and used lubricating oil were analysed. The analysis of real samples using emulsions yielded a precision value between 0.4 – 5% relative standard deviation (Goncalves, *et al*., 1998).

In another research, a method was developed in which tin and antimony are determined in used lubricating oil using electrothermal atomic absorption spectrometry. In this work the used oil sample was introduced into the flame as an oil-in-water microemulsion, this enabled calibration using aqueous standards and made sampling easy and repeatable. A permanent modifier made from a graphite tube treated with ruthenium was used to enable pyrolysis of the oil sample at elevated temperatures without appreciable loss of analytes. The analysis was done using the multi-element sequential routine provided by the atomic absorption spectrometer employed. Good recoveries for both tin and antimony were achieved and these were based on certified reference material and spiked samples respectively. Sub parts per billion limits of detection were estimated for both elements (Aucelio, *et al*., 2000).

Burguera, *et al*., 2000 presented a fast and simple procedure for the on-line preparation of a microemulsion in a flow injection system for the determination of chromium by electrothermal atomic absorption spectrometry (ETAAS) with Zeeman background correction. The whole system was controlled by a computer independent of the spectrometer. In this method, the sample solution was introduced into the hexane carrier system by injecting a 1 mL of the solution which was subsequently mixed with streams of 5% (v/v) sodium dodecysulphate, 5.0% (v/v) sec-butanol and 3.8% (m/v) sodium chloride. The flow rates of the carrier, sodium dodecysulphate, sec – butanol and sodium chloride were 1.0, 0.5, 0.2 and 0.5 mL min^{-1} respectively. The stability of the emulsion was enhanced by the sonication of the flowing solutions. An emulsified sub-sample of 200 µL was collected in a capillary of a sampling arm assembly. Thereafter, 20 µL of this sample solution were introduced by means of positive displacement with air through a time-based solenoid injector (TBSI) in the graphite tube atomizer. In order to minimise the sputtering of the sample in the atomiser a furnace program employing two drying steps at 110 and 130 °C respectively was used. Pyrolysis, atomization and cleaning temperatures of 1600, 2400 and 2500 °C were employed to achieve good peak profiles with low background signals without the use of any chemical modifier. The method exhibits a linear range for chromium from 7.0 - 50 µg L^{-1} and detection limit of 6.0 ng g $^{-1}$ which equates to 4.0 µg L^{-1}. The analysis of spiked samples gave recovery results ranging from 99.2 to 102.2% and relative standard deviation ranging from 0.6 to 0.8% confirmed the precision of the method. The agreement between values obtained from NIST (National Institute of Standards and Technology) reference material and the observed values was good and the procedure described as satisfactory for the determination of chromium in new and used lubricating oil samples (Burguera, *et al*., 2000).

Amorim, *et al*., (2007) proposed two methods for vanadium determination in fuel oil using graphite furnace atomic absorption spectrometry GFAAS. The first is based on the preparation of a microemulsion followed by direct injection into the graphite tube. The pyrolysis and atomization temperatures were selected from the temperature curves and were 1500 and 2700 ℃, respectively. This method permits analysis of vanadium with a detection limit of 0.10 µg g^{-1} and characteristic mass of 87 pg. The second method employs total acid digestion of the sample with nitric acid, hydrogen peroxide and sulphuric acid. Pyrolysis and atomization temperatures were 1000 and 2700 °C, respectively. A detection limit of 0.25 µg g^{-1} and a characteristic mass of 63 pg was achieved. Certified reference material NIST SRM 1634c-trace metals in fuel oil was analysed to confirm the accuracy of the two methods (Amorim, *et al*., 2007).The analytical characteristics i.e. limit of detection, accuracy and precision demonstrated the efficiency of the proposed method in the determination of vanadium in fuel oil samples using graphite furnace atomic absorption spectrometry. The use of the standard calibration technique with microemulsions, prepared using inorganic standards and base mineral oil made the procedure quite simple and fast. The results demonstrated that the methods could be satisfactorily applied for analysis of fuel oil samples (Amorim, *et al*., 2007).

Martins Souza, *et al*., (2004) presented a simple analytical procedure for the determination of Ni, Mo, Cr, V, and Ti in used lubricating oil by ICP-OES. Sample were prepared and introduced as detergent emulsions. The instrumental and experimental parameters were optimised to obtain sensitive, accurate and precise determination of these refractory metals in oil samples, using calibration curves prepared with triton-100 and Sc as an internal standard. By comparing the proposed methodology with the traditional ones, several practical advantages over the acid sample decomposition procedure and superior analytical performance over direct sample dilution using organic solvent procedure were found. The limits of detection and quantification in the ngg^{-1} range were achieved for all five refractory elements. The methodology was validated with lubricating oil standard reference material with excellent results (95%: n=4) for Ni, Mo, V and Ti. Recoveries in the range of 90% were achieved. These results were similar to those obtained with acid decomposed samples and can still be considered appropriate for this type of analytical problem (Souza, *et al*., 2004).

Wang, *et al*., (2003) developed a method for the simultaneous determination of twenty-one elements in organic matrices. In this procedure the samples were dispersed in concentrated nitric acid by sonication, and the resulting emulsions / suspensions were directly aspirated into an inductively coupled plasma atomic emission spectrometer (ICP-AES). Aqueous standards were used for calibration. Recoveries obtained from a 21-element metallo-organic reference material were used for validating the procedure. Analysis on a waste oil sample was done using the proposed method and a method employing microwave digestion and the results obtained compared favourably. Similar results were also obtained by diluting the sample in an organic solvent followed by ICP-AES analysis with an ultrasonic nebulizer equipped with a membrane desolvator. The accuracy of this method was also confirmed by the use of a NIST standard reference material 1084a wear metals in lubricating oil. The limits of quantitation were 6 μg g^{-1} or less for all the elements analysed and spike recoveries ranged from 83 to 105% (Wang, *et al*., 2003).

Other components of grease have also been determined, ASTM D128, (1998) covers the analysis of typical lubricating greases which consist essentially of petroleum oil and soap. The components that can be determined are unsaponifiable matter, soap, glycerine, fat, water, insoluble, free alkalinity and free fatty acids (ASTM D128, 2008).

The determination of soap involves the decomposition of the sample of grease by boiling under reflux condenser in a mixture of 50ml n-hexane and 20ml 10% hydrochloric acid. Formation of a clear oil layer is evidence of complete decomposition, digestion time is normally 3hrs, more vigorous boiling or use of a stronger HCl solution or additional n-hexane is necessary for greases difficult to decompose. For heavy greases, 50 mL of toluene may be substituted for n-hexane. The digested sample is then transferred to a separatory funnel and the aqueous layer which contains all the bases as well as glycerine is separated from the organic layer. An approximate determination of free fatty acids from soap can now be determined by titrating the organic solution with potassium hydroxide solution. From the total quantity of fatty acid found deduct the free acid and calculate the remainder as a percentage of soap (ASTM D128, 2008). In as much as constituents of lubricating grease other than metals can be determined, they might not necessarily give an insight as to the presence and degree of contamination and if they do the methods are strenuous and time consuming and will be impossible to employ on a routine basis as indicated by the determination of soap content described above. None the less some of the techniques and solvents can still be employed to develop better and easier methods.

Algeo, *et al*., 1985, evaluated new equipment and procedures for the direct determination of metals in lubricating oils, without the need for sample pre-treatment or dilution. In this work it was shown that a modified Babington principle nebulizer equipped with a sample heater is capable of producing aerosols from undiluted oils, which are suitable for introduction into an inductively coupled plasma atomic emission spectrophotometer. Additionally the work showed that heating of the oil samples before nebulisation significantly increases the output of aerosol and the variations in emission intensities due to differences in viscosity and lubricating oil manufacture are reduced. The type of organometallic complex employed in the preparation of standards is shown to be insignificant if the plasma observation region is properly selected (Algeo, *et al*., 1985).

CHAPTER 4

EXPERIMENTAL DESIGN

4.1 Chemicals and Materials

Table 4.1 below shows chemicals and materials used in the course of this work.

Table 4.1 Materials and Suppliers

Material	Supplier
65% nitric acid Extra Pure	Merck Chemicals
37% hydrochloric acid	Merck Chemicals
concentrated sulphuric acid	Merck Chemicals
1000 mg/L cobalt internal standard	Supelco
1000 mg/L S27 Multi element standard Al, Ba, Ca, Li, Na and Zn	Supelco, Spectrascan Custom blend certified reference solution
1000 mg/L S28 Multi element standard B, Mo, P and S	Supelco, Spectrascan Custom blend certified reference solution
Kerosene	Was supplied as a sample by Shell (Belgium)
Toluene ≥ 99% purity	Sigma Aldrich
Xylene anhydrous ≥ 99% purity	Sigma Aldrich
Shellsol A	Was supplied as a sample by Shell
S21 Standard Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn	Conostan Oil Analysis Standards
Low Aromatic White Spirits	Was supplied as a sample by Shell (Belgium)
Platinum Crucibles	Fischer Scientific
500 mL internal epoxy lined tin cans	Nampack
t-octylphenoxypolyethoxyethanol Triton X-100	Sigma Aldrich
Hydrogen Peroxide	Sigma Aldrich

Deionised water with a resistivity of >18 MΩ cm, produced by a Milli-Q Plus pure water generating system from Millipore was employed for all preparations of standards and sample solutions.

4.2 Sampling and Sample Preparation

500 mL internal epoxy lined tin cans with screw metal caps were used as grease sample containers. Sample containers were cleaned first with soap and warm water, and then soaked in 10% nitric acid and then air dried, to ensure that they are free from all substances which may contaminate the grease. The 500 mL can was filled with samples almost to the top and immediately capped. The sample container was labelled using waterproof and oil proof ink. The sample was then thoroughly homogenised to ensure that it is a representative sample. Samples were stored in a dry cool cupboard to prevent degradation from light, heat or other detrimental conditions. After sampling, four sample preparation techniques for the determination of metals were investigated. The standard and sample preparation for each method is described below.

Lubricating grease is a complex matrix to work with and a sample preparation technique that is most accurate and repeatable is crucial for the accurate determination of the lubricating grease product. Two mineralisation techniques were explored namely sulphated ashing and microwave assisted acid digestion. Direct dilution and emulsification do not require the destruction of the organic matrix before introduction into the instrument and these two techniques were also explored.

4.2.1 Sample Preparation for Sulphated Ashing

The sample of grease was prepared as follows:

1. 5 g of grease sample was accurately weighed into a platinum crucible, and the sample charred on a hot plate until it was no longer oily.
2. The charred sample was cooled and 1-2 mL of sulphuric acid added, this was carefully heated on the hot plate taking care to avoid sputtering of contents until fumes were no longer evolved.
3. The charred sample was placed in a Carbolite CFW 1200 muffle furnace at 525 ºC until the oxidation of the carbon was practically complete. If the ashing was not complete as indicated by the presence of a black colour of the residue, step 2 was repeated to complete the sulphasation.
4. 5 mL of reverse aqua regia was added to the residue and the mixture heated gently to dissolve the remaining solids.
5. The resulting solution was quantitatively transferred to a 50 mL volumetric flask, made to volume with deionised water.

4.2.2 Sample Preparation for Microwave Assisted Acid Digestion

A CEM Mars 5 microwave digester shown below was used to digest the sample.

Fig 4.1 Image of the CEM Mars 5 microwave accelerated reaction system

The system consists of a microwave power system with user selectable power settings (0-1200 Watts), fluoropolymer-coated microwave cavity (oven interior), cavity exhaust fan and tubing to vent fumes, programmable microcomputer that controls and monitors the power, temperature, and pressure within the reaction vessels, and is capable of storing 100 programs with up to five reaction stages per program, explosion proof reaction vessels, an alternating turntable that turns the samples 360 degrees within the microwave field, a door safety interlock system that prevents exposure to microwave emissions when the system is running.

1. About 0.2 g of grease sample was accurately weighed into a PTFE digestion vessel.
2. 8 mL of reverse aqua regia was added
3. The vessel was sealed and properly placed in the microwave system as per the manufacturer's instructions.
4. The microwave program given below was used to digest the sample.

Step	Reagent added	Power / W	Time / min
1	8 mL R-aqua regia	125	30
2		190	15
3	2 mL hydrogen peroxide	190	5

5. At the end of the microwave program the vessels were allowed to cool for a minimum of 5 minutes before removing them from the microwave system.
6. The vessels were then placed in an ice bath for about half an hour and the dissolved samples were quantitatively transferred into a 100 mL volumetric flask.
7. 2.5 mL of 100 ppm cobalt internal standard was added to the solution and brought to volume with deionised water.

8. The solution in step 6 above was then filtered and analyzed.

4.2.3 Standard Preparation for Sulphated Ashing and Microwave Assisted Acid Digestion

1. 100 ppm of both multielement standards S27 and S28 was prepared by pipetting 10 mL of standard into a 100 mL volumetric flask and made up to volume with 5% reverse aqua-regia.
2. 10 ppm, 20 ppm and 40 ppm standard solution were made by pipetting 10 mL, 20 ml and 40 mL of solution in (1) above respectively into a 100 mL volumetric flask and adding 5 mL of a 100 ppm internal standard stock solution into each of the flasks and made up to 100 mL with reagent blank from a burette. See Table 4.2 below.

Table 4.2 Preparation of standards for ashing method and microwave assisted digestion.

Std Concentration / ppm	Volume of 100 ppm solution S21/S27 / mL	Volume of 100 ppm Cobalt (IS) solution / mL	Volume of reagent blank / mL
Blank	Nil	5	95
10	10	5	85
Test Std 15	15	5	80
20	20	5	75
40	40	5	55

4.3 Direct Dilution Technique Using Organic Solvents

In this method the lubricating grease sample is diluted using different solvents and solvent mixtures to determine a solvent or a solvent combination that gives the best recovery of the relevant analytes. Table 4.3 below illustrates the solvent mixtures used.

Table 4.3 Solvent combinations used for organic solvent dissolution.

	White spirit	Toluene	Xylene	Kerosene	Shelsol A
White spirit	🟩	🟨	🟨	🟨	🟨
Toluene		🟩	🟨	🟨	🟨
Xylene			🟩	🟨	🟨
Kerosene				🟩	🟨
Shellsol A					🟩

Pure	🟩
Mixture	🟨

4.3.1 Sample Preparation for Direct Dilution

1. 5 g of lubricating grease was accurately weighed into a 300 mL beaker
2. The weighed grease was made up to 100 g with clean base oil (YUBase 4).
3. The resulting mixture was thoroughly mixed using a Silverson laboratory mixer for 8 minutes.
4. Immediately 2 g of this mixture was weighed into a sampling bottle and made up to 20 g with solvent or mixture of solvents to prevent the sample from settling out before analysis. (See table 4.3 above for the solvent combination used in this project.

4.3.2 Standard Preparation for Direct Dilution

The standards and the samples should be matrix matched and hence a certain amount of standard was weighed and made up to a specific mass with a base oil so as to maintain the same oil content in both the standards and in the sample e.g. for making a 5 ppm standard 0.2 g of the conostan oil standard S21 was weighed and made up to 2 g with base oil and then diluted to 20 g with the solvent or mixture of solvents. See Table 4.4 below for preparation.

Table 4.4 Preparation of standards for the direct dilution method.

Concentration / ppm	**Mass of Std / g**	**Mass of base oil / g**	**Mass of solvent / g**	**Final mass / g**
5	0.2	1.8	18	20
10	0.4	1.6	18	20
Test std 15	0.6	1.4	18	20
20	0.8	1.2	18	20
40	1.6	0.4	18	20

4.4 Emulsification Method

4.4.1 Sample Preparation for Emulsification

1. 5 g of lubricating grease was accurately weighed into a 300 mL beaker
2. The weighed grease was made up to 100 g with clean base oil (YU Base 4).
3. The resulting mixture was thoroughly mixed using a Silverson laboratory mixer for 8 minutes.
4. 1 mL of the mixture above was placed in a 10mL volumetric flask and 0.5 mL of concentrated nitric acid was added and the resulting mixture was sonicated for 5 minutes.
5. 0.1 mL of surfactant (triton X-100) was added and mixture was made up to 10 mL with deionised water under slow and continuous agitation.
6. The volumetric flask was vigorously shaken for two minutes and placed in an ultrasonic bath for 5 minutes. The emulsion prepared was stable for up to 40 minutes and hence had to be analysed within that time.

4.4.2 Standard Preparation for Emulsification

The standards were prepared in exactly the same way as the sample, in order to match the sample matrix, for comparison sake aqueous standards were prepared as described for microwave digestion and sulphated ashing.

1. 1 mL of base oil YUBase 4 was placed in a 10 mL volumetric flask and 0.5 mL concentrated nitric acid was added, the resulting mixture was sonicated for 5 minutes.
2. 0.1 mL of surfactant (triton X-100) was then added followed by 0.5 mL, 1 mL, 1.5 mL, 2 mL and 4 mL of multielement standard (either S21 or S27) to make 5 ppm, 10 ppm, 15 ppm, 20 ppm and 40 ppm respectively.
3. The resulting mixture was made up to 10 mL with deionised water under slow and continuous agitation.

4.5 Analysis of Standards and Samples

The samples and standards were analyzed using Perkin Elmer Optima 5300V with advanced 40 MHz free running RF generator, Win Lab software and Segmented-array Charge-coupled Device (SCD) detector.

Fig 4.2 Image of the Optima 5300V

ICP Operating Parameters

Power	:	1.3 kW
Plasma gas flow	:	15 L/min
Auxiliary gas flow	:	0.80 L/min
Nebuliser gas flow	:	0.8 L/min
Nebuliser type	:	glass concentric nebuliser
Spray Chamber	:	glass cyclonic spray chamber
Torch	:	axial high solids
Sample Uptake rate	:	1.0 mL/min
Integration time	:	10 s
Flush time	:	30 s
Replicates	:	3

Selected elements and their chosen spectral lines for all four sample preparation techniques.

Table 4.5 Elements and their selected wavelengths chosen for analyses.

Element	**Wavelength / nm**
Aluminium	308.22 ; 396.15 ; 309.27
Boron	249.677 ; 208.889
Barium	455.403 ; 493.41 ; 223.53
Calcium	422.673 ; 396.85 ; 315.88
Lithium	670.784 ; 610.36 ; 460.29
Molybdenum	202.03 ; 281.62
Phosphorus	213.62 ; 214.91 ; 253.40
Sodium	589.595
Zinc	206.200 ; 206.2 ; 213.86

Analyses were done on four lubricating grease samples using all the four sample preparation techniques and results compared with quality control samples obtained from Shell Belgium to ascertain the efficiency of the techniques used for sample preparation.

4.6 Validation Procedures

4.6.1 Limits of Detection (LOD) and Limits of Quantitation (LOQ)

Detection and quantification limits were calculated as signals based on the mean blank (x_{avg}), and the standard deviation of blank responses (S_b) by means of the equations below

$L_D = x_{avg} + 3S_b$

$L_Q = x_{avg} + 10S_b$ Where L_D refers to LOD and L_Q refers to LOQ.

x_{avg} and S_b were determined by performing ten blank measurements.

4.6.2 Selectivity

Selectivity refers to the extent to which a method can determine particular analytes in mixtures or matrices without interferences from other components. The specificity of this method was established by running a 10 ppm standard of both S27 and S28 and scanning at the selected wavelength for each element to ensure it is giving an optimised response at the selected wavelength.

4.6.3 Repeatability

Repeatability was determined by 6 determinations at 5 ppm, 10 ppm and 20 ppm analyte concentrations using one piece of equipment over a relatively short time-span and the relative standard deviation calculated.

4.6.4 Linearity

The linearity of an analytical method is defined as the ability of the method to obtain test results proportional to the concentration of analyte in the sample. To check the linearity of this method, a range of standards solution in de-ionized water at the concentrations of 0, 5, 10, 20 and 40 mg/L were analysed six consecutive times per standard at the optimum conditions. The average absorbance of each standard was calculated and used to plot the linearity graphs for all the elements analysed in this project.

4.6.5 Recovery

The recovery of this method was determined by running a series of standards i.e. blank, 5 ppm, 10 ppm, 20 ppm and 40 ppm plotting the linear graph of intensity versus concentration. A control standard 15 ppm was then run and the results obtained compared to the known concentration.

For example if the control Standard shows a calcium concentration of 14.97 ppm the % recovery would be:

$\% \text{ Recovery} = [(C_{\text{Actual}}) / (C_{\text{Expected}})] \times 100$

Where C_{Actual} and C_{Expected} are the actual and expected concentrations respectively.

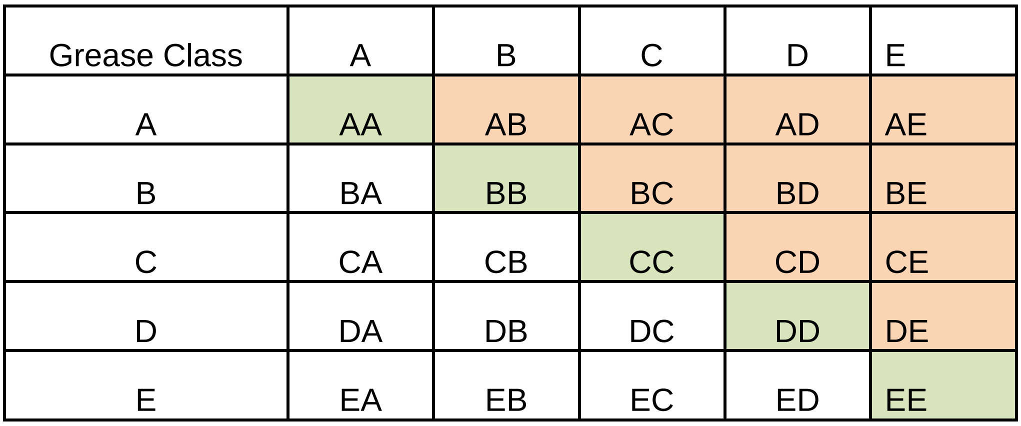
$\% \text{ Recovery} = [14.97/15] \times 100$

$= 99.8\ \%$

4.7 Flushing Matrix Experiments

These were done to determine the amount of flushing required when switching from one grease type to another. Representative samples from different family groups i.e. lithium simplex (A), lithium complex (B), calcium simplex (C), calcium complex (D) and clay based grease (E) were obtained in the middle of fill i.e. after filling at least 1000 kg of product (these were considered the quality control samples as they were expected to be free from contamination from the previous batch of lubricating grease). Samples were also obtained after flushing the line with 60 kg, 80 kg, 100 kg and 120 kg of product.

Table 4.6 Possible Inter-class Combinations for Lubricating Grease.



Grease Class	A	B	C	D	E
A	AA	AB	AC	AD	AE
B	BA	BB	BC	BD	BE
C	CA	CB	CC	CD	CE
D	DA	DB	DC	DD	DE
E	EA	EB	EC	ED	EE

Where

A	Lithium Simplex
B	Lithium Complex
C	Calcium Simplex
D	Calcium Complex
E	Clay

And

🟩 A sample was taken at the middle of fill i.e. after running 1000 kg of product.

🟧 Samples were taken after flushing with 60 kg, 80 kg, 100 kg, 150 kg and 200 kg of product.

Table 4.7 Grease combination and their contamination indicator.

Grease combination	**Indicative metal element**
AB	B
AC	Li/Ca
AD	Li/Ca and B
AE	Li
BC	Li/Ca and B
BD	Li/Ca
BE	Li/B
CD	B
CE	Ca
DE	Ca/B

Where AB indicates flushing from grease type A (Lithium Simplex) to B (Lithium Complex) and the indicative metal shows the degree of contamination and hence the amount of flushing.

4.8 Quality Assurance

For all samples and standards the mean of three replicate readings was taken. The performance of the instrument and the test procedure was monitored by analyzing a quality control sample after every fifth sample and if the control sample results are within specification the analysis was continued whilst failure to comply with the specification required that a recalibration be carried out.

CHAPTER 5

RESULTS AND DISCUSSION

5.0 Introduction

One of the main objectives of this project was to develop a simple reproducible and quick method for elemental determination in lubricating grease, as this helps in product characterisation and can be used to determine the degree of cross contamination during manufacturing. Before analysing the lubricating grease for different elements by instrumental techniques, it is important to prepare the sample in an appropriate form. In this research the following sample preparation techniques were compared:

- Mineralisation of the grease using different acids and conversion of the total metal content to a simple water soluble species,
- Direct dilution, where the lubricating grease was simply diluted with a suitable solvent, and
- Emulsification where a sample is evenly dispersed in an aqueous medium as microdroplets, stabilized in micelles or vesicles originating from the addition of a suitable detergent.

Before comparing results of the four techniques with actual samples, method development was performed using reference material. Method validation was then performed, and it is through this validation that detection limits, quantitation limits, precision, accuracy and linearity were established. Since most of the elements cannot be calculated theoretically as there is no information on their concentrations on the raw material certificate of analysis, only the more prominent metals lithium, calcium and boron were used for the microwave digestion, emulsification, sulphated ashing and direct dilution method development.

5.1 Boron, Lithium and Calcium

Complex greases are those whose basic ingredients have been fortified or treated so that they give exceptional performance in a given application (Fox, 2004). A more complex structure can be formed by using a complexing salt, thus converting the thickener to a soap-salt complex. Complex greases were developed to improve the heat resistance of soap greases, the most popular being lithium, aluminium, calcium and barium. Complex greases are similar to regular greases except that the thickeners contain two dissimilar acids (one fatty, one inorganic) which impart high temperature characteristics in the final product. The most commonly used complexing agents are dimer acids such as azelaic, adipic and boric acid. However, the latter is the most commonly used (Gow, 2010). Boron is therefore the main indicator of contamination when switching from complex grease to simplex grease. Calcium and Lithium are obviously indicators when switching from calcium soap grease to lithium soap grease and hence the importance of their determination is apparent.

5.2 Sample Analysis

5.2.1 Microwave Digestion

First, the method proposed by ASTM for elemental determination in lubricating grease, D7303 was tested. Since there were no lubricating grease standards to match the products at Blendcor (this is one of the major setbacks in the analysis of lubricants i.e. absence of reference materials), previously analysed grease samples from a more advanced overseas grease plant was used as the standard. Following the method presented in D7303 about 0.2 g of grease sample was put into a PTFE digestion vessel together with 10 mL of 32% nitric acid.

The digestion procedure used a two stage program 125 W for 15 min (stage 1) and then 190 W for another 15 min (stage 2). This digestion procedure did not adequately digest both complex grease and clay based grease samples as shown by a greasy ring lining the walls of the digestion vessels at the end of the digestion cycle, and recoveries were relatively low for all grease types as shown in Table 5.1 below.

Table 5.1 Recoveries for boron, calcium and lithium in four grease products.

Grease Type	Indicative Metal	Theoretical Concentration/ ppm	Actual Concentration/ ppm	% Recovery
Lithium Sx	Li	3516	1793	51
Lithium Cx	B	2309	1208	52
Calcium Sx	Ca	1564	772	49
Calcium Cx	B	2309	1249	54

In order to come up with an efficient microwave digestion procedure the parameters that affect the digestion process, such as sample amount, concentrated acid volumes, microwave radiation applied power, and digestion time, should be investigated. If however I were to investigate all of the parameters this would take a considerable amount of time and so a digestion procedure based on microwave digestion of other similarly complex lubricants and fuels was used.

Sample amount - It is well known that the use of closed reactors implies risk of explosions because a great deal of gas is produced in a short time, and also the use of oxidising acids for the digestion increases the amount of gas produced. In this study 0.5 g of grease was used.

Concentrated acid mixture and volume - An ideal digestion method is one with a minimum amount of solid residue or preferably none at all. Breaking down of fatty component requires drastic conditions and literature indicates that nitric acid or a mixture of nitric acid with another acid is sufficient to successfully destroy the organic matrix.

Additionally the volume of the reagents used is limited to avoid excessive dilution of the sample. A 3:1 mixture of concentrated nitric acid and hydrochloric acid (reverse aqua regia) had already been tested in the microwave by other authors (Kuss, 1992) but with similar kinds of sample. This mixture was thus applied to the digestion of lubricating grease samples. Hydrogen peroxide has a clarifying effect after digestion, and therefore the last stage of the digestion programme included the addition of hydrogen peroxide.

Radiation power and time – Taking into account the high reactivity of the grease with the mixture of nitric acid and hydrochloric acid, the heating had to be done gently to avoid destruction of the safety membranes, over a longer period of time and this in turn implies use of longer times. Gradual ramping of the operating power ensures that the digestion proceeds safely and avoids the production of large volumes of gases at one go. Hence the programme outlined in Table 5.2 below which is a modification of the initial D7303 was finally adopted for the digestion of the lubricating grease samples.

Table 5.2 Microwave program for the digestion of lubricating grease.

Step	Acid	Power / W	Time / min
1	10 mL RAR	125	15
2		190	15
3		250	15
4	2 mL H_2O_2	190	5

The best results for the four grease types were obtained with this treatment, since the samples appeared to be completely dissolved when the digestion vessels were opened. Nevertheless after cooling down, a very thin oily layer appeared on the aqueous phase. Cobalt was used as an internal standard for the quantification of the analytes because the high proportion of nitric acid in the final solution affected the transport of sample solutions to the plasma. Results shown in Table 5.3 were obtained for the revised digestion method.

Table 5.3 Recoveries for boron, calcium and lithium using the 4 stage microwave program.

Grease Type	Indicative Metal	Theoretical Concentration / ppm	Actual Concentration / ppm	% Recovery
Lithium Sx	Li	3516	3512	99.9
Lithium Cx	B	2309	2274	98.5
Calcium Sx	Ca	1564	1565	100.1
Calcium Cx	B	2309	2270	98.3

It has been proven that microwave digestion can be used to accurately prepare samples containing “volatile’ boron compounds (Nadkarni, 2005). However in this case the lower boron results may have been caused by the release of gas under high pressure causing the loss of volatile boron. However, adequate recoveries were obtained for calcium and lithium both with relative standard deviation less than 2%.

5.2.2 Sulphated Ashing

ASTM D7303 was followed for the sulphated ashing of lubricating grease samples (procedure is outlined under experimental section). This is an old technique with a relatively long procedure. It uses the same inorganic standards as the microwave digestion, and it also has its short falls when it comes to the analysis of real samples. Most apparent was the loss of volatiles to the atmosphere. Sulphur cannot be determined for the sulphated ashing as sulphuric acid is used for the ashing process. An average of nearly 65% of the boron was lost due to volatilisation during the sulphated ash procedure. This procedure has shown a higher propensity to spatter resulting in ejection of analytes from the crucible and hence low recoveries for all three elements were obtained as shown in Table 5.4 overleaf.

Table 5.4 Recoveries for boron, calcium and lithium after the sulphated ashing.

Grease Type	Indicative Metal	Theoretical Concentration / ppm	Actual Concentration / ppm	% Recovery
Lithium Sx	Li	3516	2672.0	76
Lithium Cx	B	2309	1500.8	35
Calcium Sx	Ca	1564	1376.0	88
Calcium Cx	B	2309	761.0	33

5.2.2.1 Method Validation

Method linearity was determined by analysing a blank and five standards from 5 ppm to 40 ppm of a mixed standard. Serial dilution was used to prepare the different concentrations from a 100 ppm solution. Linear dynamic ranges were obtained for all elements as shown by the correlation value. The limits of detection (LOD) ranged from 0.028 mg/L for sodium to 0.255 mg/L for boron as shown in table 5.5 below. Limits of quantitation (LOQ) were ranging from 0.09 mg/L for sodium to 0.47 mg/L for sulphur. Correlation coefficient values (R^2) for all the elements were greater than 0.99 this indicates that the calibration curves were good for analysing the digested grease samples. Recovery was determined by analysing calibration standards 5 ppm, 10 ppm, 20 ppm, 40 ppm and by running a control standard 15 ppm that was separately prepared. Recovery was then determined using the equation shown below.

$$\% \text{ Recovery} = [(C_{\text{Actual}}) / (C_{\text{Expected}})] \times 100$$

Overall recovery for all the elements was noted at 100 ± 3%, thus meeting the quality control objective for most of the analytical methods. The mean RSD for the all of the elements is under 2%.

Table 5.5 Validation figures for inorganic method (sulphated ashing and microwave digestion).

Element wavelength	Correlation Coefficient R^2	Avg % Recovery	Precision % RSD	LOD / mg/L	LOQ / mg/L
Ca	0.996	100.70	1.20	0.14	0.43
B	0.999	100.92	1.01	0.26	0.81
Al	0.999	102.85	0.76	0.10	0.31
Na	0.998	102.20	0.58	0.03	0.09
S	0.995	99.75	1.35	0.15	0.47
Mo	0.999	99.47	0.60	0.07	0.23
Zn	1.000	101.87	0.56	0.10	0.33
Ba	0.999	100.34	0.85	0.05	0.16
Li	0.999	100.05	0.74	0.06	0.20

5.2.3 Direct Dilution

In this method 5 g of lubricating grease was shear mixed with clean base oil (not containing any metal elements), just the shear mixing itself resulted in sample loss as some of the grease got stuck on the walls of the container, or on the blades of the shear mixer. The shear mixed mixture also had to be used immediately as it had a tendency to separate out thereby compromising the homogeneity of the sample. After shear mixing the mixture was then dissolved in an organic solvent for analysis by ICP. The solvents recommended by ASTM D4951 (elemental determination in lubricating oils) were first tried. The solvents low aromatic white spirit used in ASTM D 4951 for the elemental determination in lubricating oils but this solvent did not adequately dissolve the shear mixed sample and hence non- reproducible results for most metals was obtained.

Toluene and benzene are two of the solvents also tried out in this work, but increased organic content in the sample increased carbon build-up on the quartz torch, affecting the performance of the instrument in subsequent samples. Carbon accumulation on the tip of the torch injector tube is a general problem associated with samples containing high levels of organics or organic solvents. It was also noted that the use of these solvents caused plasma destabilization or even plasma extinction. The toxicity of these organic solvents requires special care to avoid any health hazards for laboratory personnel. A mixture of metal free aviation kerosene and xylene was finally used, as it dissolved the shear mixed sample much better than the other solvent combinations. Analysis of the samples with this solvent combination yielded the following results.

Table 5.6 Recoveries for boron calcium and lithium after direct dilution.

Grease Type	Indicative Metal	Theoretical Concentration / ppm	Actual Concentration / ppm	% Recovery
Lithium Sx	Li	3516	1160.0	33
Lithium Cx	B	2309	969.8	42
Calcium Sx	Ca	1564	797.6	51
Calcium Cx	B	2309	715.8	31

The direct dilution method gave the most inconsistent results, with % RSD values as high as 56% for calcium, 79% for boron and 66% for lithium. Solutions of Conostan standards diluted in the kerosene and xylene gave a broad range of linearity and good precision. However when actual samples were tested the recoveries were inconsistent, as shown in Table 5.6 above and this was attributed to the heterogeneity of the sample. Additionally there can also be alteration in concentration caused by the evaporation of solvent and metal deposition on the walls of the containers. Due to the fact that the solutions are unstable after 48 hours, standards and samples were freshly prepared.

5.2.4 Emulsification

A system based on oil in water microemulsion is very advantageous, more so for a manufacturing company like Blendcor (Pty) Ltd as there is a tremendous reduction in the cost of analysis. It is similar to aqueous solutions and therefore easier to obtain optimised instrument parameters for analysis.

It also uses cheaper inorganic standards and for this reason this sample preparation technique was explored. The composition and mode of preparation of the microemulsion was based on previous work described by Aucelio, *et al*., (2002), and was adopted for this work with a few modifications to suit the lubricating greases. The lubricating grease had to be shear mixed with a metal free base oil so as to resemble lubricating oil. Shear mixing is blending liquids with similar or greatly varying viscosities at high rotation speeds to produce a homogenous product. Aviation kerosene was added to further reduce the viscosity. The stability and homogeneity of the emulsions were evaluated visually, and timed from the initial shaking until the sudden phase separation of the emulsion components. This was achieved by keeping the mass of oil sample constant at 5% by mass, and varying the surfactant mass.

Table 5.7 Time taken for the phase separation to occur for the microemulsion mixtures.

% composition of surfactant / g	Stability time / min
1	Unstable
2	Unstable
3	Unstable
4	7.0
5	17.0
6	40.0
7	39.5
8	39.0
9	39.6
10	39.4
15	12.0
20	10.0

Detergent emulsions utilise surfactants to stabilise the oil microdroplets into the aqueous medium. Ionic surfactants especially anionic ones introduce large amounts of ions into the solution which may affect plasma conditions and usually require a basic medium to form the emulsions, which are not suitable for trace element determinations. Triton X has a hydrophilic-lipophilic balance in the appropriate range for stable oil in water emulsions and is readily available in most laboratories and hence is usually the surfactant of choice among the non-ionic surfactants. From Table 5.7 it can be seen that mixtures containing between 6-10% surfactant (Triton X100) produced emulsions that were stable for approximately 40 minutes compared to the other mixtures. Emulsions containing less than 6% of surfactant were stable for less than17 minutes. Triton X-100 concentrations below 4% did not allow the emulsification of samples. The microemulsion stability decreased with higher amounts of surfactant. For the purposes of this research the emulsion containing 6% surfactant was used. A previous addition of concentrated nitric acid was employed in order to dissolve metallic particles and to decompose metallorganic species. The volume of nitric acid was limited to 0.5 mL so as not to affect the magnitude of the analyte emission signals. The instrumental conditions were optimised to guarantee the maximum analyte signal from the microemulsion and to enable proper correlation with analyte standards. The optimised conditions for the analyses are summarised in the experimental section.

Calibration curves were established using emulsified base oil with increasing concentration of analytes from which analytical figures of merit were obtained. The recommended uptake rate of 2 mL min^{-1} for aqueous samples was used in this research which confirms the aqueous behaviour of the emulsions. Emulsified standards using metal free base oil were analysed and the figures of merit determined are shown in Table 5.8 overleaf.

Table 5.8 Analytical data obtained using emulsified base oil standards.

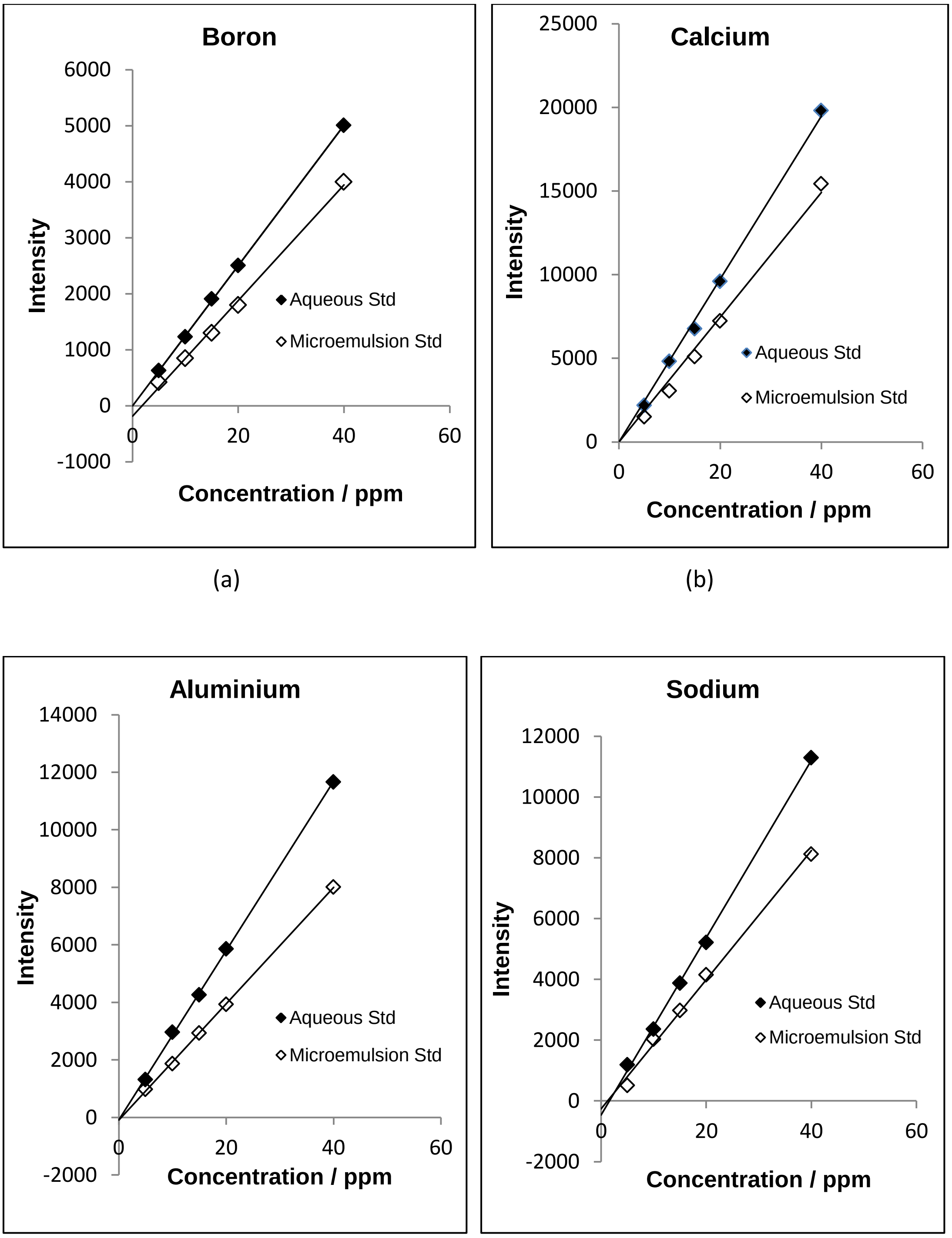
Element	Correlation Coefficient R^2	Avg % Recovery	Precision RSD %	LOD / mg/L	LOQ / mg/L
Ca	0.996	101.20	4.20	0.20	0.65
B	0.993	99.20	3.30	0.03	0.47
Al	0.999	100.40	0.80	0.03	0.03
Na	0.999	100.40	0.90	0.04	0.14
S	0.997	103.00	1.10	0.20	0.67
Mo	0.996	109.20	1.60	0.09	0.31
Zn	0.998	101.40	3.60	0.15	0.51
Ba	0.994	103.20	4.50	0.09	0.30
Li	0.997	99.90	3.90	0.09	0.31

The possibility of using aqueous inorganic standards was also investigated by making standards in 6% triton-X 100 aqueous solution. The statistical test in which the regression lines are used for comparing analytical methods was applied in order to estimate possible systematic differences between the two calibration methods. The responses obtained from a series of aqueous standards were plotted against the responses obtained from an identical series of oil emulsion standards. The calibration curves for the elements, B, Ca, Al, Na, S, Mo, Zn, Ba and Li are given in Fig 5.1 (a to i) below. The calculated values of slope and intercept with their confidence interval (at 95% confidence level), obtained from all oil matrices, and each spectral line of the studied elements, are presented in Table 5.9. For statistical reasons the values obtained were not rounded.

Table 5.9 Slope, intercept and R^2 values for both aqueous and emulsion solutions.

	Aqueous Standards			**Emulsified Standards**		
	Intercept	Slope	R^2	Intercept	Slope	R^2
Al	75.710	294.000	0.999	92.840	202.200	0.999
B	1.660	125.100	0.999	0.000	96.190	0.997
Ba	3721.000	7406.000	0.999	-3132.000	5225.000	0.999
Ca	-433.800	503.900	0.999	-807.400	403.800	0.999
Li	3421.000	20176.000	0.999	-3932.000	11007.000	0.999
Mo	-52.290	274.900	0.999	-280.700	155.400	0.997
Na	-459.900	291.600	0.999	-263.300	212.400	0.999
S	17.600	17.530	0.995	6.808	7.930	0.999
Zn	-258.400	494.200	1.000	-558.600	331.800	0.998

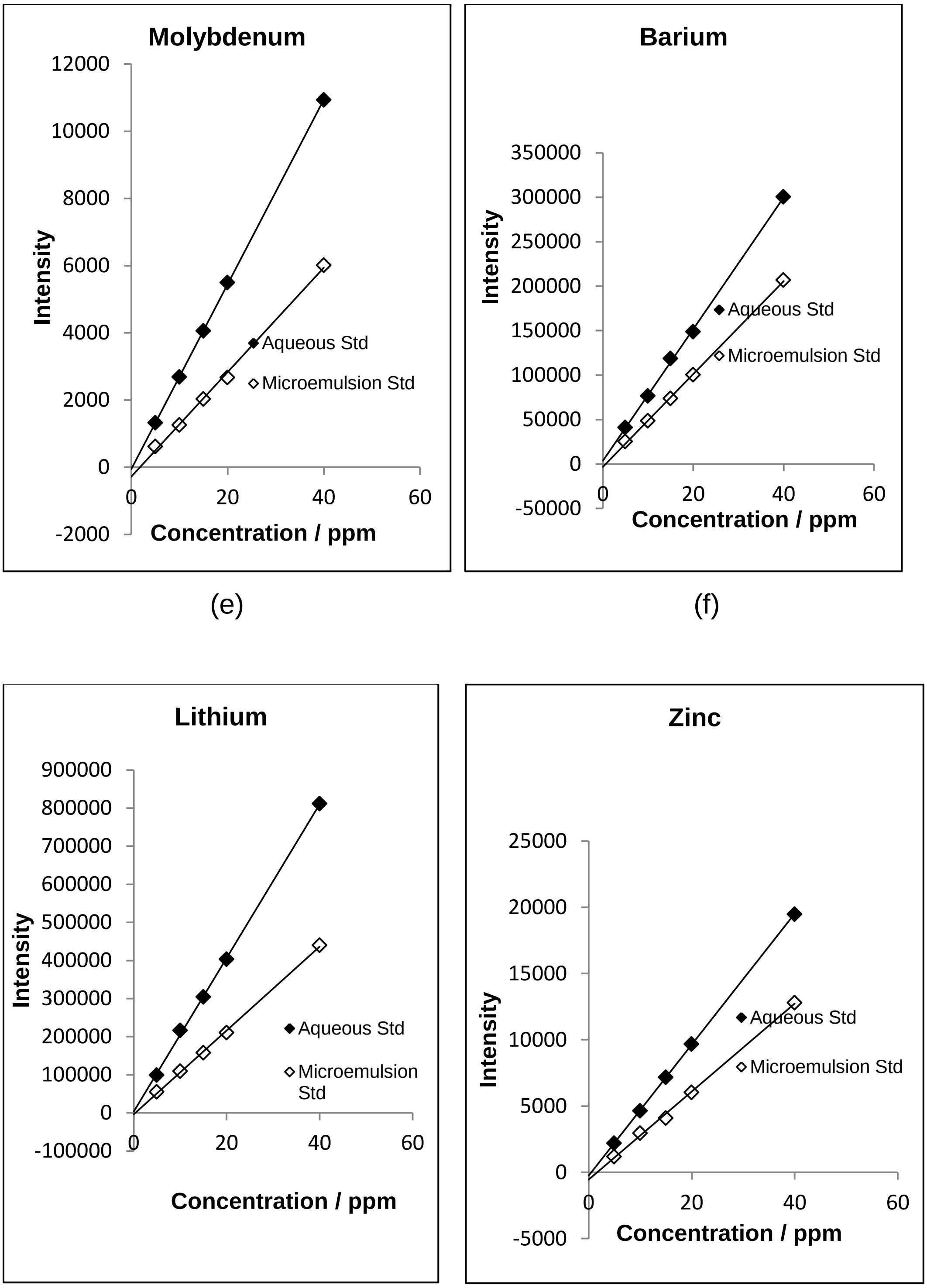
As it is shown in Fig 5.1, the calibration curves of oil emulsions did not differ significantly from aqueous ones in the most of the investigated spectra lines. However, the observed differences were attributed to the slopes and not to the intercepts, which means that there are no significant differences in the base-line measurements using either oil or aqueous emulsion.



(a) (b)

(c) (d)

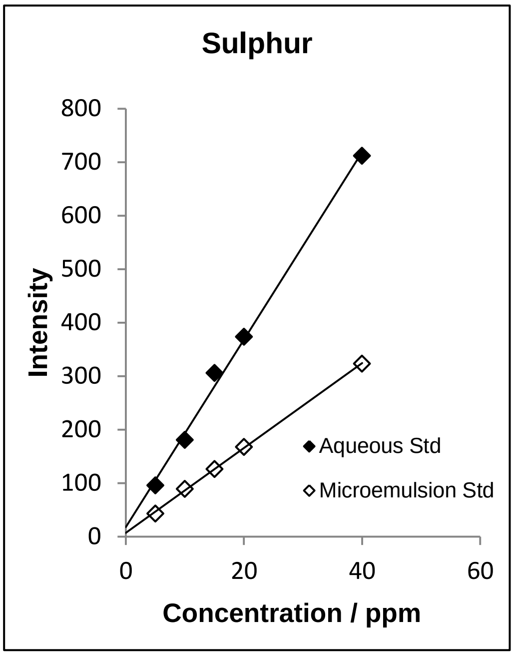
Fig 5.1 (1) Calibration curves for (a) Boron, (b) Calcium, (c) Aluminium and (d) Sodium, prepared in aqueous and in emulsified base oil media.



(e) (f)

(g) (h)

Fig 5.1 (2) Calibration curves for (e) Molybdenum, (f) Barium, (g) Lithium and (h) Zinc, prepared in aqueous and in emulsified base oil media.



(i)

Fig 5.1 (3) Calibration curve for (i) Sulphur, prepared in aqueous and in emulsified base oil media.

In order to compare the efficiencies of the emulsification and microwave digestion techniques five quality assurance samples were prepared by microwave digestion as well as emulsification and analysed, the results are as shown in Table 5.10 overleaf.

Table 5.10 Concentration in ppm obtained for 5 samples prepared by microwave digestion and emulsification.

Element	Sample No.	Concentration Values for Microwave digestion / ppm	Concentration Values for Emulsified samples / ppm
Ca	1	2348	2337
	2	346	338
	3	939	933
	4	1656	1650
	5	1720	1713
Li	1	2008	1999
	2	2528	2531
	3	2973	2969
	4	3689	3684
	5	3499	3489
Zn	1	<0.5	<0.5
	2	347	342
	3	1209	1198
	4	1467	1465
	5	1556	1549
S	1	23011	22990
	2	14425	14430
	3	10145	10143
	4	12055	12046
	5	22590	22567
B	1	<0.5	<0.5
	2	<0.5	<0.5
	3	<0.5	<0.5
	4	2231	2229
	5	2513	2510

Microwave digestion and emulsification were compared by analysing 5 quality assurance samples and performing a paired t-test at the 95% confidence interval and 4 degrees of freedom.

The null hypothesis

$H_0 : \mu_d = 0$

And the alternative hypothesis

$H_a : \mu_d \neq 0$

The test statistic

$t = d / [(s_d / \sqrt{N})]$

Where d = is the average difference equal to $\sum d_i / N$

And s_d the standard deviation of the difference

The t-test was performed for each analyte as shown for Calcium

	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
Microwave digestion	2348	346	939	1656	1720
Emulsification	2337	338	933	1650	1713
Difference	11	8	6	6	7

$d = 7.6$

$s_d = 2.073$

Therefore

$$t = 7.6 / [(2.073/\sqrt{5})]$$

$$t = 8.2$$

From the table of t-values the critical value of t is 8.61 for the 99.9% confidence level and 4 degrees of freedom. Since $t < t_{critical}$ the null hypothesis was accepted and it was concluded that the two methods gave similar results. The other t-tests for the remaining elements were obtained similarly and are shown in the Table 5.11 below.

Table 5.11 T-test results at the 99.9% confidence interval of several elements.

Analyte	t-critical	t-value	Conclusion at 99.9 % confidence level
Li	8.61	4.70	accept null hypothesis
Zn	12.90	3.31	accept null hypothesis
Ba	–	–	N/A
Al	–	–	N/A
P	–	–	N/A
S	8.61	2.80	accept null hypothesis
Mo			N/A
B	12.70	7.90	accept null hypothesis

5.3 Flushing Matrix Experiments

After validating a method for metal determination in lubricating grease a series of experiments was then performed to determine the mass of grease required to flush the filling line in order to get a product that is free from contamination from previous batch of product. In these experiments microwave digestion sample preparation technique was utilised for the subsequent determination of the flushing mass required in between product changes. Five products that are representative of the lubricating grease classes were used, unfortunately as their composition is proprietary, their names remain confidential information to Blendcor (Pty) Ltd, and hence Table 5.12 overleaf gives the codes that will be adopted for the purposes of this project.

Table 5.12 Product names and classification.

	Sample Code	Grease class	Indicative Metal/s
A	LiSx	Lithium Simplex	Li
B	LiCx	Lithium Complex	Li/B
C	CaSx	Calcium Simplex	Ca
D	CaCx	Calcium Complex	Ca/B
E	Clay	Clay based	Not applicable

5.3.1 Lithium Complex versus Lithium Simplex

A total of 10 combinations are possible from this list of samples, to begin with flushing between lithium simplex (A) and Lithium complex (B) was explored. Samples were taken from the middle of batch i.e. after 1000kg of product A has been dispensed. The latter was considered to be the “clean” sample free from any contaminants from previous products. The next product to be manufactured was lithium complex grease (B). Samples were collected at the filling line after 60 kg, 80 kg, 100 kg, 120 kg, 150 kg, 200 kg and finally 1000 kg of product B had been filled and these samples were analysed for boron.

Since both products contain lithium the best indicator for contamination is boron as lithium simplex ideally does not contain this element. All determinations were done in duplicate and the average calculated. Table 5.13 gives data on the variation of flushing mass of lithium complex (B) with the concentration of boron.

Table 5.13 Change in concentration of boron with an increase in the flushing mass of lithium complex (B).

Sample mass / kg	Boron Concentration / ppm
1000 A only	< 0.5
60 B	1154
80 B	2009
100 B	2328
120 B	2487
140 B	2511
150 B	2509
200 B	2499
1000 B only	2513

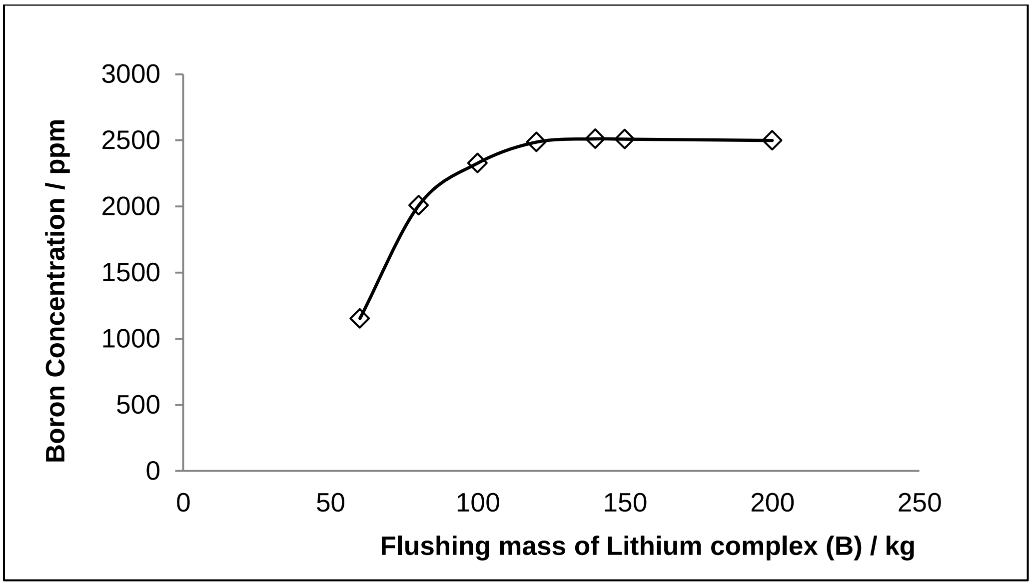


Fig 5.2 Graph showing flushing mass for lithium complex grease (B) versus concentration of boron.

From Fig 5.2 it can be seen that the initial amount of boron in the lithium complex sample B is in the 1000 ppm range. This is due to the dilution of the sample by the lithium simplex sample A i.e. contamination of sample B by sample A. Flushing the filling lines with more of sample B eventually removes all of sample A and only the “clean” sample B remains. This can be seen by the increase in the concentration of boron as the flushing mass of sample B increases. From the plot above 140 kg of B is enough to sufficiently eliminate contamination from the previous product (in this case A).

5.3.2 Lithium Simplex versus Calcium Simplex

When switching from lithium simplex (A) to a calcium simplex (C) the indicative metals can either be lithium or calcium. Ideally as more of the calcium simplex is used to flush the filling line the concentration of lithium should decrease until the grease has a negligible concentration of lithium. For this case the two lubricating greases have different colours the A (lithium simplex) is brown in color and the C is a cream color so absence of the light brown colour also assisted in determining the maximum flush mass. Table 5.14 shows the decrease in lithium concentration with increasing flushing mass of calcium simplex (C).

Table 5.14 Change in concentration of lithium and calcium with an increase in the flushing mass of calcium simplex (C).

Sample mass / kg	Lithium Concentration / ppm	Calcium Concentration / ppm
1000 A only	3499	< 0.5
60 C	2521	958
80 C	1678	1243
100 C	1112	1586
120 C	606	1875
140 C	77	2293
150 C	< 0.5	2343
200 C	< 0.5	2351
1000 C only	< 0.5	2348

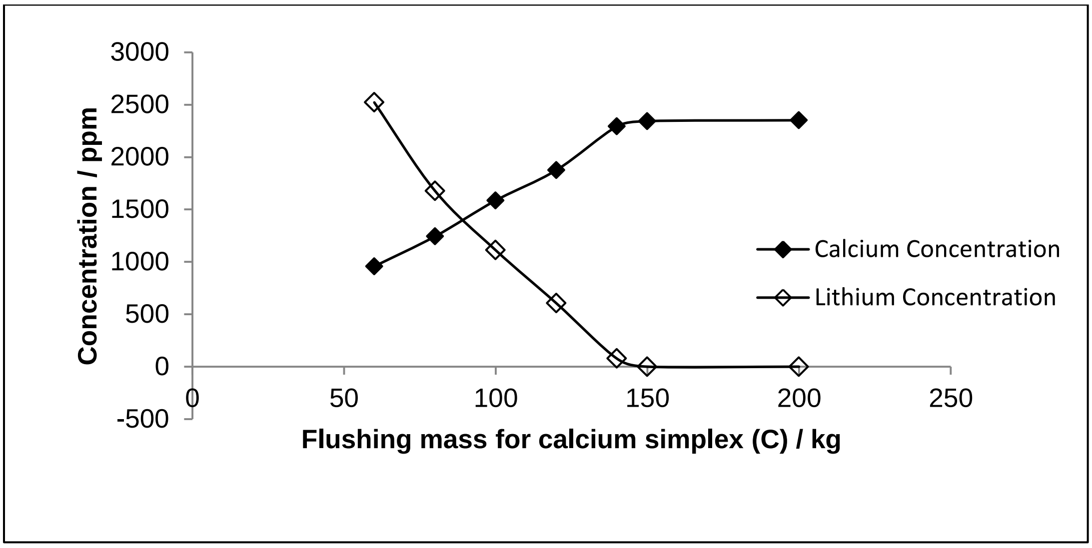


Fig. 5.3 Graph showing flushing mass for calcium simplex grease (C) versus concentration of lithium and calcium.

From the plot above Fig 5.3 it can be seen that the initial 60 kg sample of calcium simplex (C) has a concentration of calcium that is less than a 1000 ppm. This is attributed to the dilution of sample by the presence of lithium simplex (A). Flushing the filling line with more of the calcium simplex (C) results in an increase in the calcium concentration, and as more of the calcium simplex (C) is pushed through the line the concentration of lithium simplex (A) decreases until it is negligible. From the above results it can be concluded that 150 kg of the calcium simplex (C) is required to completely flush out contamination with the previous batch of lithium simplex (A).

5.3.3 Lithium simplex versus Calcium complex

When switching from lithium simplex grease (A) to a calcium complex grease (D) the filling is flushed with the calcium complex grease. Samples were taken as explained in 4.2.2, Boron, Calcium and Lithium indicate the degree of contamination and hence any of the three can be monitored. Table 5.15

below shows the variation in concentration with increase in flushing mass of calcium complex grease (D).

Table 5.15 Change in the concentration of boron, calcium and lithium with an increase in flushing mass of calcium complex grease (D).

Sample mass / kg	Boron Concentration / ppm	Calcium concentration / ppm	Lithium Concentration / ppm
1000 A only	< 0.5	< 0.5	2499
60 D	247	523	2551
80 D	755	972	1929
100 D	1131	1526	1109
120 D	1500	1997	522
140 D	1972	2593	134
150 D	2131	2644	< 0.5
200 D	2224	2643	< 0.5
1000 D only	2233	2637	< 0.5

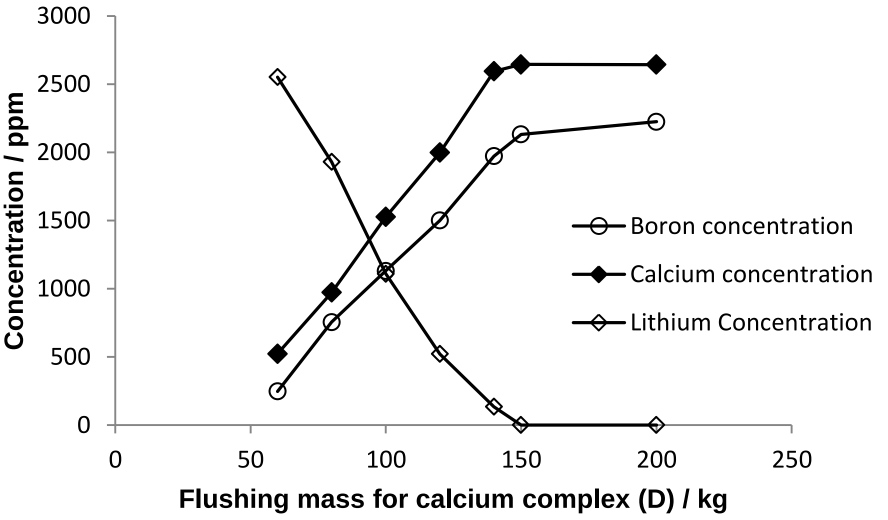


Fig 5.4 Graph showing flushing mass of calcium complex grease (D) vs. the concentration of boron, calcium and lithium.

Fig 5.4 above shows that the initial 60 kg sample of calcium complex grease (D) has a lower concentration of both boron and calcium. This is due to the dilution of the sample by the presence of lithium simplex grease (A). Flushing the filling lines with more of the calcium complex (D) eventually removes all of the contaminating lithium simplex (A) and the boron and calcium concentration increases until it matches that of a “clean” sample i.e. sample of calcium complex (D) taken after the line has been flushed with 1000 kg of the product. From the plot above Fig 5.4, 150 kg of D (calcium complex) is sufficient to eliminate contamination from the lithium simplex grease (A).

5.3.4 Lithium Simplex versus Clay based lubricating grease

Clay lubricating grease normally is free from significant metal concentration. When switching from Lithium simplex to clay based grease, lithium is an obvious contamination indicator and the concentration of lithium will decrease with increase in the flushing mass of E as shown in Fig 5.5 below.

Table 5.16 Change in lithium concentration with an increase in flushing mass of clay grease (E).

Sample mass / kg	Lithium Concentration / ppm
1000 A only	3499
60 E	2438
80 E	1879
100 E	1100
120 E	545
140 E	156
150 E	52
200 E	< 0.5
1000 E only	< 0.5

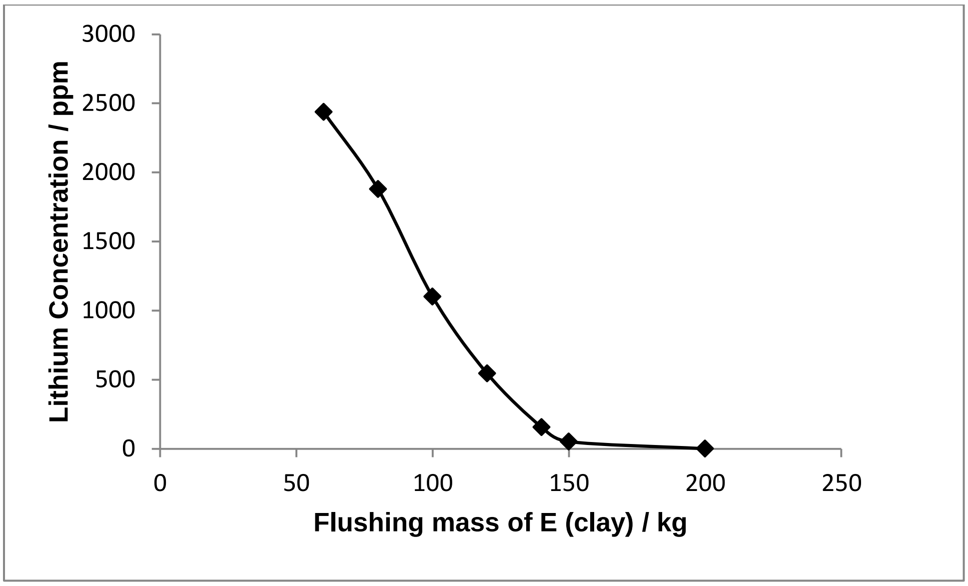


Fig 5.5 Graph showing flushing mass of clay based grease (E) vs. concentration of Lithium.

From Fig 5.5 above it can be seen that the initial amount of lithium in the clay based grease sample E is above 2000 ppm, as more of the clay based grease is pushed through the flushing line this dilutes the contaminating lithium simplex grease resulting in a decrease in the lithium concentration until it is negligible which is ideal for the clay based grease. Figure 5.5 shows that 200 kg of clay based grease (E) is sufficient to remove contamination from a previous batch of lithium simplex grease (A).

5.3.5 Lithium Complex versus Calcium Simplex

When switching from lithium complex grease (B) to calcium simplex grease (C) both the concentration of lithium and boron should decrease and the concentration of calcium increases with increasing flushing mass of calcium simplex grease as shown in Fig 5.6 overleaf.

Table 5.17 Change in concentration of calcium, boron and lithium with an increase in the flushing mass of calcium simplex grease (C).

Sample mass / kg	Calcium Concentration / ppm	Boron Concentration / ppm	Lithium Concentration / ppm
1000 B only	< 0.5	2319	3499
60 C	478	1920	2958
80 C	925	1460	1933
100 C	1350	1130	1124
120 C	1730	940	631
140 C	1968	130	143
150 C	2067	34	12
200 C	2344	< 0.5	< 0.5
1000 C only	2348	< 0.5	< 0.5

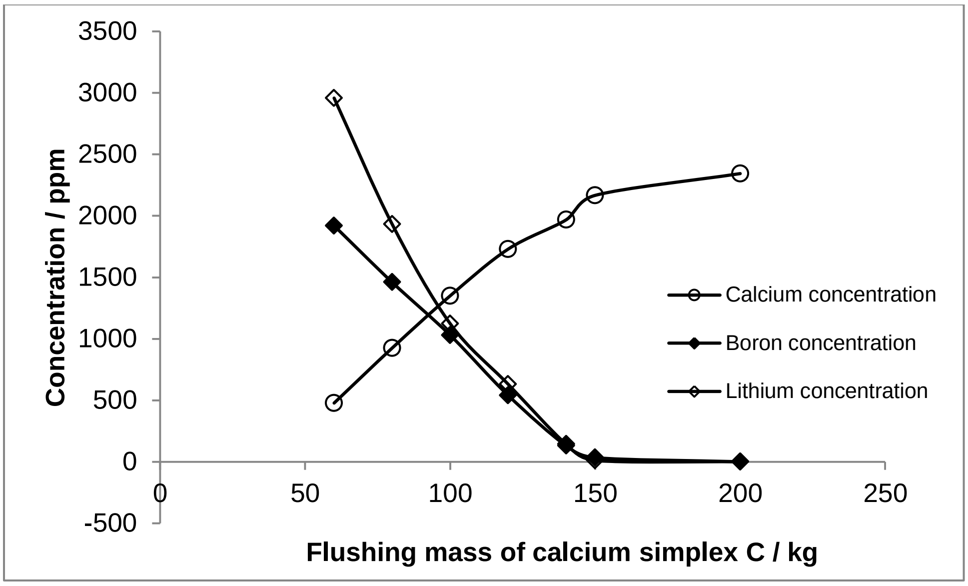


Fig 5.6 Graph showing flushing mass of calcium simplex (C) vs. concentration of calcium, boron and lithium.

From Fig 5.6 above concentrations of both boron and lithium decrease with increase in flushing mass of calcium simplex grease (C). As more of the calcium simplex grease (C) is passed through the filling line, the calcium concentration increases until it equals the theoretical concentration of calcium in calcium simplex grease (C). From the data presented in Fig 5.6 it can be seen that 150 kg of C is sufficient to flush the filling line and remove any contamination from a previous batch of lithium complex (B).

5.3.6 Lithium Complex versus Calcium Complex

When switching from a lithium complex (B) to a calcium complex (D) the contamination indicators are either calcium or lithium.

Table 5.18 Change in concentration of calcium and lithium with an increase in flushing mass of calcium complex grease (D).

Sample mass / kg	Calcium Concentration / ppm	Lithium Concentration / ppm
1000 B only	< 0.5	3516
60 D	351	3001
80 D	940	2734
100 D	1334	2097
120 D	1680	1640
140 D	1960	823
150 D	2035	101
200 D	2342	< 0.5
1000 D only	2344	< 0.5

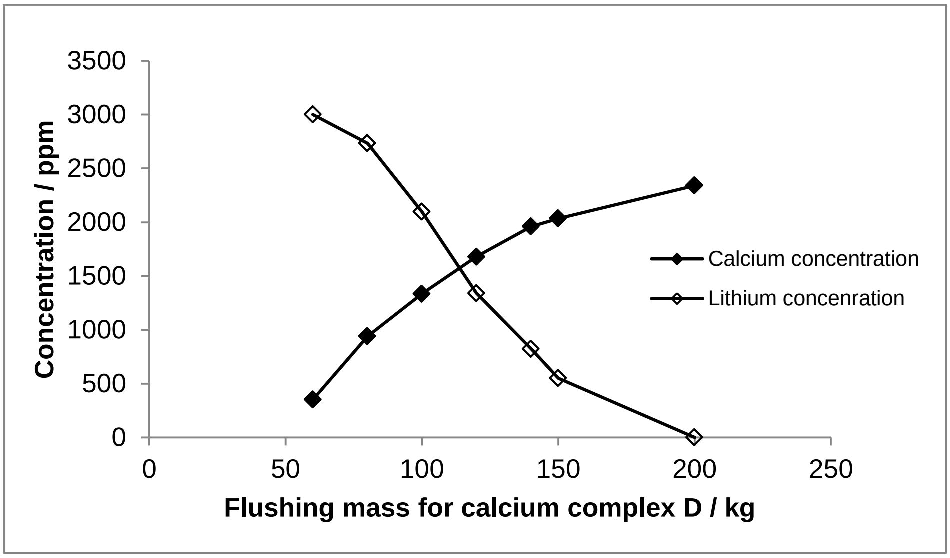


Fig 5.7 Graph showing flushing mass of calcium complex (D) vs. calcium and lithium concentration.

From Table 5.18 above it can be seen that the concentration of calcium is lower (351 ppm) while that of lithium higher (3001 ppm). As more of the calcium complex grease (D) is passed through the filling line, the lithium concentration decreases while the calcium concentration increases to almost equal the expected theoretical calcium concentration in the calcium complex grease (D). Fig 5.7 shows that 200 kg of calcium complex grease (D) is required to flush the filling line and remove contamination from lithium complex (B) efficiently.

5.3.7 Lithium Complex versus Clay Grease

When flushing the filling line from lithium complex grease (B) to clay grease (E) both the concentrations of lithium and boron should decrease with increase in flushing mass of clay grease (E) as shown in Fig 5.8 below. Samples were collected as in the other flushing experiments described above and the data obtained with ICP-OES shown in Table 5.19.

Table 5.19 Boron and lithium concentration with increasing mass of E.

Sample mass / kg	Boron Concentration / ppm	Lithium Concentration / ppm
1000 B only	2513	3499
60 E	2499	2438
80 E	1980	1879
100 E	1232	1100
120 E	487	645
140 E	97	56
150 E	< 0.5	< 0.5
200 E	< 0.5	< 0.5
1000 E only	< 0.5	< 0.5

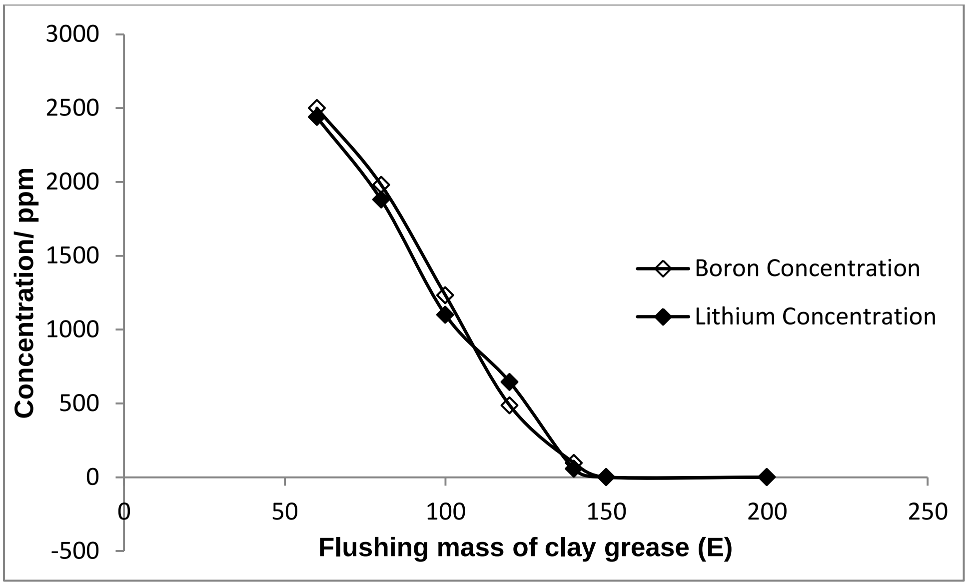


Fig 5.8 Graph showing flushing mass of clay based grease (E) vs. concentration of boron and lithium.

From Fig 5.8 it can be seen that the initial amount of both lithium and boron in the clay based grease are 2438 ppm and 2499 ppm respectively. This is due to the presence of the lithium complex grease (B) with the clay based grease (E). However as more of the clay based grease E is passed through the filling line, more of the lithium complex grease is flushed out resulting in a decrease in the boron and lithium concentration in the clay based grease sample E. Fig 5.8 shows that 150 kg of sample is enough to flush the filling line and remove contamination of clay based grease E with a previous batch of lithium complex grease (B).

5.3.8 Calcium Simplex versus Calcium Complex

When flushing calcium simplex grease (C) with calcium complex grease (D) boron is the indicative metal.

Table 5.20 Change in concentration of boron with an increase in the flushing mass of calcium complex (D).

Sample mass / kg	Boron Concentration / ppm
1000 C only	< 0.5
60 D	< 0.5
80 D	< 0.5
100 D	13
120 D	137
140 D	1205
150 D	1820
200 D	2330
1000 D only	2333

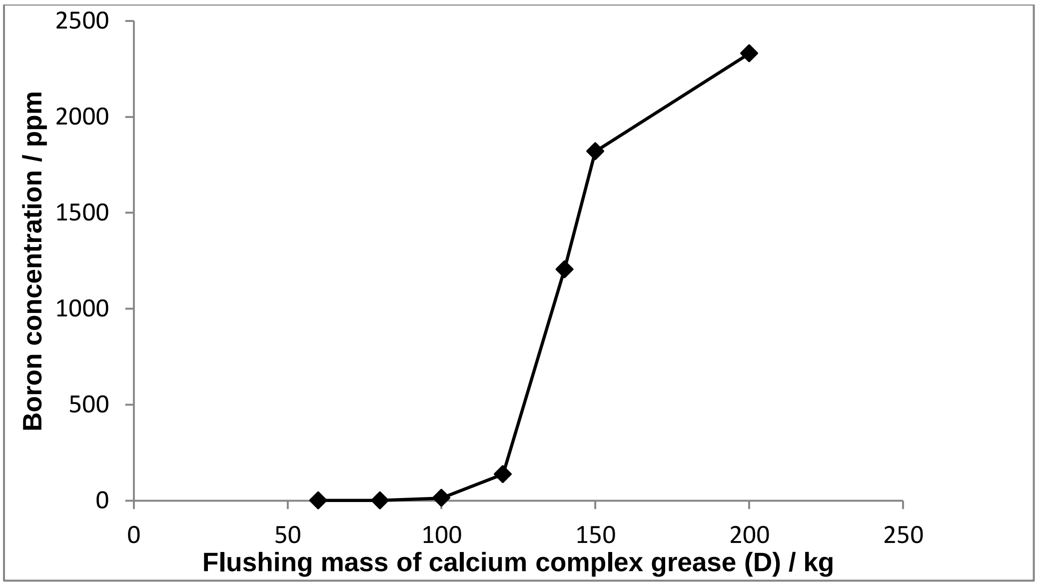


Fig 5.9 Graph showing flushing mass for calcium complex grease (D) vs. concentration of boron.

From Fig 5.9 it can be seen that the initial amount of boron in the calcium complex grease sample (D) is almost negligible. This is due to the dilution of the sample by the calcium simplex grease (C) i.e. contamination of sample D by sample C. Flushing the line with more of calcium complex grease eventually removes all of calcium simplex (C) and the concentration of boron increases until it matches boron concentration in the “clean” calcium complex grease. After flushing with 200 kg of calcium complex the concentration of boron in the sample is in the same range as the expected theoretical concentration, therefore 200 kg sufficiently flushes the line.

5.4 Quality Assurance

A control chart is a popular statistical tool for monitoring and improving quality in the manufacturing sector. It was originated by Walter Shewhart and was later extended by W. Edward Deming to the quality improvement in all industrial processes. The upper and lower control limits (UCL and LCL) are calculated according to the formula below.

$$UCL = CL + 3s$$
$$LCL = CL - 3s$$

Where s is the standard deviation of the monitored parameter and CL is the control limit.

After determining the amount of flushing required the flushing process was statistically monitored by use of Shewart type control charts. The monitoring was done on all the lubricating grease classes for a period of one month. Ten samples were collected for each batch and analysed for the indicative metal e.g. boron for the complex greases, the mean and standard deviation where used to plot the control chart.

The theoretical concentration of Boron in Lithium complex (LiCx) is 2309ppm, this value was considered to be the control limit (CL), for the first batch to be monitored B1 the standard deviation of 10 samples was found to be 9.2 hence

$$\begin{aligned} UCL &= 2309 + 3(9.2) \\ &= 2336.6\text{ppm} \\ LCL &= 2309 - 3(9.2) \\ &= 2281.4\text{ppm} \end{aligned}$$

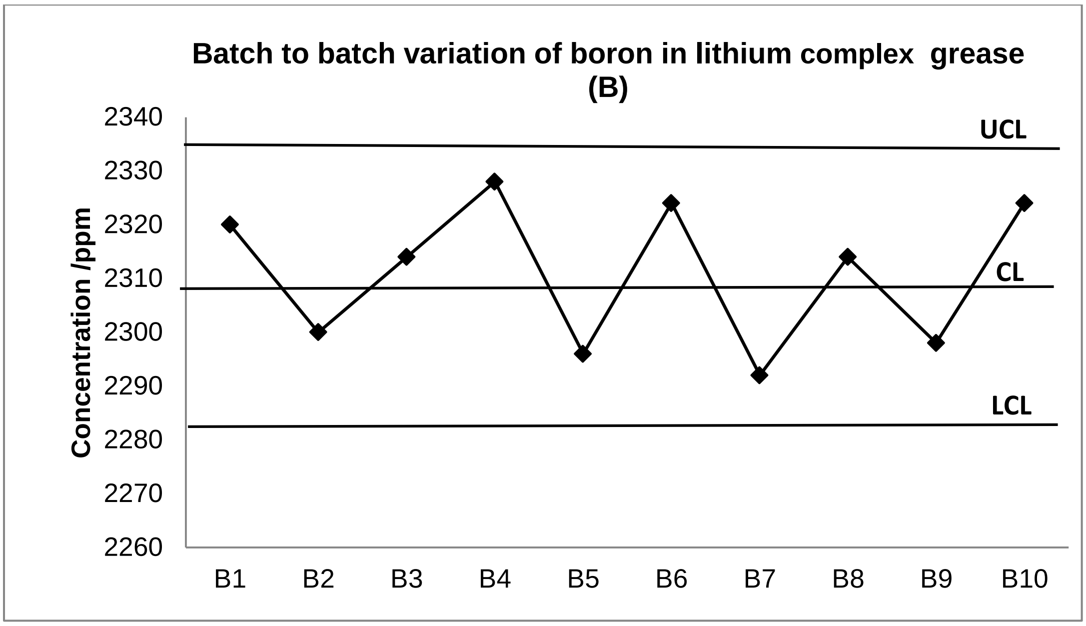


Fig 5.10 Graph showing batch to batch variation of Boron in LiCx grease (B).

The control charts for the other lubricating grease classes were obtained similarly and are shown in the control charts below. Boron concentration is in statistical control as shown in Fig 5.10 above.

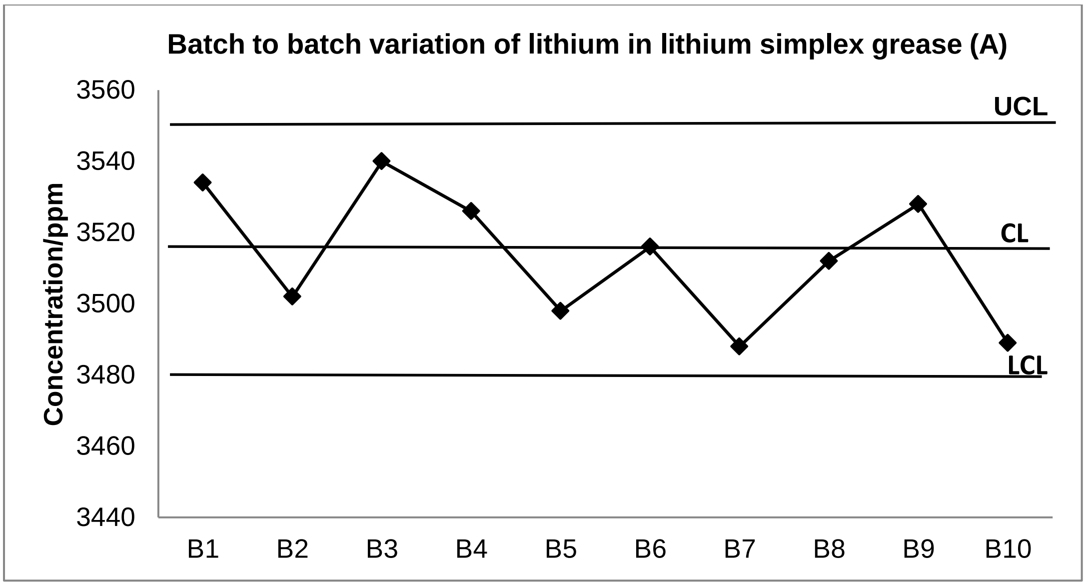


Fig 5.11 Graph showing batch to batch variation of Lithium in LiSx grease (A).

Lithium is in statistical control as shown in Fig 5.11 above, all the points for the 10 batches are between the lower and upper control limits.

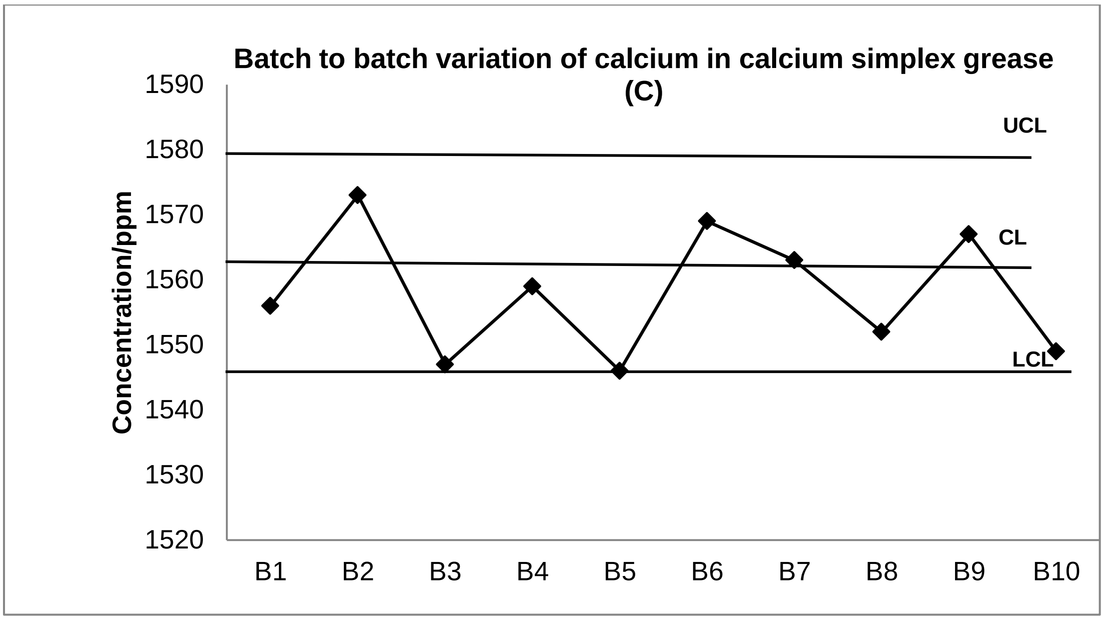


Fig 5.12 Graph showing batch to batch variation of Calcium in CaSx grease (C).

Batch 3 and 4 are on the lower control limit and will not be rejected as the still lie within product specifications.

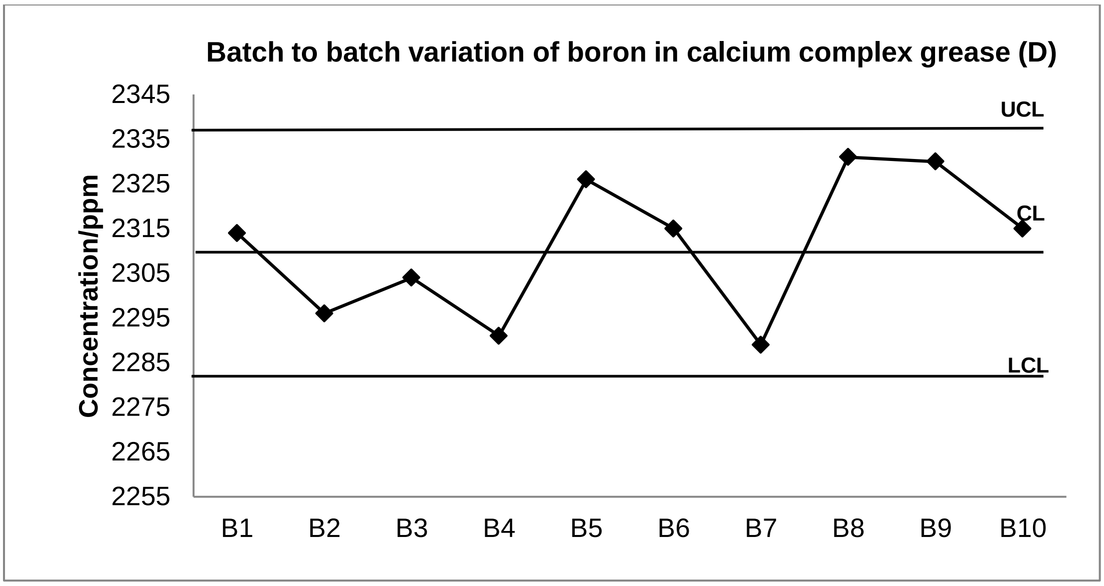


Fig 5.13 Graph showing batch to batch variation of Boron in CaCx grease (D).

Calcium concentration was in statistical control for the 10 batches monitored and as can be seen from Fig 5.13 above all the points are in between the lower and upper control limits.

CHAPTER 6

CONCLUSIONS

One of the main objectives of this research was to develop a routine, easy and reproducible method for elemental determination in lubricating grease. Grease is a complex matrix to work with from the perspective of the analytical laboratory, and hence sample preparation posed a challenge in this study.

Ashing method had lower sensitivity than both emulsification and microwave assisted acid digestion methods. An average of nearly 65% of the boron was lost due to volatilisation during the sulphated ash procedure. This procedure has shown higher propensity to spatter resulting in ejection of analytes from the crucible, and hence low recoveries for Li (76%) and Ca (88%) were obtained. Despite the fact that it uses cheaper inorganic standards, it is time consuming requiring 5 hours in the muffle furnace and this would not be ideal for routine analysis.

Solutions of Constan standards diluted in kerosene and xylene gave a broad range of linearity and good precision for the direct dilution method. However, when actual samples were tested the recoveries were inconsistent with % RSD as high as 56% for calcium, 79% for boron and 66% for lithium. This was attributed to the heterogeneity of the sample as the xylene-kerosene mixture did not completely dissolve the grease sample resulting in a higher viscosity mixture.

The best results for the elemental determination were obtained with a four-stage microwave assisted acid digestion. It uses relatively short sample preparation time compared to the ashing method. The recoveries for the more volatile elements like boron are greatly improved since it is a closed system. The method uses inorganic standards which are much cheaper compared to organo-metallic standards required for the direct dilution method. The limits of detection (LOD) ranged from 0.028 mg/L for sodium to 0.255 mg/L for boron. Limits of quantitation (LOQ) were ranging from 0.09 mg/L for sodium to 0.47 mg/L for sulphur. Correlation coefficient values (R^2) for all the elements were greater than 0.99 indicating that the calibration curves were good for analysing the digested grease samples.

The preparation of emulsion standards was found to be less time consuming and as cost efficient as aqueous calibration. The emulsification method reduces the organic content of the oil sample thereby reducing the background noise inherent to dilution with organic solvent. Similar operating conditions to those used in aqueous calibrations can be used as the properties of the emulsion are closer to aqueous than oil matrix. No time consuming clean- up is required in the emulsification method as in the case of the dilution method. The limits of detection (LOD) ranged from 0.03 mg/L for aluminium to 0.20 mg/L for calcium and sulphur. Limits of quantitation (LOQ) were ranging from 0.30 mg/L for barium to 0.67 mg/L for sulphur. Correlation coefficient values (R^2) for all the elements were greater than 0.99 implying that the calibration curves were also good for analysing the emulsified grease samples.

Although the limits of detection for the emulsification method are higher than those for the aqueous method for all the elements analysed in this work, emulsification proved to be an equally efficient method. A t-test performed at the 99% confidence level and 4 degrees of freedom, showed that the two sample preparation techniques gave similar results.

This work not only centred on analytical method development, but also extended to real life application of the developed method in a lubricating grease plant and also tackled some environmental, quality and budget aspects. Before the initiation of this project, Blendcor (Pty) Ltd was accumulating an impossible amount of lubricating grease waste which could not be used for any economic benefit. As a result of the developed flushing procedure there has been a significant decline in non-conformity as evidenced by the Shewart control charts. This method allows in-process products to be analysed and corrections can be made before the packaging stage. It also enables an exhaustive product characterisation which may be required by customers. The amount of flushing waste has significantly decreased and this entails lower disposal cost for waste. As a result of this research it was noted that shortening the filling lines can also minimise the amount of flushing required and at the completion of this project Blendcor (Pty) Ltd was embarking on a project to shorten their filling lines. Emulsified samples can be used with inorganic standards which are more cost effective than metallo-organic standards and hence this method can also be extended to lubricating oils instead of direct dilution method that is in currently in use.

In conclusion, this work has shown that the emulsification of lubricating grease as a sample preparation technique for routine analysis of grease is the recommended method.

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