



Joana Rita Batista Marques

Physicochemical characterization of waste lubricating oils

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Joana Rita Batista Marques

Physicochemical characterization of waste lubricating oils

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Orientadores:

Prof. Doutora Margarida Maria João de Quina

Prof. Doutor Licínio Manuel Gando Azevedo Ferreira

Instituições:

Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra

CIEPQPF - Centro de Investigação em Engenharia dos Processos Químicos e dos Produtos da Floresta

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*'Research is to see what everybody else has seen,
and to think what nobody else has thought.'*

- Dr. Albert Szent-Gyorgyi

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RESUMO

O presente trabalho tem como principal objectivo a caracterização de amostras de óleo lubrificante usado com vista à sua regeneração por processos que envolvam tratamentos alcalinos. A regeneração de óleo usado com recurso a pré-tratamentos alcalinos é atualmente utilizada em Portugal. Neste âmbito, foram recolhidas 133 amostras as quais foram submetidas a um teste empírico de coagulação de modo a categoriza-las em quatro classes (A, B1, B2 e C).

Adicionalmente, foram avaliadas as seguintes propriedades físico-químicas para todas as amostras: tensão superficial a 30°C, teor de água, número total de acidez (TAN), índice de saponificação (IS) e viscosidade cinemática a 40°C. Foram ainda realizadas análises com vista à identificação quantitativa e qualificativa dos elementos químicos presentes nas amostras através da técnica de fluorescência de raios X por dispersão de energia e ainda a identificação de grupos funcionais através da espectroscopia no infravermelho por transformada de Fourier.

Os resultados obtidos foram agrupados com base nas quatro classes de coagulação. Foi possível concluir que podem existir diferenças estatisticamente relevantes em algumas propriedades. Designadamente, foi evidente que o TAN da classe B2 é particularmente baixo (cerca de 0,54 mg KOH/g) relativamente às outras classes. Em relação ao IS, foi a categoria C que apresentou um valor mais elevado (cerca de 32,97 mg KOH/g), o que significa que estas amostras apresentam grande tendência a coagular quando tratadas com KOH. A análise elementar mostrou que o teor de magnésio, fósforo e enxofre também pode ser discriminatório. Os espectros de FTIR não foram conclusivos para diferenciar as amostras com base na sua classe de coagulação.

Globalmente, o TAN foi o parâmetro mais determinante para distinguir as diferentes categorias de óleos. Os resultados do TAN sugerem também que os de aditivos empregues na formulação destes lubrificantes, podem estar envolvidos no fenómeno de coagulação observado nas amostras da categoria C. As amostras da categoria C exibem maiores teores de matéria saponificável pelo que são as mais susceptíveis à ocorrência de reacções de saponificação.

Palavras-chave: Óleo usado; Caracterização de lubrificantes; Número total de acidez; Número de saponificação; Aditivos

ABSTRACT

This work addresses the characterization of used lubricant oil (ULO) samples aiming to its regeneration through alkaline treatments. Waste oils regeneration via alkaline processes is process implemented in Portugal. Some ULO, when submitted to alkaline conditions experience coagulation, which stands as a hindrance to its regeneration. In this context, 133 samples were obtained and submitted to an empirical coagulation test in order to categorize them into four categories (A, B1, B2 and C)

Additionally, the following physiochemical properties were measured in all samples; surface tension at 30°C, water content, total acid number (TAN), saponification number (SN) and kinematic viscosity at 40°C. Furthermore, it was also performed elemental analysis aiming to a quantitative and qualitative identification of the chemical elements present in the waste lubricant oil samples through energy dispersive X-ray fluorescence technique and also analysis to exiting functional groups using Fourier transform infrared spectroscopy technique.

The results obtained were separated according to the four coagulation categories. It was possible to conclude that some properties display statically relevant differences. Specifically, TAN of category B2 is particularly low (about 0.54 mg KOH/g) comparing to other categories. Regarding SN, category C showed the highest values (about 32.97 mg KOH/g), which means this samples are more likely to experience coagulation when treated with KOH. Elemental analysis, showed that content of magnesium, phosphorus and sulphur can also allow some differentiation. The Fourier transform infrared spectroscopy analysis was not conclusive enough to allow a sample differentiation based on coagulation category.

Globally TAN was the most useful property to distinguish the different categories. TAN results also suggest that the additives employed in the oils formulation might be involved in the coagulation phenomena observed in samples from category C. Samples from category C display higher contents of saponifiable matter then the remaining categories, and thus more suitable to experience a saponification reaction.

Keywords: Used oil; Lubricants characterization; Total acid number; Saponification number; Additives

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ACRONYMS

ULO – Used lubricating oil

TAN – Total acid number

IS – Index of saponification

PCB - Polychlorinated biphenyl

FTIR – Fourier transform infrared spectroscopy

EDXRF - Energy Dispersive X-ray Fluorescence

ICP-OES - inductively coupled plasma optical emission spectrometry

GC/MS - Gas chromatography–mass spectrometry

NMR - Nuclear magnetic resonance

AAS - Atomic absorption spectroscopy

1. Introduction

1.1. Scope and goals

The technological world is highly dependent on the use of lubricating oils which allows not only the proper functioning of machinery and engines, but it also protects them of wear, contamination and oxidation processes. After a certain period of use, lubricants experience deterioration processes and contamination of other fluids such as fuel and brake fluid. Under these conditions, the oil must be changed because it no longer has lubricating properties needed for the proper functioning of the equipment, and it is in this context that waste oils arise, whose chemical composition is extremely complex and highly hazardous to the environment. Waste oil may constitute an environmental problem, and an economical problem loss if handled improperly, becoming a waste rather than a usable resource.

The solution to both problems is the valorization of this resource in a circular economy perspective. By recycling waste oil, it can be avoided simultaneously the waste of a valuable resource, and carbon dioxide emissions from the production of new lubricating oils.

Currently there are three ways in which waste oil can be valued: re-refining, other forms of recycling, and energy recovery through direct combustion. In order to oil can proceed to these routes, it must possess certain properties, otherwise it will remain with the status of a residue. Specifically, in the process of re-refining, the lack of knowledge of some properties of used oil is an obstacle to the normal functioning of the process. Often re-refining of oil undergoes a pre-treatment with a strong base (KOH) to neutralize acidic constituents and remove contaminants. If the oil is then sent to distillation columns the phenomena of coagulation may occur, which blocks the columns and hampers its normal operation.

The mechanism behind waste oil coagulation phenomena is unclear. It can be due to saponification reactions or aggregation of colloidal particles. Therefore, it would be beneficial to foresee if a sample will coagulate by analysing its characteristics so that samples that will coagulate do not be mixed, allowing a maximum yield in the regeneration process. This way, a previous characterization can be a helpful tool for increasing the yield of valorization processes.

Thus, the main objective of this work is the characterization of used lubricant oil (ULO) aiming its valorization through alkaline regeneration processes. In order to accomplish this objective, the experimental work involved the following steps:

- Study of the behaviour of the coagulation phenomena through an alkaline treatment with sodium hydroxide in order to identify the different coagulation classes;
- Determination of physicochemical properties, functional groups and elemental analysis;
- Statistical analysis of the results in order to correlate the properties measured with coagulation behaviour.

Before the characterization of samples, a coagulation test reproducing the conditions that the oil samples will experience in the regeneration process was performed to classify samples according to their coagulation result. The coagulation tests led to four different categories: A – oil did not change when submitted to the test; B1 – oil displayed an increase in viscosity; B2 – oil formed a precipitate; C – the total oil sample coagulated.

This work was accomplished in the scope of the project CONUR II, which is a continuation of the previous project CONUR I, with the financial support of SOGILUB (Sociedade de Gestão Integrada de Óleos Lubrificantes Usados Lda).

1.2 Structure of the thesis

This dissertation will be organized in six chapters. The first chapter consists in an introduction to used lubricating oils, in which the scope and motivation of the work is presented as well as a summary description of the structure of the thesis. The second chapter corresponds to the theoretical background on the subject. First, relevant information on lubricating oil origin is given as well as the different types of base oil that are currently most widely used: mineral base oil and synthetic base oil. Next, a description of the most common additives used in lubricating oils is made with special focus on how they behave while in service use. Also, the most relevant physicochemical properties of lubricating oil to this work are analysed.

In Chapter 2, important matters on used lubricating oils are reviewed. A description of the main contaminants and their possible sources in used oil is made. Also, management of used oils practices is analysed as well as relevant European and Portuguese legislation. Finally, at the end of Chapter 2, is given an overview on used oil valorisation routes and environmental concerns.

In Chapter 3 a literature review is made on published papers regarding waste lubricating oils characterization. In Chapter 4 the experimental methodologies employed to perform the characterization of samples is indicated, as well as the sampling process. In Chapter 5 the results obtained are presented and discussed. Finally, in Chapter 6 the main conclusions are summarized and some future work proposals are made.

2. Theoretical background

This chapter is divided in two sections: the first one is about fresh lubricating oils, and the second part is related to waste lubricating oils.

2.1. New lubricating oils

2.1.1. Base oils

Base oil is the main raw material for producing lubricants along with additives. It can be produced from different sources. When obtained by the refining of crude oil is known as mineral base oil, while base oil obtained through chemical synthesis is called synthetic base oil. In average, base oil accounts for about 95% of lubricants weight, hence their importance. Base oil produced through crude refining can be divided in two categories, naphthenic or paraffinic, depending on their hydrocarbon properties. The crude oil composition determines the type of mineral base oil (Speight and Exall 2014; Mang and Dresel 2007).

Paraffins are hydrocarbons also known as alkanes with saturated linear or branched-chain structures. Alkanes, present some attractive lubricating properties such as low viscosities and boiling points. They also show a good relation between viscosity and temperature, which means a small change in the lubricating oil's viscosity with increasing temperature (Mortier, Fox, and Orszulik 2010). In general alkanes are reasonably resistant to oxidation and have particularly good response to oxidation inhibitors. However paraffinic based oil with linear alkanes (n-paraffins) have the inconvenient of crystallizing waxy substances at low temperatures as a result of their high melting point. Waxy substances restrain flow movement, because of their solid behaviour, which is crucial for a proper lubricating function. Therefore, paraffinic lube oil presents adverse flow properties in cold environments. To overcome this problem the base oil needs to be dewaxed which can be obtained through solvent dewaxing (Speight and Exall 2014; Mang and Dresel 2007). Nonetheless, paraffinic base oils have other lubricating characteristics that make them very attractive. According to Speight and Exall (2014), they account for 85% of the world's base stock market.

Naphthenes or alicyclic are hydrocarbons with saturated cyclic structures based on five and six membered rings. They have the advantage of lower melting points, meaning they do not crystallize

wax as easily as paraffinic base oil do at low temperatures. Another advantage is that alicyclics usually have better solvency capacity for additives, making them easier to manipulate. On the other hand, alicyclics show an inferior viscosity/temperature relation and thus they are not very suitable for applications where wide temperature changes occur. Also they show less stability in terms of oxidation (Mortier, Fox, and Orszulik 2010).

Mineral base oil make up for most of lubricating base fluids, but the market for synthetic lubricating oil is expanding. Synthetic oils are used in applications in which mineral oils do not have the required level of lubricant performance or when a synthetic oil can provide a performance and cost advantage over a conventional mineral oil (Brown et al. 2009). These lubricants are expensive and usually used in very specific applications as a result of their outstanding physical and chemical properties. They are more suitable for extreme operating conditions such as very high temperatures and pressures (Mang and Dresel 2007). Synthetic oils are durable and provide resistance to oxidation and to formation of deposits. There are also available synthetic blends, with no more than 30% v/v of synthetic oil. These blends combine the benefits of synthetic base oil performance with the lower cost of crude derivative oil. The chemical basis used to prepare synthetic base oil are mostly esters, phosphate esters, polybutenes, synthetic hydrocarbons, polyalkylene glycols and silicone oils (Speight and Exall 2014; Mang 2014; Brown et al. 2009).

Synthetic hydrocarbons or poly alpha-olefins (PAO) are produced through polymerization process of hydrocarbon molecules also known as α -olefins, using catalysts. They are capable of working productively in a large range of temperatures (Brown et al. 2009), including low temperature (Speight and Exall 2014). A peculiar aspect about PAO is that in some oxidation tests, without the contribution of additives, mineral oils actually display a better performance. This can be attributed to occurrence of the natural antioxidants present in the mineral oils (Mang and Dresel 2007).

2.1.2. Additives

Lubricating oil is a blend of base oil and additives. Without the aid of additives, development of new or improved machinery would not be possible. Additives are synthetic substances used to impart specific properties to the finished oils (Rizvi 2009; Rudnick 2006). They can enhance natural properties, add new ones, or even suppress an unwanted existing one. Some additives act by reducing the rate at which adverse changes occur. For instance, the oxidation rate of the lubricant would be much higher without additives, given that the rate of oxidation of a hydrocarbon doubles with each 10°C increase in temperature (Rizvi 2009; Speight and Exall 2014). Some additives

influence the lubricants chemistry and others the physical properties. Usually there are several additives present at the same time. According to Speight and Exall (2014), the main functional additives are dispersants, antioxidants, detergents, viscosity index improvers, extreme-pressure additives, and anti-wear agents:

i) Antioxidants

Lubricating oil often are exposed to oxidative conditions due to air/oxygen, high temperatures and metals acting as catalyst. Also, oxidation products can act as catalysts themselves, speeding up the process even more (Awaja and Pavel 2006). Besides that, oxidation products are harmful and corrosive (Rudnick 2006; Speight and Exall 2014). According to Rudnick (2006), oxidation is the primary cause for oil degradation, hence the importance of using oxidation inhibitors. Base oil has naturally occurring antioxidants though not sufficient to prevent the formation of the harmful products of oxidation like resins, lacquers and acidic compounds (Rizvi 2009). According to Torbacke (2014), this mechanism begins with the collision of oxygen with a hydrocarbon chain, forming radicals, which are very reactive chemical species, and carboxylic acids (that attack metal surfaces, generating carboxylic salts and increasing the rate of oxidation). This step is known as initiation and is followed by propagation. In the propagation step radicals attack hydrocarbons giving way to new radicals in a chain reaction. The termination step can evolve either from the action of antioxidants or a radical-radical reaction. There are three types of antioxidants: metal deactivators, that inhibit the catalytic activity of metals; radical scavengers, which are the main type and convert radicals to alcohols and ring-stabilized radicals; hydroperoxide decomposers prevent oxidation by converting hydroperoxides to alcohols, which otherwise would initiate a new oxidation chain reaction (Torbacke, Rudolphi, and Kassfeldt 2014; Speight and Exall 2014; Rudnick 2006).

ii) Detergents

Detergents are metal salts of organic acids and maintain lubricated metal parts clean. A display of an overbased detergent with a core of calcium carbonate can be seen in Figure 2.1. They assume particular importance in high temperature applications due to the formation of deposits and sludge as a result of oxidation or combustion (Torbacke, Rudolphi, and Kassfeldt 2014). They have the ability to neutralize the acidic products of combustion (sulphuric and nitric acid) and prevent deposits by suspending polar oxidation products in the lubricant (Rizvi 2009; Rudnick 2006).

iii) Dispersants

Dispersants are required to prevent the deposition of particles in the lubricated parts, maintaining harmful debris such as sludge and soot dispersed or suspended (Torbacke, Rudolphi, and Kassfeldt 2014; Mortier, Fox, and Orszulik 2010). Soot usually forms in the combustion chamber of diesel engines due to incomplete oxidation of the fuel, whereas sludge results from thermal oxidation of the oil (Mortier, Fox, and Orszulik 2010). Some of these particles might be granular and abrasive, and dispersants act by separating small particles. Dispersants dissolve polar contaminants such as dirt in the lubricant through physical action (Mortier, Fox, and Orszulik 2010). The polar head group of dispersants adsorb to the surface of the contaminants and, and the non-polar hydrocarbon tail points outwards, acting like a physical barrier that prevents the particles do aggregate to one another (Rudnick 2006).

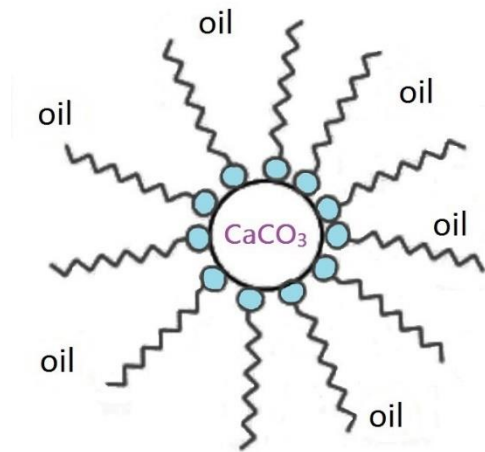


Figure 2.1 - An overbased detergent with a core of calcium carbonate (adapted from "Lubricants: Introduction to Properties and Performance", 2014).

iv) Viscosity index improvers

Viscosity is one of the most important parameters in lubricating oils because it determines the performance in different ranges of temperature. For instance, at high temperatures the viscosity tends to decrease, and at low temperatures it shows the opposite behaviour. The viscosity index reflects the changes in viscosity in relation to changes in temperature (Awaja and Pavel 2006; Speight and Exall 2014). A high viscosity index means a small change of viscosity with temperature, while a low viscosity index number means the opposite. Without the aid of additives, lubricants would not be able to have an adequately perform at elevated temperatures (Mang and Dresel 2007). Viscosity index improvers are polymer chain molecules with short hydrocarbon

branches (Torbacke, Rudolphi, and Kassfeldt 2014). At elevated temperatures, the polymer configuration changes, the polymeric chain stretch (as a result of an increase in thermal energy) and the molecules solubility increase (as a result of the chain length growth). Consequently, the lubricants viscosity increases as well. The thickening efficiency is proportional to the molecular weight or the length of the polymer chain. For low temperatures these molecules adopt a coiled form occupying a small volume and therefore have no significant contribution to viscosity (Rizvi 2009; Torbacke, Rudolphi, and Kassfeldt 2014). Additives can be obtained using ester polymers such as polyalkylmethacrylate (PMA), olefin-based polymers such as polyisobutylene (PIB) or olefin copolymers (OCPs) (Torbacke, Rudolphi, and Kassfeldt 2014).

v) Anti-wear and extreme-pressure additives

Wear is a mechanical phenomenon of physical loss of material that occurs from the contact between two surfaces, leading to imperfections (Mortier, Fox, and Orszulik 2010; Rudnick 2006). When those imperfections rub against each other they cause friction and subsequently start breaking apart (Callister and Rethwisch 2012; Speight and Exall 2014). Therefore, this class of additives act by forming layers on the metal surface through adsorption or chemisorption avoiding scuffing and wear in the lubricated surfaces (Mang 2014; Torbacke, Rudolphi, and Kassfeldt 2014). When the lubricating fluid is no longer present or suffers a rupture due to increase in load and the surfaces are in contact with one another, friction takes place and subsequent increase in temperature. At such temperatures, these additives decompose and react with the metal forming an inorganic layer that is able to prevent direct contact between the metal surfaces which allows the temperature (Stepina and Vesely. V 1992). The most common anti-wear additive is zinc dialkyldithiophosphate (ZDDP), although it can be used as antioxidant and detergent. Extreme-pressure additives are used in situation where the system is exposed to severe stress, high speed or high temperature such as heavily loaded gears and metalworking fluids. They protect the machine by preventing the welding of the moving parts (Torbacke, Rudolphi, and Kassfeldt 2014; Mang and Dresel 2007; Rudnick 2006).

vi) Corrosion inhibitors

Corrosion is a process of material degradation due to the deterioration of its mechanical or other physical properties. It consists in electrochemical or chemical reactions between usually a metal and the surrounding environment. Atmospheric oxygen and moisture are the main environmental conditions that trigger a corrosive reaction on a metal surface (Callister and Rethwisch 2012). Metallic corrosion is a serious problem, given that approximately 5% of an industrialized nation's

income is spent on the prevention of corrosion plus maintenance or replacement of the degraded material. Corrosion inhibitors protect the metal surface from the attack of oxygen, moisture (from the combustion of fuel) and acidic products. They are molecules with long alkyl chains and polar groups that are adsorbed to the metal surface forming hydrophobic layers and acts as a barrier film against corrosive agents (Mang and Dresel 2007; Mortier, Fox, and Orszulik 2010). An inconvenience associated with these additives is that they compete with other polar additives for the metal surface such as anti-wear and extreme pressure additives. There are several categories of corrosion inhibitors (Rudnick 2006). Some examples are nitrites, chromates, hydrazines, carboxylates, silicates, oxidants, sulfonates, amines, amine carboxylates, borates, amine borates, phosphates, amine phosphates.

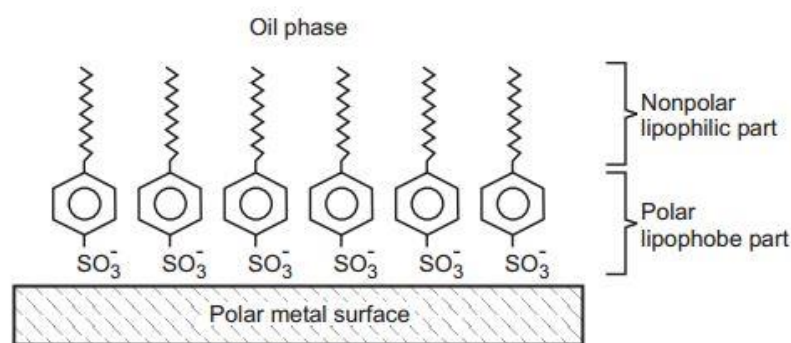


Figure 2.2 - Display of an anticorrosion additive (adapted from "Lubricants and Lubrication" 2007).

2.1.3. Physicochemical properties

According to Speight and Exall (2014) the main properties of lubricants are viscosity, viscosity index, pour point and flash point, density, Total Acid Number (TAN) and saponification value, which will be analysed in the next sections:

i) Viscosity and viscosity index

Viscosity is a property that measures the internal friction in a fluid (the force resisting motion between the fluid molecules) (Mang and Dresel 2007; Stepina and Vesely. V 1992). It relates the applied shearing stress to the velocity gradient it produces in the liquid (Speight and Exall 2014). Viscosity is a property of high importance given that it determines the fluid friction, the load-

carrying capacity of the lubricant film and its resistance to movement (Stepina and Vesely. V 1992). A high viscosity usually means a thicker lubricant film, and low viscosity will originate a thinner one (Torbacke, Rudolphi, and Kassfeldt 2014). The viscosity index (VI) is a number that reflects the level of change in viscosity due to changes in temperature (Speight and Exall 2014). The original method attributes a VI equal to 100 to an oil from Pennsylvanian crude, which is paraffinic base oil that changes very little its viscosity with temperature, and a VI of 0 to a naphthenic Mexican Gulf crude oil whose viscosity changes dramatically with temperature (Stepina and Vesely. V 1992; Torbacke, Rudolphi, and Kassfeldt 2014; Mang and Dresel 2007). Nowadays it can be found oils with VI higher than 100 because of synthetic base oils that possess a higher inherent viscosity index (Torbacke, Rudolphi, and Kassfeldt 2014).

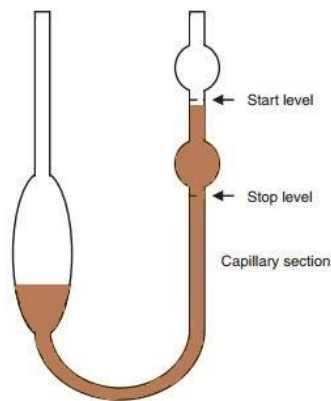


Figure 2.3 - Kinematic viscosity measured through a capillary viscometer (adapted from "Lubricants Introduction to Properties and Performance" 2014)

ii) Pour point and flash point

The pour point is the lowest temperature the lubricant can still flow (Torbacke, Rudolphi, and Kassfeldt 2014). This property assumes great importance in environments where cold weather are prominent or low temperatures are achieved (Speight and Exall 2014). The flash point is the lowest temperature at which the lubricants vapor will form an inflammable mixture with the air (Mang and Dresel 2007; Torbacke, Rudolphi, and Kassfeldt 2014). It is possible to know if an oil is contaminated with volatile substances such as gasoline through the flash point since these contaminants considerably lower the lubricants flash point (Speight and Exall 2014). Besides this, oxidation will also lower the flash point of a lubricant given that it forms volatile compounds (Speight and Exall 2014). In the selection of a lubricant, it is important to choose one whose flash

point is above the maximum temperature in which the equipment will run, for obvious security reasons (Torbacke, Rudolphi, and Kassfeldt 2014).

iii) Density

Density corresponds to the mass of a substance per unit volume of substance at a given temperature, usually 20°C (Stepina and Vesely. V 1992). The density of a lubricant is correlated to its chemical composition, namely higher amount of aromatic compounds lead to higher density (Speight and Exall 2014). Inversely, the presence of saturated compounds will lower the lubricants density. The information about the lubricants density is necessary to calculate kinematic viscosity through dynamic viscosity, giving a hint to the lubricants composition (Stepina and Vesely. V 1992).

iv) Total acid number

The total acid number (TAN) is a measure of the concentration of free acidic constituents in lubricating oil and it is expressed as milligrams of KOH required to neutralise a unit mass of material (Stepina and Vesely. V 1992; Speight and Exall 2014). In new lubricants the acidic content is correlated to the type and concentration of specific additives, while in used oil the total acid number can indicate the oils degradation degree, more specifically the extent of oxidation (Mang and Dresel 2007). Therefore, TAN of a lubricating oil in use should be monitored so that it can change in time, avoiding corrosion of the lubricated system (Torbacke, Rudolphi, and Kassfeldt 2014).

v) Saponification number

The saponification number (SN) or saponification value is the number of milligrams of potassium hydroxide (KOH) consumed by 1 g of sample, in this case lubricating oil, under conditions specified in ASTM D94 (ASTM International 2002; Slade 1997). It reflects the amount of fatty saponifiable material on the lubricant oil, though one must be careful when interpreting the results given that other substances that also react with KOH may be present and thus increasing the apparent saponification number (Speight and Exall 2014).

2.2.Used lubricating oils

Used (or waste) lubricating oil is the fluid rejected as unfit for further machinery lubrication. This is due to oil deterioration in service as a result of physical or chemical contamination in the process of use. The degradation rate is influenced by the time in service, the operating system temperature as well as the severity of the operation and surrounding environmental conditions (Rizvi 2009). Therefore, used lubricants are composed by base oil, additives and different contaminants, that can be either product of chemical deterioration or from external origin. When a lubricant can no longer perform its initial purpose it is considered a waste. This chapter will be dedicated entirely to insight further on used lubricating oil matters as well as the process/route of its valorization (the process of transforming used lubricants into fine base oil). Environmental concerns regarding used oils will be also evaluated.

2.2.1. Mechanisms of degradation and main contaminants

At a certain point of the lubricants life, its properties change and are no longer suitable for its initial purpose. When a lubricant reaches that point, it needs to be replaced. The loss of efficiency in the lubricants performance is usually due to the oil degradation in service caused by the presence of contaminants. Lubricant degradation can be the result of many factors, but the main one is oxidation. The products resulting from the lubricants oxidation can be soluble and cause an increase in viscosity oil, or insoluble, such as resins like varnish, sludge and sediment formation (Speight and Exall 2014; Rizvi 2009). Besides, oxidation products can be acidic which may increase TAN. The temperature to which the lubricant is submitted determines the oxidation rate. In mineral oils at temperatures lower than 60°C the oxidation rate is very low, but as oil temperature rises the oxidation rate rises as well (Rizvi 2009; Totten 2006). In addition, contaminants like water, metals and the amount of air in the lubricant can also increase oxidation rate (Rizvi 2009; Awaja and Pavel 2006). In Figure 2.4 it is shown the influence of contaminants on oxidation rate. Another important factor on lubricating oil degradation is additive depletion. Additives render lubricant with greater stability and resistance to changes (Totten 2006; Rizvi 2009).

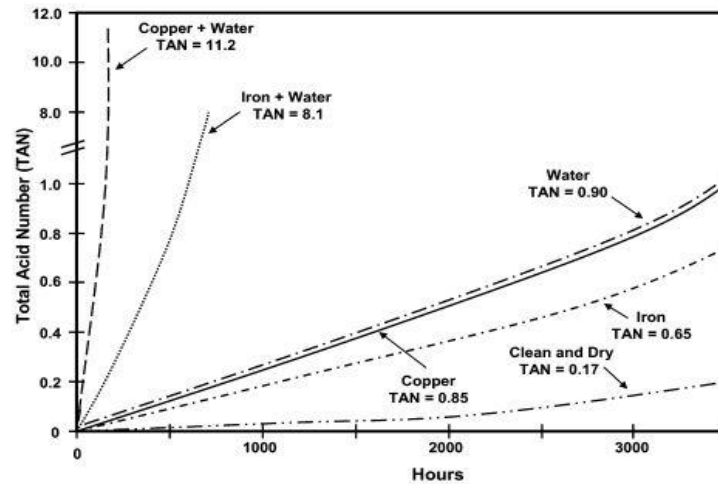


Figure 2.4 - Catalytic effects of contaminants on oil oxidation (ASTM D943).

According to Rizvi (2009) the reduction in the additives concentration by the end of use may be 46% for detergents, 16% for ashless dispersant, 45% for zinc dialkyl dithiophosphate, 45% for oxidation inhibitor package, and 9% for viscosity modifiers.

Another mentionable mechanism of oil degradation is thermal breakdown. This occurs when the temperatures rise above the point of thermal stability of the oil. The lubricating oil must not only lubricate the moving parts of the system, instead it also has to cool down the machinery, leading to an increase in the lubricant temperature that can sometimes be above its thermal stability point. High temperatures can also trigger a positive feedback on the oils degradation if it leads to the lubricant to vaporize and thus promote additives depletion. While in service, the lubricating oil is contaminated with foreign substances and products of oil deterioration (Awaja and Pavel 2006; Speight and Exall 2014).

Foreign substances may arise from the lubricated metal surfaces due to wear or corrosion, water from the cooling system or product of fuel combustion, carbonaceous particles from incomplete fuel combustion and even fuel itself that may enter the crankcase of the engine such as gasoline or diesel (Awaja and Pavel 2006; Speight and Exall 2014). Contaminants present in the oil vary according to the type of application of the oil, the additives package, the type of engine or machinery and the type of fuel (Speight and Exall 2014). Another form of contamination may occur during storage and collection. This form of contamination is much more severe given that the sources are less foreseeable. Polychlorinated biphenyl compounds (PCBs), visible in Figure 2.5, are substances listed as human carcinogenic and can be found in used oils even though in a

low concentration because in some places waste PCB are blended with used oils for disposal. Besides PCB, antifreeze fluid is also commonly found combined with used oils. Another group of contaminants of concern is halogenated solvents like perchloroethylene (tetrachloroethane), methylene chloride, trichloroethylene, and 1,1,1-trichloroethane, that can be used as cleaning agents (Totten 2006).

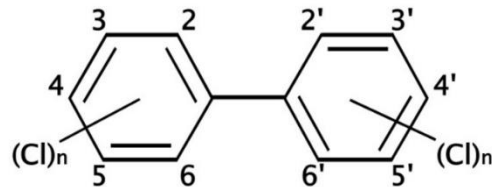


Figure 2.5 - Chemical structure of PCBs

Given that these contaminants are not part of the lubricant composition, their presence is a way to know that the used lubricant has been mixed improperly with other substances. Regarding the products of oil degradation, the most prominent contaminants are (Speight and Exall 2014; Awaja and Pavel 2006):

- oil-soluble products generated during oil oxidation;
- sludge from incomplete combustion of fuels;
- lacquer from subjecting sludge in the oil to high temperature operation;

Contamination control is very important to prolong the lubricants life. Usually a sort of filtration system is put in place, though it never removes all the contaminants from the lubrication system. However, the filtration system can still contain the level of contamination to a certain degree that ideally is below the components tolerance level. The extent of the lubricants contamination is influenced by many different factors that interact through complex ways, such as the rate of contaminant entry to the system, rate of wear debris production, type of filtration implemented in the lubricated system, filter characteristics, fluid loss and contamination tolerance of the system parts (Totten 2006). In addition, it is also important to mention that used engine oils may contain PAHs, hazardous substances formed during combustion (King et al. 2001).

2.2.2. Management of used oils

Used lubricant oil (ULO) is a hazardous waste that must be handled carefully, not only because it is a threat to the environment if not properly managed, but also because it is a valuable resource. According to the Compendium of Recycling and Destruction Technologies for Waste Oil compiled by the United Nations Environment Programme (UNEP 2012), management of waste oil has a particular importance due to the large quantities that are generated globally by the transport and industrial activities. Data provided by the Report from the Commission to the Council and the European Parliament of 19 July 2006 on implementation of the Community waste legislation on the matter of waste oil management, in 2003 nearly 2 million tonnes of waste oils were collected, meaning a collection rate of 81%. From the 2 million tonnes collected, 44% went to regeneration and 46% were treated by combustion. On a global scale, these numbers change significantly. According to UNEP (2012) the estimated global collection of waste oils is around 15 million metric tonnes (MMT) of the estimated 45 million metric tonnes of new oil produced globally, which means that only 33% are collected. This can be explained by the fact that in many places of the world the collection of waste oil is not yet well established and the cost of doing so can be discouraging. To avoid this kind of situations, governments play an important role. Legislation and regulations can be the most important tool of a good waste oil management process. According to Totten (2006), Germany and Italy subsidize the collection and re-refining of used oils as an encouragement. In Portugal, the Decreto Lei n° 153/2003, 11th July 2003, in Chapter IV states waste oil management procedures that organizations must follow on the collection, transportation, storage and treatment of used oils. It also establishes penalties to be applied in case of improper disposal of used oils and incorrect management activities.

2.2.3. European and Portuguese legislation overview

An important tool for a proper management and handling of used oil is through legislation. Even though the consequences of an incorrect handling of used oils can have global repercussions, the legislative measures regarding waste oils vary from country to country. In the EU the first important regulation was Waste Oil Directive 75/439/EEC of 16 June 1975. This Directive establishes the measures that the Member States (MS) must follow in order to minimize the environmental impact of the disposal of waste oils. MS must ensure the collection of waste oils, and follow the waste hierarchy: the priority must be given to regeneration by re-refining process and whenever such is not possible, combustion, destruction and storage of used oils may be considered. Directive 75/439/EEC strictly prohibits discharges into inland surface water, ground

water, territorial sea and drainage systems. It is also prohibited to make any discharge of used oils into the soil. Mixing used oils with PCB and PCT or any toxic and dangerous wastes is also forbidden. This Directive was amended by Directive 2008/98/EC which establishes the European law on the matter of waste in general and not only on waste oil. Another mentionable document is Directive 2000/76/EC which regulates the incineration of waste, including used oils. This document stipulated in which conditions a used oil can follow the path of energetic valorization via combustion as well as the conditions in which is strictly prohibited the burning of used oils. Regarding Portuguese legislation, the Decreto Lei n° 153/2003 provides the rules to properly manage used oils, as well as new oils, transposing the European Directive 75/439/EC of 16 of June 1975 repealed by Directive 2008/98/EC of 22 of November 2008. In Table 2.1 is possible to see the technical specification waste oil must meet before proceeding to regeneration according to Portuguese Legislation. In 2005, the Portuguese law licenced a company named “Sogilub” to manage oil collection and disposal under the guidelines of Despacho n° 662/2005. In clause n° 5 of this document is introduced a tax of 63€/m³ for the lubricant manufactures to pay in order to support the used oil management system. Sogilub must accomplish:

- collecting 70% of the used oils generated annually;
- recycling at least 50% of the collected used oil;
- valorization of all the collected used oil;

The technical specification that the collected, treated and recycled used oil must have before and after the valorization process are also addressed on the document

Table 2.1 - Technical Specification waste oil must meet before proceeding to regeneration according to Portuguese Legislation.

characteristic	unit	minimum value	maximum value
PCB	ppm	-	50
water	weight percentage	-	10
sediments	weight percentage	-	3
coagulation	-	no	no
total chlorine	ppm	-	2000
flash point	°C	180	-

According to EU regulation for the classification of waste, Commission Decision 2014/955/EU (amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC of the European Parliament and of the Council) that came into force on 1st June 2015, waste lubricant

oils are classified mainly in Chapter 13 (oil wastes and waste of liquid fuels) as hazardous. For example, code 130204* refers to “mineral-based chlorinated engine, gear and lubricating oils”. The asterisk mark means that the waste has at least one of the fifteen hazardous properties (HP1 to HP15). Used oil is a hazardous probably due to harmful / toxic, irritant, carcinogenic or ecotoxic properties.

2.2.4. Used oil valorisation

Used oil should be disposed properly not only to reduce its environmental impact, but also because of its potential as valuable resource. There are currently many options to recycle and recover used oil, but the preferable options are the ones in line with waste management hierarchy (UNEP 2012). A mentionable option to recover used oil is reconditioning. Reconditioning involves the removal of impurities such as solids and water through basic physical methods (settling, filtration, centrifuging, heating and dehydration) but it does not remove oil-soluble contaminants. This pathway allows the lubricant to be used again in the same or related application and through this way extends its useful life (Rizvi 2009). Recycling of used oil may involve a series of changes and treatment steps that will allow reuse of this asset. In Table 2.2 is possible to see the technical specifications waste oils must meet in order to be able to go to recycling route according to Portuguese legislation. The recycling processes consist mainly of two commercial regeneration methods of waste oils: reclamation and re-refining (Rizvi 2009; Mang 2014).

Reclamation is a recycling process applied to industrial lubricants, with particularly incidence in hydraulic oils, that consists of a higher degree of reprocessing (UNIDO 2003). The process for used oil reclamation involves mechanical purification and chemical processes. These include settling, centrifuging and filtering, followed by clay and alkali treatment to remove polar oxygenated compounds and acidic contaminants. Though reclaimed lubricant oil quality is either the same or lower than the one prior to its use, reclamation offers an opportunity for reuse in the original application (Rizvi 2009; Mang 2014).

On the top of the waste oil hierarchy is the process of used oil re-refining. Re-refining is a process that also aims to recover a valuable resource. Re-refining is the most complex recycling process, consisting in re-refining used oil to obtain mineral base oil just as good or even better than the original base stock that gave origin to the used oil being re-refined through petroleum refining techniques (Mang 2014; Rizvi 2009). Any petroleum-based lubricant can be produced through this pathway. According to a study led by UNIDO (2003), the safest route for waste oil is to re-refine it. In this process, first the contaminants are removed from the used lubricant, and then the oil is distilled and molecules reformed to produce new base oil. Initially a pre-treatment is applied to reduce contaminant levels and impurity content through application of heat, filtration and treatment with acids, caustic and other chemicals. Other steps in re-refining include vacuum distillation, solvent extraction, thin-film evaporation, hydrogenation and catalytic hydrotreating (Mang 2014; Speight & Exall 2014; Rizvi 2009). The quality of the base stock produced by re-

refining is highly influenced by the type of used oil (Mortier et al. 2010;). Nonetheless, re-refined base oil must meet the same specification as unused crankcase oil (Mang 2014; Speight & Exall 2014). According to Rizvi (2009), for every gallon of used oil that is re-refined, nearly 50% is converted into base oil, 25% distills as light ends fuels, 15% remains as bottom asphalt and 10% is water. Regarding other recycling options, re-refining provides significant energy savings and fewer environmental impacts (UNIDO 2003). According to Grice et al. (2014) the life cycle carbon footprint of re-refined oil is 81% lower than base oil that is not re-refined.

Another disposal route is combustion of used lubricant as a fuel. For instance, waste engine oil can be a good fuel given that is essentially composed of hydrocarbons and it does not contain a heavy residual fraction like heavy fuels usually do (Audibert 2006). Regarding to the other previously mentioned disposal routes for used oil, the most efficient in terms of energy conservation is combustion of used lubricant as fuel (Mortier et al. 2010). The most common application of used oil is as a fuel for industrial furnaces due to the lower price relatively to other fuel oils (Mang 2014). Some pre-treatment of the used lubricant may be required to make sure that emissions of PCBs, PAH's, dioxins and heavy metals do not exceed the regulated emission standards (Mortier et al. 2010; Pawlak 2003). A very popular use is in cement production, with the advantage of retaining in the cement the hazardous contaminants present in the used oil (Mortier et al. 2010; Mang 2014).

Table 2.2 - Technical Specifications waste oils must meet in order to be able to go to recycling route according to Portuguese Legislation.

characteristic	unit	minimum value	maximum value	test method
density at 15 °C	-	0.855	0.925	ASTM D-4052
flash point	°C	65	-	ASTM D-93
water content	weight percentage	-	3	ASTM D-95
sediments content	weight percentage	-	0.75	-
ramsbottom carbon residue	weight percentage	-	2	ASTM D-524
total chlorine	ppm	-	2000	-
PCB/PCT	ppm	-	50	H.P.G.C.-ECD
total sulphur	weight percentage	-	1	ASTM D-1552
lead	ppm	-	750	ASTM D-5185
nickel	ppm	-	15	IP-288
chromium	ppm	-	5	ASTM D-5185
copper	ppm	-	200	ASTM D-5185
vanadium	ppm	-	5	IP-288
cadmium	ppm	-	1	ASTM D-5185

2.2.5. Environmental issues

As already mentioned, used oil is a hazardous waste, since poses a threat to the environment and human health if not handled correctly. For example, UNEP (2012) highlights that many people change their own car motor oil rather than having it done in professional shops. The oil leaked on soil migrates downward by gravity through the soil, and it may reach groundwater. According to UNEP (2012), the used oil from one oil change can contaminate 1 million gallons (3785411.78 Liters) of drinking water unfit to drink. New motor oil has lighter hydrocarbons that pose a threat to aquatic organisms on the short term, while used motor oil contains a greater content of metals and heavy polycyclic aromatic hydrocarbons (PAHs) with a long-term effect. The PAH content of used motor oil can be 670 times higher than the one in new motor oil (Vazquez-Duhalt 1989). Of all the toxic components on used oil, aromatics are considered to be the ones that pose a major threat to the environment for their relative persistence and chronic effects, including carcinogenicity, mutagenicity and teratogenicity (Irwin, R.J., M. VanMouwerik, L. Stevens and Seese 1997). The metals present in used oil that poses a greater concern are most of all lead, and to a lesser extent zinc, chromium, barium, arsenic and cadmium (Irwin, R.J., M. VanMouwerik, L. Stevens and Seese 1997; Totten 2006). The presence of used motor oil in the soil dramatically interferes with the development of the microbial communities. The biological cycles are affected, plant development is inhibited, and metal content of remaining plants is increased. In aquatic environments, the presence of used motor oil causes a change in microbial communities, a decrease in primary production of phytoplankton and damages shell fish (Vazquez-Duhalt, 1989). The presence of used oil in the environment also has impact on mammals and birds, such as toxic contamination, destruction of food resources and habitats, reduced reproductive ability and for some species oil vapours damage their central nervous systems, lungs and livers. Another matter of concern in respect to the environment is the emission of metals and PAHs to the atmosphere due to uncontrolled burning of used oils, that may be adsorbed by air-borne particulate matter that eventually is deposited in soil and water. Emissions of dioxins and furans, which are highly carcinogenic substances, is also a matter of concern and constitute a more worrying form of pollution to the environment (UNEP 2012). Of all the diverse constituents of used oil, the most carcinogenic components are poly-aromatic hydrocarbons (PAHs) with 3–7 rings such as benz-o-pyrene, benz-o-anthracene, and chrysene (Mang 2014).

3. State of the art

In this chapter a review of existing studies regarding used lubricating oil characterization is made as well as relevant work on the subject highlighted. The aim of this chapter is to get an insight of current practises and seek information that can be helpful for the development of this work. Used oil is a very complex waste, and for that reason it is very difficult to characterize. Besides that, new technologies allied with new additives emerging on the market further complicate a general characterization process. Currently in the literature there are limited published works on this regard and some of the existing ones are outdated. Nevertheless, used oil characterization as an integrated part of valorization processes is still a developing field and there are some relevant papers on the subject of this dissertation that will be presented on this chapter.

Regarding physicochemical characterization of used oil, only a few studies can be found in the literature, as it is possible to see in Table 3.1. Ouffoue et al. (2013) contributed to waste oil characterization field by carrying a physicochemical characterization of waste oils and an analysis to detect potential organic pollutants contained or hidden in these oils. They measured parameters such as density at 15°C, kinematic viscosity at 40°C, water content, flashpoint, sulphur content, pour point, calorific value, ash content in accordance with ASTM protocols of analysis. They concluded that through physicochemical analysis it was possible to indicate the presence of minerals and metals in used oils in a concentration 30 times higher to that of new lubricating oils. Rahimi et al. (2012), in their used oil analysis study measured viscosity at 40 and 100°C, viscosity index, flash point; pour point, specific gravity, colour, total acid and base numbers and water content. Their results showed a decreasing trend in concentration of additive elements and increasing in concentration for wear elements. Al-Ghouti and Al-Atoum (2007) in their study measured viscosity, flash point, pour point, and copper corrosion and concluded that physical and chemical oil analysis can be an effective tool for assuring the quality of recycled oil.

Throughout the literature is possible to see that the most employed techniques of characterization of used oil samples are those based in spectroscopic methods, as seen in Table 3.2. These methods of analysis rely upon the interaction between electromagnetic radiation and matter and measure the amount of radiation emitted or absorbed by molecules or atomic species of interest. For used oil analysis, Fourier transform infrared spectroscopy (FTIR) is the most common technique. Kupareva et al. (2012), concluded that FTIR alone is not adequate to determinate aromatic compounds in the oil samples. A study performed by Zięba-Palus and Kościelniak, (1999), with the intent to analyse motor oil focussing on the determination of additives for the sake of criminal

purposes, used FTIR technique and concluded that FTIR results alone were not conclusive. Al-Ghouti and Al-Atoum, (2009), also used this technique in their analyses to determine the extent of the differences occurring between the virgin and used recycled oil. Dominguez-Rosado and Pichtel, (2003), compared the chemical composition of fresh oil, used motor oil, and naturally weathered used oil, and successfully used FTIR spectra to identify functional groups in the different samples. Another spectroscopic technique widely used is inductively coupled plasma atomic emission spectroscopy (ICP-AES) also referred to inductively coupled plasma optical emission spectrometry (ICP-OES). It has been used to detect trace metals. In this technique inductively coupled plasma is used to produce excited atoms and ions which emit electromagnetic radiation in characteristic wavelength. In an effort to better understand the possible processes that alter the oil composition, Abdul et al., (2015), performed a study on the heavy metal distribution in virgin, used, waste and recovered oil in term of their additives, contaminants and wear elements using ICP-OES analysis. They found this technique very useful for differentiation purposes. Another spectroscopic method used to characterize used oil samples than can be found in literature is nuclear magnetic resonance spectroscopy (NMR), which is a technique based on the magnetic properties of certain atomic nucleus. In Kupareva et al., (2012), characterization involved NMR technique and the results provided more detailed information regarding the hydrocarbon structure of the used oil samples and also confirmed some data obtained by FTIR spectroscopy. In the chemical characterization study of fresh, used and weathered motor oil performed by Dominguez-Rosado and Pichtel, (2003), NMR was also applied and the results of used oil analysis showed the presence of new aromatic peaks compared with new motor oil. Additional spectroscopic techniques found in the literature are atomic absorption (AAS) and X-ray fluorescence (XRF) spectroscopy. AAS uses the absorption of optical radiation by free atoms in gaseous state, and XRF measures the fluorescent or secondary X-ray emitted from a sample when excited by a primary X-ray source. Both techniques allow to determine the presence of certain elements in the sample, and mostly used to determine the presence of heavy metals. In Zięba-Palus and Kościelniak (1999), combined FTIR, XRF and AAS spectrometry techniques and concluded that the AAS method delivered the most useful and reliable information regarding elemental composition of the oil samples examined. Christensen and Agerbo (1981) performed a determination of sulphur and heavy metals in crude oil and petroleum products combining energy-dispersive X-ray fluorescence spectrometry (EDXRF) technique and the fundamental parameter approach to provide a method for determining part-per-million levels of sulphur and heavy

metals. Their results proved to be accurate in a range of 2-5%, proving that EDXRF is a good technique for the determination of metal content.

Hereafter spectroscopic approach, gas chromatography–mass spectrometry (GC-MS) was the most commonly found technique employed in used oil characterization literature. GC-MS is an analytical technique that combines both gas-chromatography and mass spectrometry. In mass spectrometry (MS), chemical species are ionized and the ions are separated by their mass-to-charge ratio, and in gas chromatography (GC), the sample components of a vaporized sample are separated as a result of their partition between a mobile gaseous phase and a stationary liquid or solid phase contained within the chromatographic column. Yang et al. (2015) performed a study of virgin and used lubricants characteristics aiming to identify contamination or adulteration sources through chemical fingerprint analysis and used GC-MS for this purpose. The separation and analyses of target compounds in the oil samples were accomplished using this method. Lu and Kaplan (2008) studied the difference in chemical composition for fresh and used motor oils and their partitioning effect in water. The selected technique was also GC-MS.

Overall, both physical and the chemical properties measurement are good used oil characterization techniques. When combined, they allow more conclusive results, and thus a more robust study.

Table 3.1 - Literature review: studies that included physicochemical characterization of ULO.

Ref.	Analytical techniques	Materials and methods	Properties measured	Main conclusions
Ouffoue et al. 2013	Density	ASTM 4052	Physical and chemical parameters; functional groups focusing on volatile hydrocarbons, hydrogen sulphide, mercaptans in order to detect potential organic pollutants	Through the physicochemical analysis carried it was possible to indicate the presence of minerals and metals in used oils in a concentration 30 times higher to that of new lubricating oils
	Kinematic viscosity	ASTM 94		
	Ash content	ASTM 482		
	Water content	ASTM 95		
	Calorific value	ASTM 4868		
	Pour point	ASTM 94		
	Flashpoint	ASTM 94		
	Sulphur content	ASTM 4294		
Rahimi et al. 2012	Dräger semi-quantitative colorimetric method	No specifications were made		
	ICPOES	No specifications were made	Elemental analysis, functional groups, physical and chemical properties	The results showed a decreasing trend in concentration of additive elements and increasing in concentration for wear elements
	FTIR	FTIR spectrum was recorded on a FTIR spectrum Perkin Elmer model Spectrum 65 using KBr pellets		
	Viscosity	ASTM D445		
	Viscosity index	ASTM D2270		
	Flash point	ASTM D4095		
	Viscosity index	ASTM D5920		
	Flash point	ASTM D7745		
	Viscosity index	ASTM D9570		
	Flash point	ASTM D11395		
Viscosity index	ASTM D13220			
Al-Ghouti and Al-Atoum 2007	ICP-AES	3 g of the oil sample were weighed and diluted in a 50 ml flask. Samples were prepared by dilution of these solutions, 20, 50 or 100 times, depending on the species of metal being determines, using xylene	Elemental analysis, functional groups, physical and chemical properties	They concluded that FTIR and quantitative element analysis might be accepted as a good feature for differentiation between virgin and used recycled engine oil samples and also that physical and chemical oil analysis can be an effective tool for assuring the quality of purification method.
	FTIR	It was used a resolution of 4cm^{-1} at 64 scans and KBr disks; spectra were recorded with a range of 4000 to 400cm^{-1}		
	Viscosity	ASTM D-445		
	Flash point	ASTM D-92		
	Pour point	ASTM D-97		
	Copper corrosion	ASTM D-130		

Table 3.2 – Literature review: characterization with a spectroscopic approach.

Ref.	Analytical techniques	Materials and methods	Properties measured	Main conclusions
Abdul et al. 2015	ICP-AES	The samples were dissolved in oil soluble solvent, (kerosene) prior to analysis with ICP-OES. The oil analysis was based on ASTM D-5185	Elemental analysis focusing on the concentration of heavy metals	The results showed no significant change for additive content in in virgin and used oil samples.
Yang et al. 2015	(GC/MS)	Samples were eluted with hexane (12 mL), a mixture of hexane: dichloromethane (1:1 v/v, 15 mL), and 15 mL of dichloromethane.	Functional groups focusing on total petroleum hydrocarbons and polycyclic aromatic hydrocarbons	The used oil analysis showed a mixed signature of lube oil and fuel oil such as diesel, biodiesel and gasoline.
Kupareva et al. 2012	(GC/MS) FTIR NMR spectroscopy CHNS/O analysis	Sample was diluted with hexane to 2 mL; Helium was the carrier gas; Heating rate was of 8 °C/min from 80 to 340 °C Potassium bromide (KBr) discs were used; Spectra was obtained in a range of 4000 - 500 cm ⁻¹ The solvent applied was Deuterated chloroform (CDCl ₃) It was used a FlashEA 112 organic; The technique used was based on quantitative "dynamic flash combustion"	Elemental and functional groups analysis in order to determine chemical composition	FTIR alone is not adequate to determinate aromatic compounds in the oil samples. Different techniques complement each other to determine the chemical nature of samples. NMR results show that paraffinic hydrocarbons of the fresh oil are more linear and have longer chains than those in the used oil.
Lu and Kaplan 2008	(GC/MS)	The heating rate was 4 °C/min, from 40 °C to 310°C and held for 30 min	Chemical analysis of the hydrocarbon composition and compounds extracted by water washing	The presence of one to two-ring aromatics, such as alkylbenzenes, naphthalene, and alkyl-naphthalenes were found to be the most notorious differences between unused and used motor oils.

Table 3.2 – (continuation).

Ref.	Analytical techniques	Materials and methods	Properties measured	Main conclusions
Dominguez-Rosado and Pichtel 2003	FTIR (GC/MS) NMR spectroscopy	Sodium chloride (NaCl) polished discs (25 X 2 mm) were used and four scans were carried in a range of 4000-400 cm ⁻¹ . Deuterated chloroform (CDC1 3) was added to 5 mL of the oil sample and a number of 16 scans was used; The heating rate was 12°C/min from 45°C to 325°C It was placed 0.5 g of used oil in a digestion flask and 4 mL of concentrated H ₂ SO ₄ added: A temperature of 440°C was used and 10 mL of water added and refluxed for 2min.	Functional groups and elemental analysis	The results showed that used oil contained new aliphatic and aromatic hydrocarbon compounds such as 1,3,5-trimethyl benzene, p-xylene and methyl ester undecanoic acid and regarding metal content the numbers were below the ones found in previous papers
Zięba-Palus and Kościelniak 1999	FTIR XRF AAS	Spectra was recorded in a range of 600-3800 cm ⁻¹ . To place the samples, it was used a NaCl absorption cell of 0.04 mm thickness: The resolution used was 4cm ⁻¹ 5 ml of sample was filled in the measurement cell and analysed directly; The chamber environment was helium A background correction unit and an automatic gas control unit were used with an air-acetylene flame; Aqueous standard stock solutions were used for calibration.	Elemental and functional groups analysis for the determination of additives in oil samples for criminal purposes.	Infrared spectroscopy supported by quantitative elemental analysis delivers good information on additives and can be recommended. Also, results obtained through only FTIR were not conclusive. AAS method delivered the most useful and reliable information regarding elemental composition of the oil samples.
Christensen and Agerbo 1981	EDXRF	Samples are analysed directly without any kind of sample preparation. An open cell arrangement consisting of a spectro cup and a very thin Mylar window (<4 µm) is used as a sample holder	Elemental analysis mostly focusing heavy metals and sulphur	Their results proved to be accurate in a range of 2-5%, proving EDXRF to be a good technique to the determination of metal content in used oils.

4. Materials and methods

In this chapter, it will be described the experimental procedures and analytical methods that were applied to characterize the used oil samples during the bench scale studies. Agitation of samples was promoted prior to all procedures in order to accomplish a proper blending of sample and preventing separation of components.

4.1.Sampling

According to the results observed in the coagulation test (procedure detailed in the next section), four categories were identified: A – oil samples viscosity did not change after the coagulation test; B1 – oil samples displayed an increase in viscosity; B2 – oil samples formed a precipitate or a partial coagulation; C – all of the oil matrix coagulate. Within the scope of the project CONUR II, about 30 samples from each of these categories were initially requested to Sogilub (120 samples) aiming to have an equilibrated distribution of each category. For reasons beyond this work, instead it was received 63 samples from category A, 14 samples from category B1, 19 from category B2 and 37 from category C, in a sum of 133 samples. The samples were numbered from S1 to S133. In Table 4.1 is displayed a Summary report of coagulation category samples.

Table 4.1 - Summary report of coagulation category samples.

Category	Number of samples	Reference
A	63	S1 to S63
B1	14	S64 to S77
B2	19	S78 to S96
C	37	S97 to S133
Total	133	

4.2. Coagulation test

The coagulation test was performed to all of 133 used oil samples received in the laboratory. The coagulation test consists in the following steps:

- 1) 100 g of sample were weighted into a stainless-steel cup;
- 2) 10 g of an aqueous solution of 50% KOH (w/w) were mixed with the sample;
- 3) The mixture is gradually heated until 180 °C. In certain cases, anti-foaming might be required in order to avoid excessive foam formation;
- 4) When the sample reaches 180 °C, insert immediately the stainless-steel cup in a water bath at 15 °C to facilitate the cooling process;
- 5) Wait until the sample cooled down to room temperature, and classify the result of the test in categories A, B1, B2 and C.

Indeed, if the sample shows fluidity and no increase in viscosity is observed, then the result is negative and the terminology used to distinguish negative samples was the letter A. The result was considered positive when the sample showed no fluidity at all, or in other words, a soap was formed. The terminology for positive samples was the letter C. In many occasions, the results were ambiguous and so there was the need to add more results criteria. If the sample showed fluidity but an increase in viscosity is observed, it would be categorized as B1. Another possibility was the formation of precipitates or positive behaviour in some parts of the sample while the other parts maintained fluidity. This type of results was categorized as B2.

4.3. FT-IR analysis

In order to identify the functional groups, present in used oil samples, FT-IR (Fourier Transform Infrared) analyses were made. Structural features of a molecule, regardless if they are functional groups attached or the backbone of the molecule, produce characteristic and reproducible absorption peaks in the infrared spectrum (Meyers 2006). For this reason, infrared spectrum represents a fingerprint of the substance being analysed and thus an excellent tool for the identification of functional groups (Stuart 2004). An IR spectrometer emits radiation that reaches the sample, where some of the radiation is absorbed and vibrational excitation occurs, and the rest of the radiation is transmitted (Skoog et al. 2013). The instrument used in this work was spectrometer Jasco FT/IR – 4200, and spectrums were obtained within the mid infrared

wavenumbers 4000-400 cm^{-1} using 64 scans/sample with a resolution of 4 cm^{-1} . In order to perform measurements potassium bromide (KBr) pellets were used. The pellets were prepared by properly grinding KBr and weighting 80 mg and using a pneumatic press. Because FTIRs are very sensitive (Smith 2011), only a few milligrams of sample were placed on the surface of the pellet forming a translucent thin layer that allows a good transmittance. A background spectrum was taken with KBr pellets before proceeding to the scanning of the oil samples in order to have a spectral response of the instrument that will be removed so that the spectrum obtained is strictly due to the sample. All material used to perform the analyses were cleaned with ethanol.

4.4. Energy dispersive X-ray fluorescence (EDXRF)

Energy-dispersive X-ray fluorescence (EDXRF) is an analytical method used for qualitative as well as quantitative determination of elements in a sample based on the fact that when elements are irradiated with high-energetic X-rays there is a certain probability of emitting characteristic X-rays, which are unique for each element (Meyers 2006). The EDXRF spectrometer irradiates the sample with X-rays and an energy dispersive detector combined with a multi-channel analyser collects the fluorescence radiation that the sample emits while at the same time the different energies of the characteristic radiation from each of the many elements of the sample is separated (Schneider 2011; Meyers 2006). In this study, an elemental analysis was performed using EDXRF for measuring the concentration of: magnesium (Mg), aluminium (Al), silicium (Si), phosphorus(P), sulphur(S), chlorine (Cl), calcium (Ca), chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), sodium (Na), manganese (Mn), molybdenum (Mo), lead (Pb) and barium (Ba). In Table 4.2 is possible to see which elements are usually associated with different additive packages.

Table 4.2 - Elements associated with different kind of Additives.

Additives	Elements
Detergents	Ca, Ba, Mg
Anti-Wear and extreme-pressure	Cl, S, P, Cu, Zn
Antioxidants	Ca, Mo, Ba, Cu
Rust and Corrosion Inhibitors	P, S, Zn

The equipment used was a Nex CG Rigaku spectrometer, with an analysing capacity ranging from sodium ($_{11}\text{Na}$) to uranium ($_{92}\text{U}$). It was poured 4 g of sample into special cells with a very thin transparent film surface. This technique does not require a sample preparation, and thus the oil samples were directly analysed.

4.5. Total acid number (TAN)

TAN is a measure of the amount of the acidic constituents present in the lubricant and can be determined by titrating with a base according to standard ASTM D664. The method requires the preparation of a specific solvent with 500 mL of toluene, 495 mL isopropanol (IPA) and 5 mL CO_2 -free water. An appropriate amount of sample was weighted according to the expected TAN for the sample. In Table 4.3 is possible to see the appropriate sample size to be used for different expected TAN value. The sample must be free of visible sediments. The sample was then poured into a titration vessel to which 125 mL of the solvent was added and mixed. Before proceeding with the measurements, the electrode was placed for about 5 min into distilled water. A titration of a blank solution (only solvent) was made. After that, the titration was performed using an isopropanol potassium hydroxide solution (KOH in IPA) of 0.1 mol/L. The results obtained are expressed in terms of milligrams of KOH needed to neutralized one gram of substance. The results were obtained through software tiamoTM where a curve of consumed titrant against the potential measured was displayed. Eq. (4.1) was used to calculate the TAN of the sample expressed in mg KOH/g sample:

$$TAN = \frac{(V_{last\ EP} - V_{blank}) \times c_{KOH} \times f \times M_A}{m_s} \quad (4.1)$$

where $V_{last\ EP}$ is the volume of titrant consumption in mL to reach the last equivalence point (EP); V_{blank} is the titrant consumption in mL to reach the equivalence point for blank; c_{KOH} is the concentration of titrant in mol/L (0.1 mol/L); f is the correction factor for the concentration of titrant and is dimensionless; M_A is the molar mass of KOH (56.106 g/mol); and m_s is the sample weight in grams (g). Usually one equivalent point is achieved, but if the solution has strong acids, several EP could be observed, and the last one is used for calculations. After every sample titration, the electrode and burette tip were thoroughly cleaned using first the solvent mixture, then IPA and lastly distilled water. The equipment used to perform measurements was the volumetric titrator Metrohm 905 Titrando, and the electrode Solvotrode EasyClean with an electrolyte solution of

lithium chloride saturated in ethanol. Table 4.3 indicates the mass of the sample as a function of the expected TAN.

Table 4.3 - Sample size according to the expected TAN value.

TAN [mg KOH/g sample]	Sample weight [g]	Weighing accuracy [mg]
0.05-0.9	10 ± 2	100
1-4.9	± 0.5	20
5-19	1 ± 0.1	5
20-99	0.25 ± 0.02	1
100-250	0.1 ± 0.01	0.5

4.6.Saponification number

Saponification number (SP) measurements were performed to determine the amount of constituents in the ULO that will saponify under specific test conditions. The equipment used was the volumetric titrator Metrohm 905 Titrando and a Solvotrode electrode with an electrolyte solution of tetraethylammonium bromide (TEABR) in ethylene glycol. The SN was determined in compliance with standard ASTM D94. First a blank determination was carried. To prepare the blank solution, 25 mL of alcoholic KOH 0.5 M solution and 25 mL of butanone were placed in an Erlenmeyer, heated under magnetic stirring and connect it to a condenser after refluxing begins. After 30 min, the Erlenmeyer was taken from the plate of agitation and 50 mL of naphtha was poured down the condenser. Titration of the blank occurs without reheating, using 0.5 M hydrochloric acid (HCl) at a flowrate of 2 mL/min. The samples were weighed in an Erlenmeyer in accordance with the expected SN. Because used oil is difficult to dissolve, 25 mL of White Spirit (Stoddard Solvent) solution were added to the sample first, and only then 25 mL of butanone was added to the sample, followed by 25 mL of alcoholic solution of KOH (0.5 M). Then, the same refluxing and heating procedure described to the blank was applied to the sample. Samples were titrated while hot with no reheating using 0.5 M HCl. The SN is expressed as the amount of required milligrams of KOH to saponify 1 g of sample, according to

$$SN = \frac{(V_{blank} - V_{EP1}) \times f \times c(HCl) \times M_A}{m_S} \quad (4.2)$$

where V_{blank} (mL) is the amount of titrant consumed until the equivalence point in blank solution; V_{EP1} (mL) is the amount of titrant consumed until the first equivalence point is reached when determining the sample; $c(\text{HCl})$ is the concentration of titrant (0.5 M); M_{A} is the molar mass of KOH (56.106 g/mol) and m_{s} is the amount of sample in grams (g) according to Table 4.4. Even though the intent of this experiment was to quantify saponifiable material present in ULO, there are other substances that may increase the SN by also consuming alkali and acids and that must be taken into account when looking at the results (ASTM International 2002). In Table 4.4 is possible to see the appropriate sample size according to the expected saponification number.

Table 4.4 - Sample size according to the expected saponification number.

Expected SN [mg KOH/g sample]	Sample weight [g]
200 – 250	1.7 – 1.4
250 – 300	1.3 – 1.2
> 300	1.1 – 1.0

4.7. Surface tension

Surface tension measurement of ULO samples were performed using a Sigma 70 Tensiometer applying the Wilhelmy Method. The temperature used for all samples were 30 °C and the interactive phase was air. To initiate the procedure, no sample preparation was required. Prior to measurements, the Wilhelmy plate was thoroughly cleaned using a burner flame to remove any residual organic contaminants and after cooled down to room temperature, it was emerged in ethanol. After drying, the probe was attached to the scale of the tensiometer with a thin metal wire and oriented to the interface perpendicularly. The Wilhelmy plate material was made of platinum, though the results obtained do not depend on the material of the plate as long as the plate is wetted by the liquid. The calculations were made by KSV's Sigma software. The measurements are made by means of recording the force exerted onto the probe due to wetting and applying it to calculate the surface tension, γ , according to the Wilhelmy Equation, Eq. (4.3):

$$\gamma = \frac{F}{l \times \cos(\theta)} \quad (4.3)$$

where γ is the surface tension of the sample (mN/m); l is the wetted perimeter ($= 2w+2d$, where w is the plate width and d is the plate thickness of the Wilhelmy plate, Figure 4.1) expressed in meters; F is the force on the plate due to wetting measured by the tensiometer (millinewtons); and θ is the contact angle between the liquid phase and the plate, which in this case is equal to zero due to complete wetting (Davis and Dykstra 2012). An illustration of the Wilhelmy plate method can be seen in Figure 4.1 for better understanding.

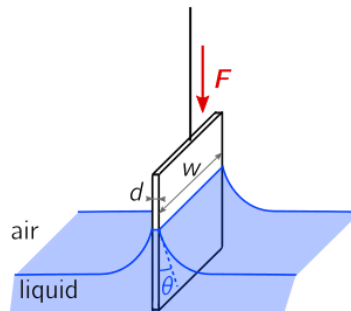


Figure 4.1 - Wilhelmy Plate

4.8. Kinematic viscosity

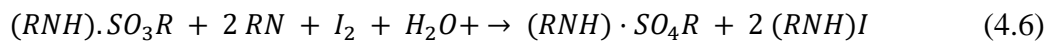
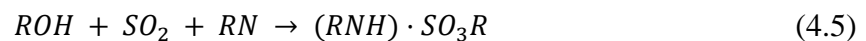
Kinematic viscosity measurements of used oil samples were performed at 40 °C using an Anton Parr-SVM 3000 Stabinger Viscosimeter. No sample preparation was required. The standard test method for dynamic viscosity and density of liquids by Stabinger viscometer (and the calculation of kinematic viscosity) ASTM D 7042 was applied. The calculations that allowed to obtain the kinematic viscosity values were made possible by the employment of the following equation:

$$KV = C \times t \quad (4.4)$$

where KV is the kinematic viscosity number of the sample in cSt; C is the intrinsic constant of the viscometer capillary tube in (mm^2/s^2) and t is the flux time (s) that samples took to flow from the lower to the upper meniscus mark of the viscometer.

4.9. Water content

The presence of water, a contaminant in lubricating oils, increases the oxidation rate contributing to a fast depletion of oxidation inhibitors and also according to Stern and Girdler 2007 causes certain oil additives to precipitate. Water content analysis were carried using a Mettler Toledo C20 Karl Fischer Coulometric Titrator and using HYDRANAL Coulomat Oil and CG as reagents. The analysis was performed in compliance with standard ASTM D6304. To perform the water content measurements, four drops of oil sample were injected in the titration vessel of the equipment. Note that no sample preparation is required. Karl Fischer titration is based on a twostep reaction where sulphur dioxide initially reacts with an alcohol (ROH) to form an ester intermediate which is neutralized by an appropriate organic base (RN) followed by oxidation of the alkylsulfite salt to an alkylsulfate salt by iodine that consumes water in a ratio of 1:1 to iodine (Stern and Girdler 2007; Mettler-Toledo, n.d.). The stoichiometry of this reaction is the following:



As long as the iodine reacts with the water present in the sample there will be no free iodine in the titration cell, and a high voltage is required to maintain the specified polarization current at the electrode. When all the water has reacted, free iodine will be present causing a current drop below a certain value that terminates the titration (Stern and Girdler 2007; Mettler-Toledo, n.d.).

4.10. Statistical methods

Most of the results were analysed based on inferential statistics methods. Hypothesis testing assumes true a certain condition (the null hypothesis) until new evidence suggests otherwise. The goal is to be able to determine statistically if the different coagulation categories are characterized by different properties. To that purpose, it will be assumed that the four categories are equal, which corresponds to the null hypothesis. The alternative hypothesis is that they are different. The significance level, denoted by α , is the probability of a type I error occur (rejection of the null hypothesis in favour of the alternative hypothesis - there is a difference in the set of data being compared). The typical significance level value is 0.05 and that was also the value used in this study (Bartolucci et al. 2015). The decision rule employed in hypothesis testing is: if the p-value is greater than α , the null hypothesis prevails; on the contrary, if the p-value is equal or lower to

the significance level, than the null hypothesis is rejected and the alternative is assumed true. A large p-value (>0.05) indicates weak evidence against the null hypothesis

- One way analysis of variance (ANOVA)

ANOVA is a method to compare the variation within groups to the variation between groups being study. Such inference is translated to a means group comparisons. The null hypothesis is that all means being compared are equal, and the alternative hypothesis is that at least two means are different from each other. The test statistic for analysis of variance is known as F-statistic or F-ratio, and can be translated as the ratio between the variation between group means and variation within groups. If there is a much larger variation between groups than within groups, then the group means will have a larger separation and will be considered different from one another. This means that if the null hypothesis is valid, then the expected F-statistic value should be close to 1. On the other hand, if the alternative hypothesis prevails, the F-statistic value should be much superior to 1.

- T-test for means

The t-test assesses if the means of two categories statistically differ from one other. This statistic test follows a t-distribution under the null hypothesis. If the calculated t-value is near zero, then there is much support for the null hypothesis, and it succeeds; if the calculated t value differs much from zero, then there is not much evidence for the null hypothesis, and the alternative hypothesis prevails. As t value increases, the p-value decreases, meaning rejection of the null hypothesis.

- Mean Diamonds

To display the results through graphical information it was chosen the Mean Diamonds because it allows the visualisation of information on the distribution of the results in an arrangement easy to understand. A mean diamond highlights the data mean and confidence interval. The top and bottom of each diamond represent the 95% confidence interval for each set of data. The horizontal range of each diamond along the X-axis is proportional to the number of samples. The line across the middle of the diamond indicates the mean value

5. Results and discussion

In this chapter, the results obtained throughout the experiments for the characterization of used oil samples will be presented and analysed. Statistical tools used in the analysis of experimental data will also be addressed in this chapter. For the statistical analysis of the results JMP Pro 12 software was used. The results obtained from the measurements of the properties of all the analysed samples can be seen in Annexes.

5.1. Physicochemical properties

As already mentioned, in this work it was intended to characterize different waste oil samples in order to identify compounds that can hinder the regeneration process involving alkaline treatment due the occurrence of phenomena of oil coagulation. Because the interest resided in samples that were positive (samples C) or displayed a different behaviour when subjected to the conditions of the test (samples B1 and B2), and also because of the time available was limited, no characterization of samples that remained unaffected under the coagulation test (samples A) was made. Nevertheless, to be able to compare the different coagulation classes in a more accurate way, it was necessary to collect the characterization results of samples A performed in the previous project, CONUR I. Characterization results from CONUR I of categories B1 and B2 was also used to fill the lack of samples from those categories.

5.1.1. Surface tension

The results plotted as means diamond of the surface tension measurements can be seen in Figure 5.1. As aforementioned, some information on the characterization of samples from CONUR I was added to the analysis to have a more equally balanced distribution of samples. Surface tension maximum values, as well as minimum values, were from samples from categories C (whose range was from 22.70 mN/m to 30.89 mN/m) and B2 (whose range was from 22.81 mN/m to 30.06 mN/m). The F ratio obtained for surface tension was 0.31. By analysing the F ratio value is not possible to take any conclusion given that, to assume the null hypothesis the F ratio should be close to 1. Also, if at least one of the means effect is greatly different from another, F should be much larger than 1. On the other hand, the obtained t-value of 1.992 is much different

from zero, giving no support to the null hypothesis, thus allowing more credit to the alternative hypothesis. This means that at least one of the coagulation categories differ from the others. From values listed in Table 5.1, it is possible to see the Connecting Letters Report, which explicit which categories are alike through the attribution of a letter to each category. Categories not connected by the same letter are significantly different. In this case, were assigned the same letter to all categories, and so no categories were found to be significantly different. In Table A.3, all categories are compared to each other individually in terms of the p-value. As it was already mentioned on the previous chapter, if the p-value is greater than 0.05 (confidence level), the null hypothesis cannot be rejected. All of the compared categories present a p-value much superior to the confidence level. This supports greatly the null hypothesis, which means that in surface tension measurements, all four coagulation categories are indistinguishable. Hence, it can be concluded that surface tension it is not a good indicator of whether the oil sample being analysed will coagulate under the coagulation test conditions or not.

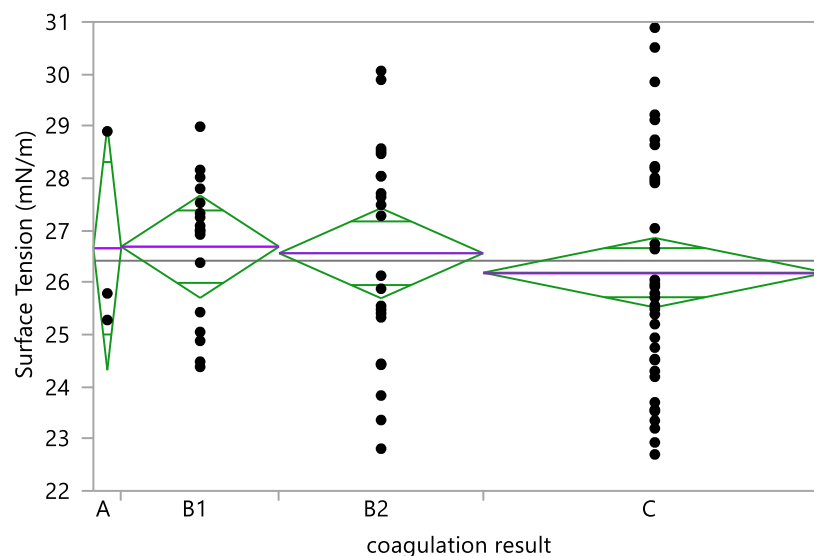


Figure 5.1 - One-way analysis of surface tension (mN/m) by coagulation result.

Table 5.1 - Connecting Letters Report for Superficial Tension.

Coagulation Category	Connecting Letter	Mean	Maximum (mN/m)	Minimum (mN/m)	Standard deviation
B1	a	26.68	28.98	24.38	1.33
A	a	26.65	28.89	25.28	1.59
B2	a	26.56	30.05	22.81	2.01
C	a	26.18	30.88	22.69	2.22

5.1.2. Water content

Water is a contaminant in waste lubricating oils and it was analysed if the presence of this contaminant could be related to the phenomena of coagulation. This property was measured at the Enviroil facilities and due to reasons beyond this work scope, the Karl Fischer Coulometric Titrator used to perform measurements stopped working, and so for that reason samples S4, S5, S6, S13, S16, S19, S23, S28 and S121 (see Table A.1) could not be measured. Figure 5.2 shows the means diamond for the water content of oil samples grouped in the 4 categories. On average, samples B2 displayed the lowest water content (about 2.21 %) and samples C the highest (about 5.8 %), although samples A have similar water contents to samples C (about 5.72%). The F ratio obtained for this property was 2.77, suggesting that the null hypothesis is not true. Such is reinforced by the t-value of 1.982, which should be close to zero in order for the null hypothesis to prevail. On Table 5.4 is displayed the Connecting Letters Report for water content, in which categories with different assigned letters are significantly different. The coagulation category B2 highlights the most, being the only category assigned with a different letter. On Table A.11, pairwise comparisons are made using Student's t-test and is possible to see the obtained p-values for each pair compared. Only coagulation category B2 compared to categories A and C present a p value lower to alpha. This means that for all the other pairs, the null hypothesis prevails and no distinction is made possible through water content analysis. Category B2 is significantly different then categories A and C, but no significant distinction can be seen between category B2 and category B1. Overall, although is possible to see a different statistical behaviour in category B2 in water content analysis, it is little rigorous to state that water content analysis is a good indicator for the sample behaviour during the coagulation test.

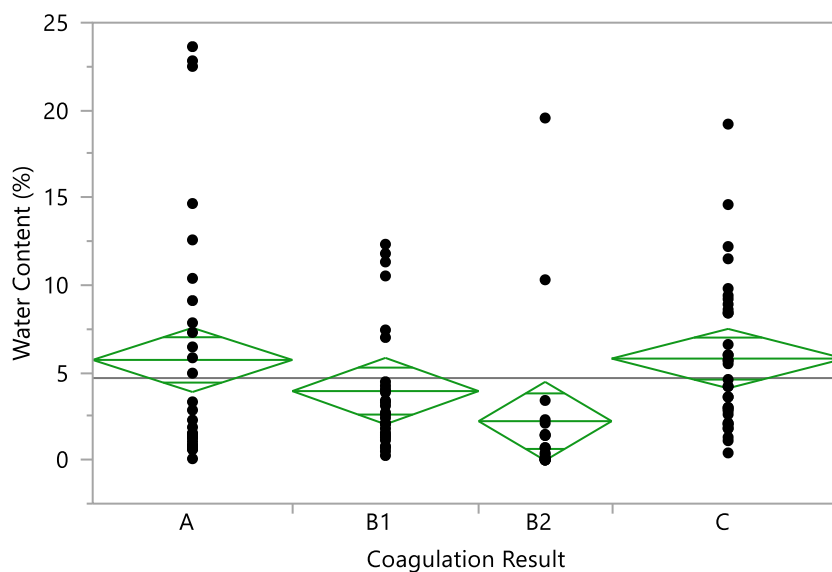


Figure 5.2 - One-way analysis of water content by coagulation result.

Table 5.2 - Connecting letters report of water content.

Level	Connecting Letter	Mean	Maximum (%)	Minimum (%)	Standard deviation
C	a	5.81	19.17	0.44	4.16
A	a	5.72	23.63	0.07	6.89
B1	a,b	3.94	12.33	0.25	3.52
B2	b	2.21	19.55	0.03	4.58

5.1.3. Total acid number

The means diamond obtained from total acid number (TAN) measurements are plotted in Fig. 5.3. Sample S69 measurement was excluded because the equipment was displaying anomalies and therefore the result obtained wasn't reliable. In category B2, there were nine samples identified in Tables A.6 and A.7, whose TAN result was lower than the quantification limit of the equipment. Categories A and B1 displayed the highest TAN (about 2.55 and 2.29 mg KOH/g respectively), while samples from category B2 have a particularly low TAN (about 0.54 mg KOH/g). The F ratio obtained was 23.05, a value quite far apart from one, stating that the coagulation categories for this property are very different. In fact, such is validated by p-value results obtained for the pairwise comparison of the different coagulation results. The pairwise comparison results of each coagulation category for TAN can be seen in Table A.8. As indicated in this table and Table 5.6

categories B2 and C are distinctly different from the other categories. Categories A and B1 are undifferentiated from each other, hence were attributed the same letter in the connecting letters report. The t-value of 1.981 is in compliance with the previous statistic results for this property. Total acid number in used oils gives an indication of its degradation degree by measuring the amount of milligrams of KOH required to neutralize one gram of oil. Higher TAN values mean higher degradation degree. Therefore, the results suggest that samples from categories A and B1 underwent a more accentuated degradation process. That could be because the lubricating oils were in duty for a longer period of time and were depleted of additives or because the conditions of service were more oxidative. It is possible that additives added into lubricants that originated samples B2 and C could have been less consumed, allowing the antioxidants additives retard the lubricant degradation by oxidation. This suggests that additives might be involved in the coagulation phenomena observed in samples C, and to a lesser degree, in samples B2. The results obtained for the Total Acid Number appear to be a good indicator to predict the used oil sample behaviour under the coagulation test conditions.

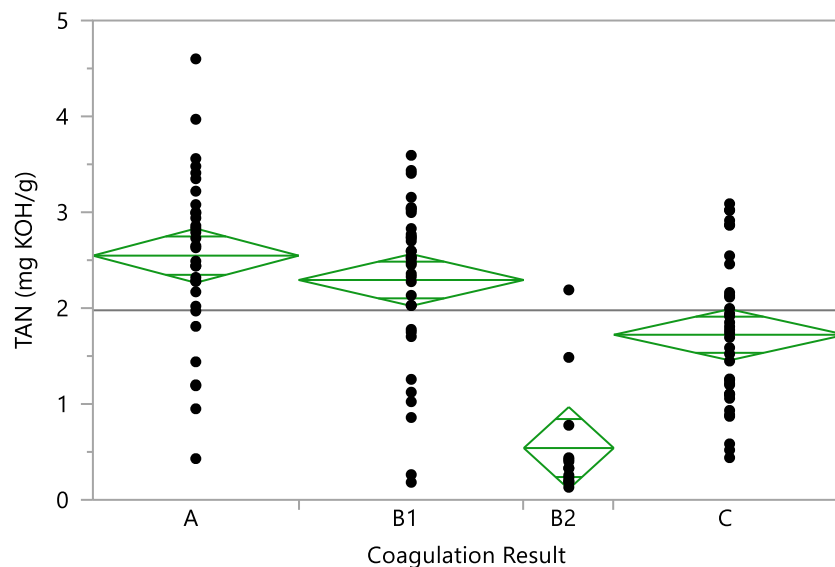


Figure 5.3 - One-way analysis of TAN by coagulation result.

Table 5.3 - Connecting letters report for TAN.

Coagulation Category	Connecting Letter	Mean	Maximum (mg KOH/g)	Minimum (mg KOH/g)	Standard deviation
A	a	2.55	4.61	0.43	0.88
B1	a	2.29	3.59	0.18	0.83
C	b	1.72	9.11	0.44	1.41
B2	c	0.54	2.19	0.13	0.57

5.1.4. Kinematic viscosity

Figure 5.4 shows means diamond calculated from the statistical procedure applied to measurements of kinematic viscosity at 40 °C. Unlike what was expected, category A displayed the higher values of kinematic viscosity (about 94.8 cSt). Samples B2 displayed the lowest values (39.7 cSt). The obtained results state the rejection of the null hypothesis. The F-value obtained was 15.59 and the t-value 1.980. In Table 5.4 is presented the Connecting letters report where is possible to see the attribution of different letters to categories that are significantly different. Categories B2 and C are indistinguishable from each other, but differentiable from negative coagulation result categories A and B2. The latter display differentiable behaviour from one another. This is expected giving that category B1 are samples that displayed an increase in viscosity when submitted to the coagulation test. In Table A.8 it is possible to see each category being compared to one another in terms of p-value, where only category A displayed a p-value lower to the significance level when compared to categories B2 and C. Oxidation products dissolved in the lubricant cause an increase of oil viscosity, and that could explain why the spread of results of categories A and B1 tends towards high kinematic viscosity values. This results are in compliance with the results obtained for the TAN value reinforcing the idea that samples A and B1 are in a more advanced stage of degradation, meaning depletion of additives. This suggests once more that additives are involved in the coagulation phenomena.

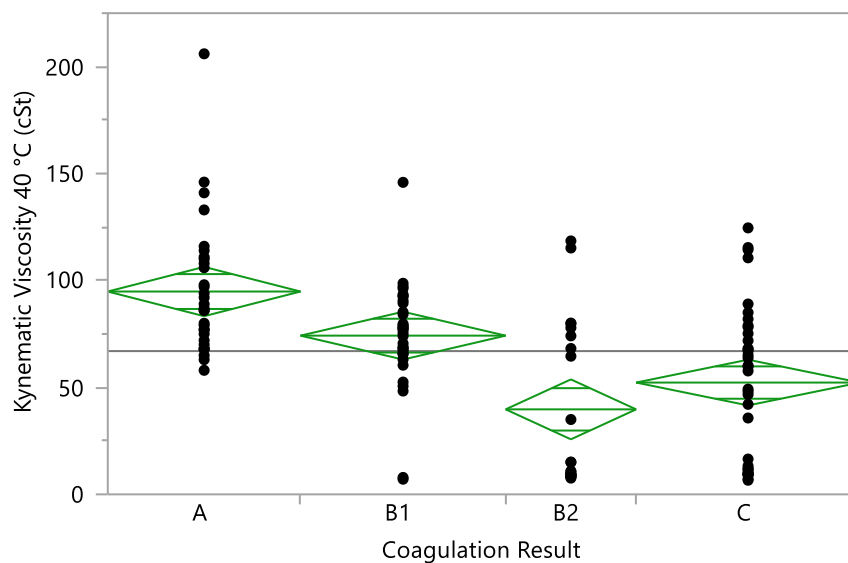


Figure 5.4 - One-way analysis of kinematic viscosity by coagulation result.

Table 5.4 - Connecting letters report for kinematic viscosity.

Coagulation Category	Connecting Letter	Mean (cSt)	Maximum (cSt)	Minimum (cSt)	Standard deviation
A	a	94.8	205.7	57.6	30.3
B1	b	74.2	145.9	7.1	24.5
C	c	52.3	124.6	6.6	35.3
B2	c	39.7	118.5	7.6	37.7

5.1.5. Saponification number

The statistical analysis of the Saponification Number measurements allowed to calculate means diamond represented in Fig. 5.5. Samples S19, S101, S102 and S128 were removed from analysis because the equipment displayed unusual behaviour at the time of the measurement, hence this samples outlier behaviour. As expected, category C displays the highest saponification number (about 33.0 mg KOH/g), while category B2 displays the lowest (about 1.9 mg KOH/g). The F ratio obtained for the Saponification Number results was 29.15 and the t-value 1.980. In the Table 5.10 of the Connecting Letters Report one can notice that to each one of the categories C and B2 was assigned a different letter, meaning they are significantly different from all the other categories. Categories A and B1 received the same letter and therefore are indistinguishable. Such is

reinforced by the obtained p-values, visible in Table A.14, where categories are compared to each other pairwise. The saponification results are in compliance with what was expected. Samples from category C display higher contents of saponifiable matter reinforcing the idea that a saponification reaction occurs when those samples are submitted to the coagulation test conditions. Samples A and B1 once more display similar range of values, which in this case is a low content of saponifiable matter. However, samples B2 also display low values of saponification number, which was unforeseen given that samples B2 present a similar behaviour to samples C in the coagulation test, only less accentuated. This suggests that the phenomenon responsible for coagulation in samples C and partial coagulation in samples B2 is from different natures. The results strongly suggest that the mechanism behind the coagulation result of samples C is a saponification reaction.

It is possible that in C samples a saponification reaction occurs, while in B2 samples what is observed is due to a flocculation process.

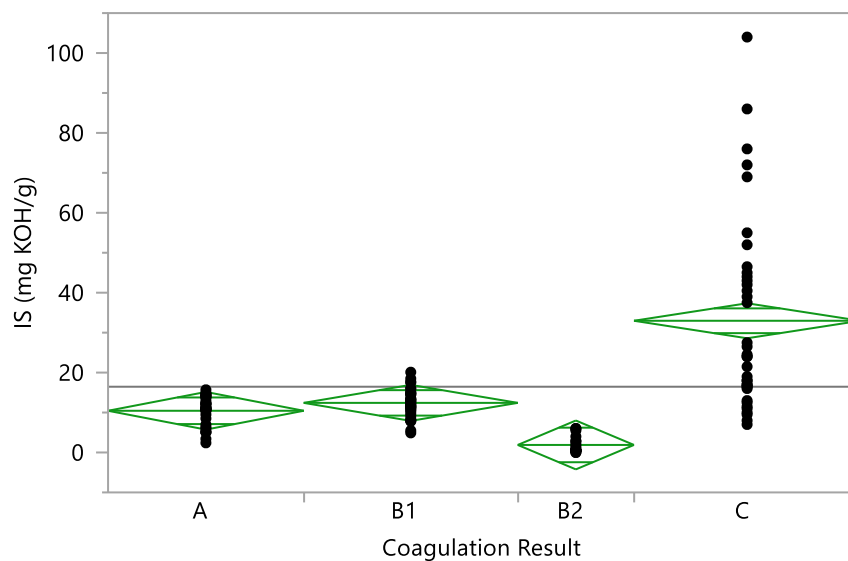


Figure 5.5 - One-way analysis of saponification number by coagulation result.

Table 5.5 - Connecting letters report for saponification number.

Coagulation Category	Connecting Letter	Mean (mg KOH/g)	Maximum (mN/m)	Minimum (mN/m)	Standard deviation
C	a	33.0	104.0	7.0	23.6
B1	b	12.4	20.1	4.9	3.4
A	b	10.4	15.7	2.4	3.6
B2	c	1.9	6.0	0.0	2.0

5.2. Functional groups analysis (FT-IR)

FT-IR analysis were performed to all samples. No clear distinction between spectra of different categories of coagulation result was made possible given that the absorption bands observed do not differ much. However, the overall spectra of samples from category C tend to display a more intense absorption bands than the rest of the categories at the following wavelengths:

- 1750 cm^{-1} , which is related to compounds with carbonyl groups from esters, ketones, or acids, more specifically to five- and seven-membered cyclic ketones (Kupareva et al. 2012);
- 1154 cm^{-1} , which can be attributed to polymethacrylate stretching vibrations. Polymethacrylate is an additive used as viscosity modifier and pour-point depressant (Al-Ghouti and Al-Atoum 2007; Kupareva et al. 2012) .
- 1112 cm^{-1} , associated with sulfurized isobutylene, an extreme-pressure additive (Wooton 2003).
- 1020 cm^{-1} , that is related to P-O-C aliphatic asymmetric stretching due to ZDDP (zinc dithiophosphate), a very common additive, specially used as extreme-pressure additive (Wooton 2003; Kupareva et al. 2012).

In all analysed samples, there were bands related to the presence of additive traces. Additives such as Zn, Ca and Mg salts or organic acids are associated with the several observed bands at $600\text{--}1300\text{ cm}^{-1}$ and $1500\text{--}2000\text{ cm}^{-1}$ (Al-Ghouti and Al-Atoum 2007; Dominguez-Rosado and Pichtel 2003). Polymethacrylate stretching vibration band is also visible in the spectra displayed by oil samples from other categories besides category C, the only difference being that in C samples this band is much more intense. According to (Zięba-Palus, Kościelniak, and Łacki 2001) the differences in the intensity of this bands might be due to differences in the concentration of the polymethacrylate in the oil samples. Besides the already mentioned band at 1154 cm^{-1} , bands at 1701 and 1731 are also associated with polymethacrylate stretching bands and visible in the used oil spectras (Kupareva et al. 2012; Al-Ghouti and Al-Atoum 2007). Bands at 1305 cm^{-1} and 1230 cm^{-1} , indicate the presence of succinimides, which are dispersion additives. Another additive whose presence was also visible in spectra of samples A, B1 and B2, but with less intensity than in samples C, was ZDDP at $1050\text{--}920\text{ cm}^{-1}$ wavelength. According to studies reported by Kupareva et al. (2012) and Dominguez-Rosado and Pichtel (2003), bands at $2954\text{--}2856\text{ cm}^{-1}$, an intense band at 1463 cm^{-1} and another band at 1376 cm^{-1} observed in FTIR results may be related

to C-H vibration and a mixture of compounds with small chain lengths. According to Kupareva (2012), a band at 1457 cm^{-1} may be related to the formation of carcinogenic nitrosamines due to chemical transformation of amines from oil additives and that band is constantly observed in all samples. Regarding contaminants, a peak around 3400 cm^{-1} is related to H-O-H bending vibrations of water and a peak at 720 cm^{-1} might be due to formation of nitrates from the oxidation of nitrogen oxide compounds according to (Dominguez-Rosado and Pichtel 2003). In Figure 5.6 and Figure 5.7 is displayed a representative FTIR spectrum of samples from category C and B2, respectively. While in Figure 5.8 and Figure 5.9, it can be seen a representative FTIR spectrum of samples from category B1 and A, respectively

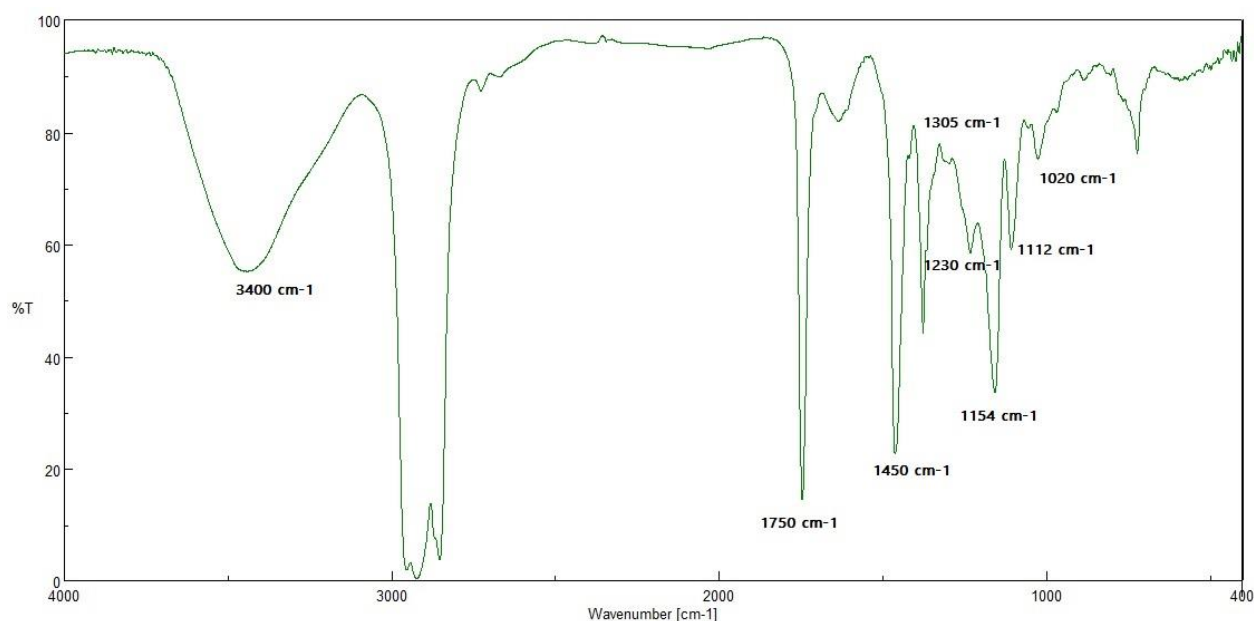


Figure 5.6 - FTIR spectra of sample S103, representative of overall samples from category C.

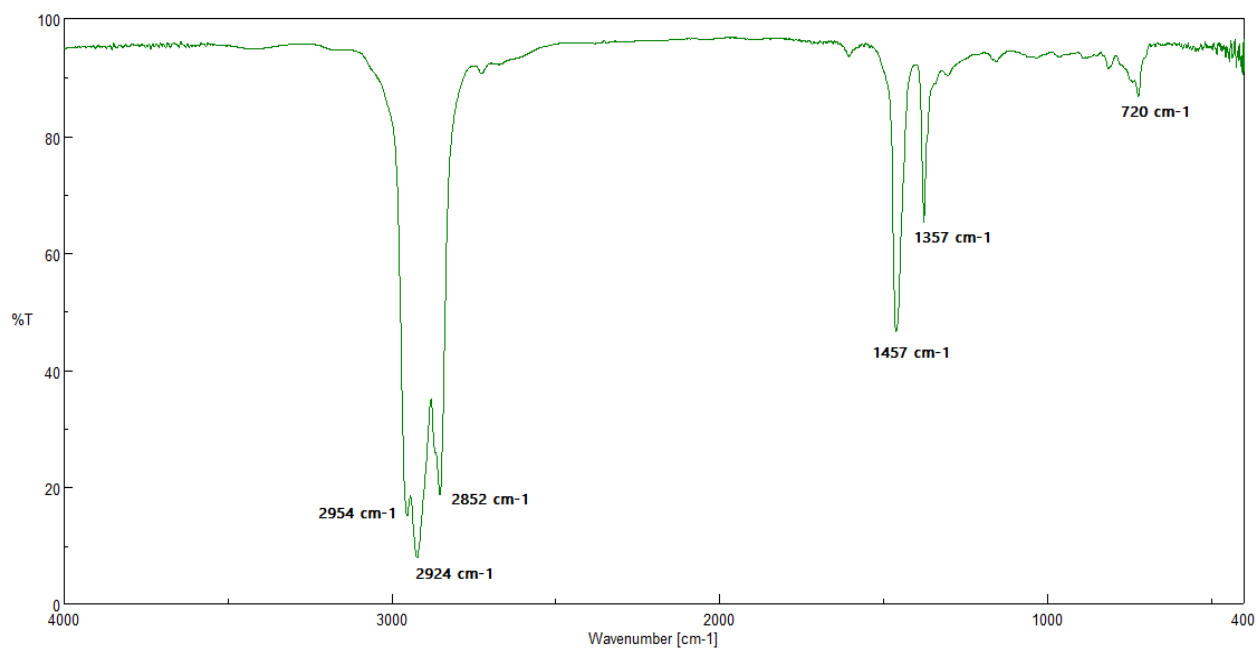


Figure 5.7 - FTIR spectra of sample S89, representative of overall samples from category B2.

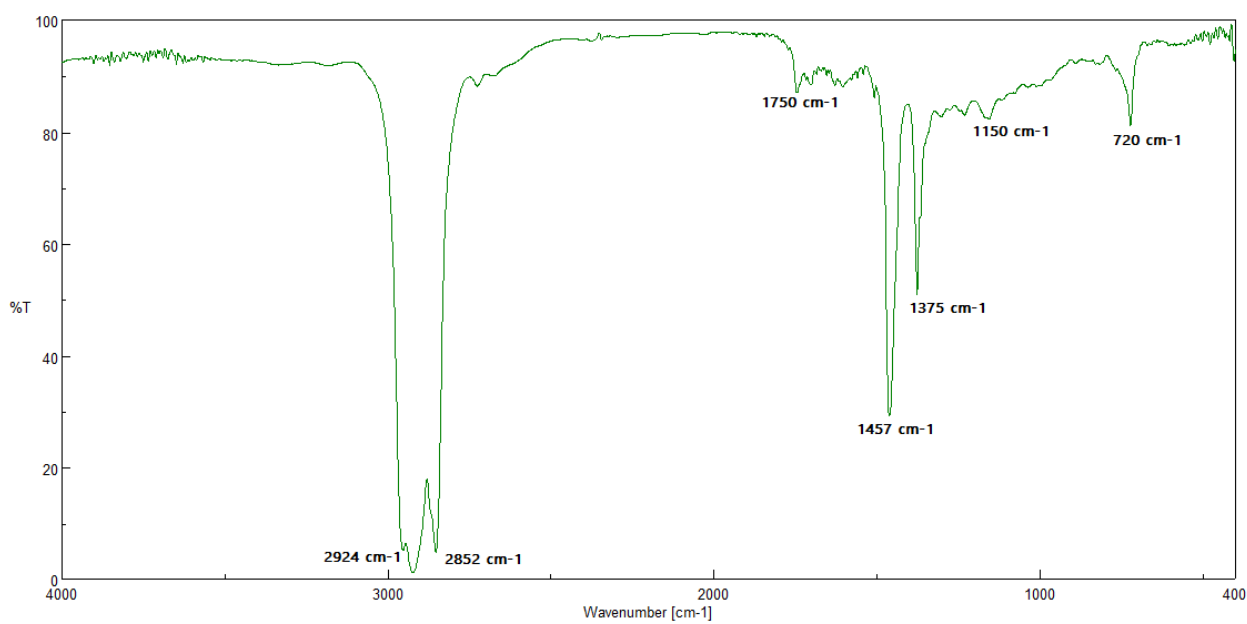


Figure 5.8 - FTIR spectra of sample S49, representative of overall samples from category B1.

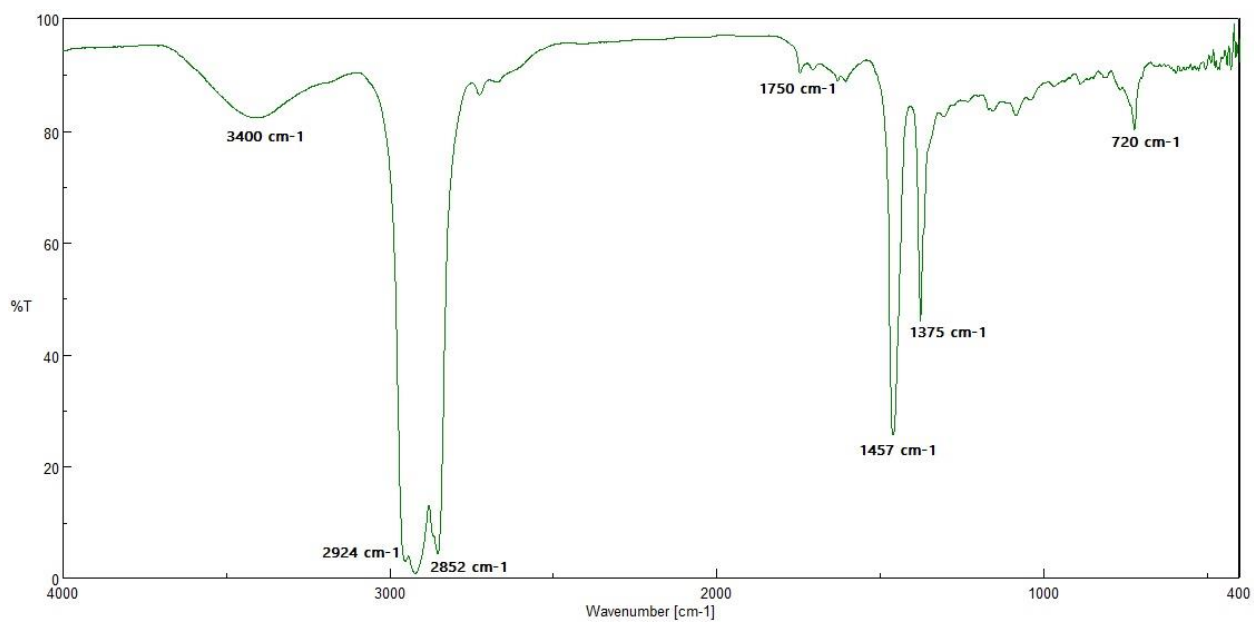


Figure 5.9 - FTIR spectra of sample S125, representative of overall samples from category A.

5.3.Elemental analysis (EDXRF)

Elemental analyses were carried out by EDXR technique. Some elements results had to be excluded from the analysis because their results were not reliable due to limitations of the EDXRF apparatus. Elemental analysis was made to all CONUR II samples with the exception of the majority of samples from category A due to the same reasons mentioned in Physicochemical Properties. The objective of this analysis is to see which additive package components are present and at which concentration as well as the identification of foreign contaminants All the results obtained are displayed in Table A.16 and Table A.17.

5.3.1. Magnesium

The presence of magnesium was only detected in samples of categories B2 and C, as shown in Figure 5.10. Both categories B2 and C display similar magnesium contents (about 30 ppm). The results seem to suggest that the presence of magnesium might be linked to the lubricant coagulation phenomena. However, though all the magnesium results are associated to samples B2 and C, not all these samples had detectable levels of magnesium. While in category B2, 12 out of 19 samples had magnesium, only 9 in 37 category C displayed presence of this element. The source for magnesium in these oil samples comes from additive packages. Magnesium is an additive used as detergent and dispersant to maintain suspension of particulate matter, or from wear of metal surfaces. Magnesium can also come from rust and corrosion inhibitors. The F ratio obtained for this element was 0,1868 and t- value 1.993, thus the null hypothesis is rejected. From Table A.18 it is noticeable that both categories were attributed the same letter in the Connecting Letters Report, and thus are not significantly. In Table 5.73 is possible to see that only category B2 pairwise comparisons have a p-value smaller than the significance level.

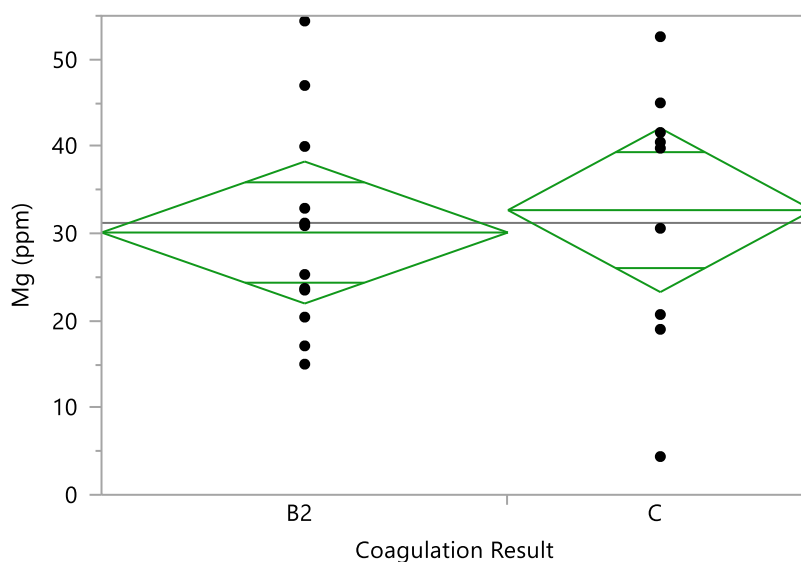


Figure 5.10 - One-way analysis of magnesium content by coagulation result.

Table 5.6 - Connecting Letters Report for magnesium content.

Coagulation Category	Connecting Letter	Mean (ppm)	Maximum (ppm)	Minimum (ppm)	Standard deviation
B2	a	19.02	54.40	15.00	11.99
C	b	7.95	52.60	4.39	15.31

5.3.2. Aluminium

The results obtained for the concentration of aluminium in waste oil samples are displayed in Figure 5.11. Samples from category C show higher contents of aluminium (about 131.7 ppm). On the contrary, category B2 displayed the lowest values with a concentration of about 45.7 ppm. The F ratio obtained was 10.62 and the t-value 1.993, and so at least one of the categories is differentiable. In Table 5.7 is displayed the Connecting Letters Report where one can see that the categories are not significantly different given that they share the same letter with at least another category. Through the p-value pairwise comparison, in Table A.19, only category C displayed a p-value lower to the significance level when compared to categories B2 and B1. No distinction between category C and A is made possible. Aluminium in waste lubricant oils is usually due to scuffing on piston skirts. Other sources such as certain types of bearings or heat exchangers are

possible. The content of aluminium in used oil samples results don't allow to infer any prediction regarding the coagulation result.

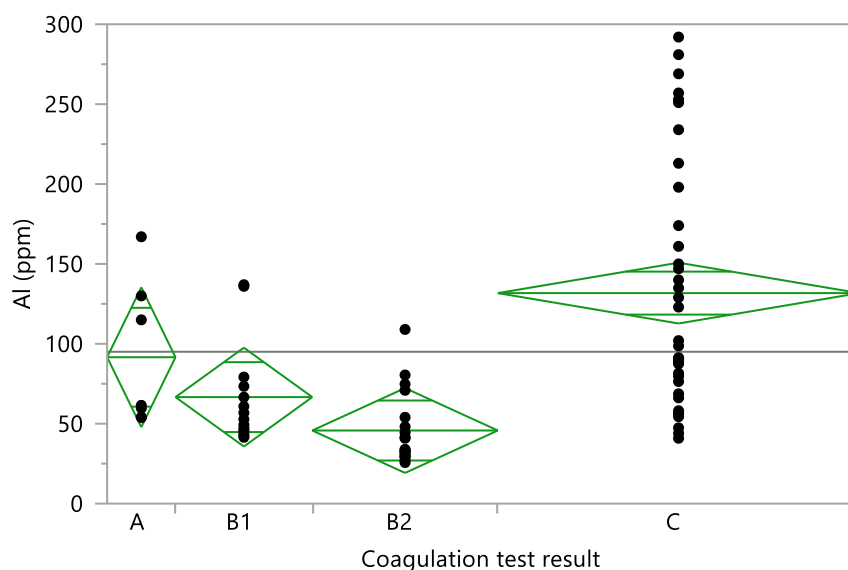


Figure 5.11 - One-way analysis of aluminium content by coagulation result.

Table 5.7 - Connecting Letters Report for aluminium content.

Coagulation Category	Connecting Letter	Mean (ppm)	Maximum (ppm)	Minimum (ppm)	Standard deviation
C	a	131.74	292.00	40.90	75.58
A	a, b	91.60	167.00	53.90	30.61
B1	b	66.64	137.00	41.50	30.61
B2	b	45.74	109.00	25.70	22.00

5.3.3. Phosphorus

Figure 5.12 illustrates ANOVA results for concentration of phosphorus in the analysed oil samples. Category B2 displays once more the lowest concentration values (about 57.2 ppm). The F Ratio obtained for this element was of 29.71 and the t-value of 1.993. Only a differentiation of samples from category B2 is possible. Analysing Table 5.16 it is possible to conclude that only to category B2 was assigned to a different letter from the remaining categories. For all the other categories were assigned the same letter, and thus are not significantly different. The same

conclusion can be reached by analysing the Ordered Differences Report, in Table A.20, where a pairwise comparison of the p-value is made. Only category B2 displayed a p-value lower to the significance level. Phosphorus is used as an additive for anti-wear, anti-oxidant, extreme-pressure and corrosion inhibition. This element analysis does not allow to predict the coagulation result.

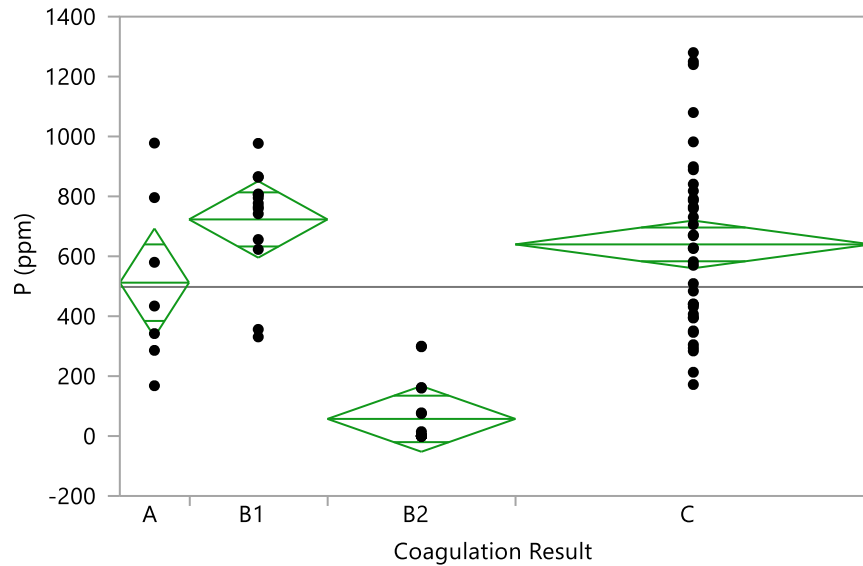


Figure 5.12 - One-way analysis of phosphorus content by coagulation result.

Table 5.8 - Connecting Letters Report for phosphorus content.

Coagulation Category	Connecting Letter	Mean (ppm)	Maximum (ppm)	Minimum (ppm)	Standard deviation
B1	a	723.14	977	331	175.91
C	a	639.75	1280	172	289.63
A	a	512.00	978	168	175.94
B2	b	57.24	300	14.7	102.53

5.3.4. Sulphur

ANOVA results obtained for sulphur are plotted in Figure 5.13. Sulphur content in samples A, B1 and C do not tend to be much different (6597.4, 6812.9, and 6574 ppm respectively), while category B2 sulphur contents are much lower (about 981.8 ppm). The F Ratio obtained from statistical analysis of this element was of 4.52 and the t-value of 1.993. Once more, category B2 displayed the most atypical behaviour. In the Connecting Letters Report, displayed in Table 5.9, all categories were connected by the same letter, with the exception of category B2, which is significantly different from the other categories. The same is true for the p-value pairwise comparison, visible in Table A.21, where it is possible to see that only category B2 displayed p-values lower to the significance level. The source of sulphur in the analysed samples can be due to two origins. The first one is base oil that gave origin to waste lubricant, because sulphur is a constituent of base oils from mineral sources. The second one is from additive packages formulated for protection against wear and corrosion. Given that protection against wear of the lubricant parts is one of the main purposes of lubricating oil, it is plausible to assume that all samples had in their formulation this type of additive. Hence, it is possible that samples that display high concentrations of sulphur are from mineral origin and samples from category B2 are from synthetic origin.

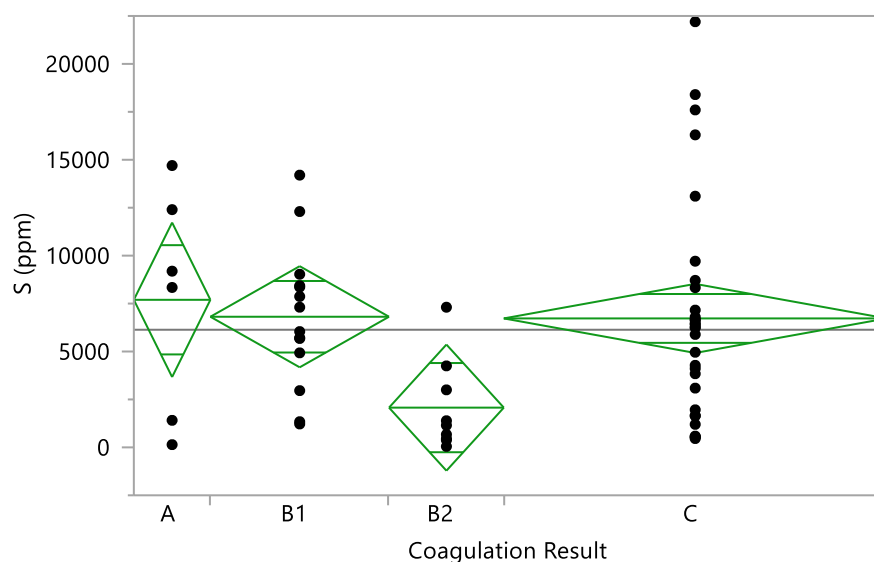


Figure 5.13 - One-way analysis of sulphur content by coagulation result.

Table 5.9 - Connecting letters report for sulphur content.

Coagulation Category	Connecting Letter	Mean (ppm)	Maximum (ppm)	Minimum (ppm)	Standard deviation
B1	a	6812.86	14200	1220	3572.58
A	a	6597.43	14700	142	5329.28
C	a	6574.03	22200	459	5594.19
B2	b	981.83	7310	49.72	2258.13

5.3.5. Calcium

Calcium is used as a detergent and dispersant additive in lubricant oils. It improves cleaning and dispersion capacity. Figure 5.14 shows the variance of values obtained for each category.

Category B1 displays the highest calcium contents (about 2069 ppm) and category B2 the lowest (about 120,7 ppm). For this element, the statistical results of the F Ratio and t-value were 24.65 and 1.993 respectively, both indicating the rejection of the null hypothesis. Results for samples B2 exhibit the most distinct behaviour as expected from what was observed in previous results. In the Connecting Letters Report shown in Table 5.10 is possible to see that once more only category B2 was significantly different from all the other categories. Regarding the pairwise comparison of the p-value, as displayed in Table A.22, category B2 has a p-value lower to then the significance level in every comparison. Category C has a p-value lower to the significance level when compared to category B1 and B2. Thus, while the rejection of the null hypothesis is valid when category C is compared to B1 and B2, the same is not valid regarding category A. This means calcium analysis is not a good indicator of weather the coagulation result of an oil sample will be negative (A) or positive (C).

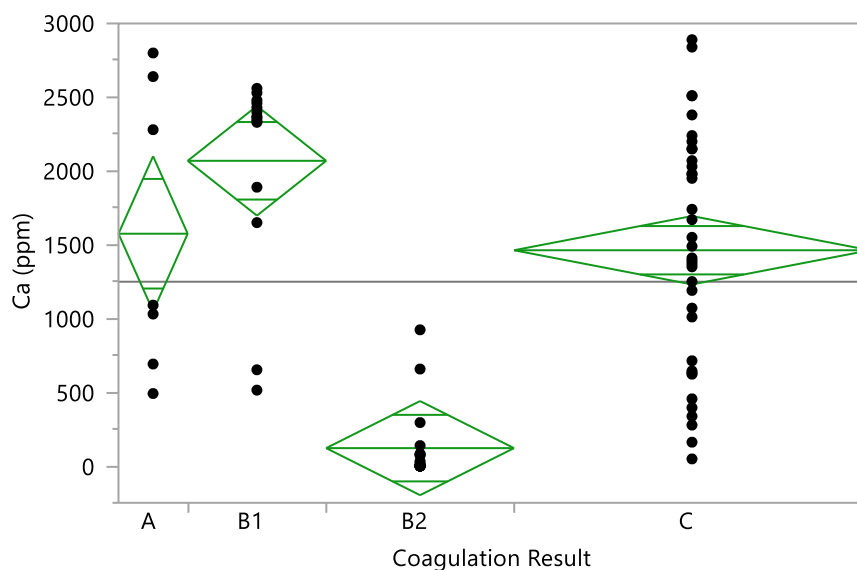


Figure 5.14 - One-way analysis of calcium content by coagulation result

Table 5.10 - Connecting letters report for calcium content analysis.

Coagulation Category	Connecting Letter	Mean (ppm)	Maximum (ppm)	Minimum (ppm)	Standard deviation
B1	a	2069	2560	514	652.78
A	a, b	1574.57	2800	491	896.07
C	b	1462.52	2890	47.61	787.42
B2	c	120.77	923	18.42	302.48

5.3.6. Zinc

Zinc is an element associated with anti-wear, anti-oxidant and corrosion inhibitor additives. Again, category B1 displays the highest concentration (about 1007 ppm of zinc), and category B2 the lowest (about 58.9 ppm of Zn). Results for the concentration of zinc in oil samples (Fig. 5.15) are in compliance with the other results regarding elemental analysis, given that once more category B2 clearly stands out from the remaining categories. The F Ratio for this element is 26.85 and the t-value 1.994. In Table 5.11 it is possible to observe that again only category B2 is significantly different from the remaining categories, hence was attributed a different letter. Category C shares the same letter with category A, and thus, both categories are not significantly different. The same is reinforced by the results obtained in the pairwise comparison, as it can be seen in Table A.23. Thus, zinc analysis does not allow to take any conclusions regarding coagulation result.

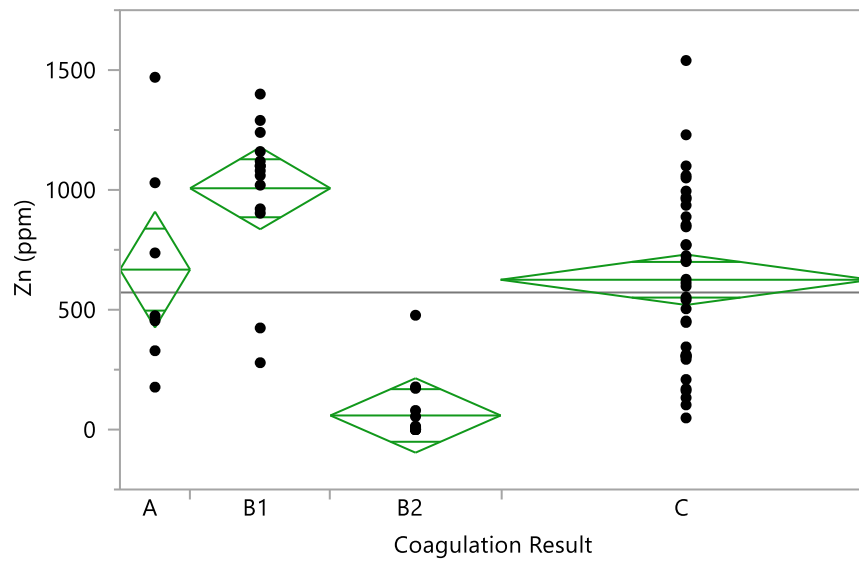


Figure 5.15 - One-way analysis of zinc content by coagulation result.

Table 5.11 - Connecting letters report for zinc content analysis.

Coagulation Category	Connecting Letter	Mean (ppm)	Maximum (ppm)	Minimum (ppm)	Standard deviation
B1	a	1006.93	1400	279	297.45
A	b	667.43	1470	177	417.14
C	b	625.21	1540	48.63	353.40
B2	c	58.89	178	2.45	67.07

6. Conclusions and future work

In this work a physicochemical characterisation of 133 used oil samples was carried in an attempt to identify a parameter that could separate samples according to their four coagulation categories. Some properties display statically relevant differences between categories. TAN and IS analysis displayed the best results in terms of distinguishing the different categories. Samples C display higher IS and thus more likely to occur saponification. TAN results also suggest that negative samples (A and B1) underwent a more accentuated degradation, given that samples from these categories overall display higher TAN values (about 2.55 and 2.29 mg KOH/g respectively). Categories C and B2 TAN was lower (about 1.7 and 0.54 mg KOH/g respectively). Such might be due to the a less consumed additive package in the lubricants that originated samples B2 and C, allowing the antioxidant additives retard the lubricant degradation by oxidation. Thus, additives might be involved in the coagulation phenomena observed in samples C. The kinematic viscosity results are in compliance with the results obtained for the TAN value, given that categories A and B1 display higher viscosity values (about 94,94 and 74,22 cSt respectively). Oxidation products dissolved in the lubricant cause an increase of oil viscosity, thus high viscosity values are expected in more degraded samples. Elemental analysis, showed that content of magnesium, phosphorus, sulphur and calcium can allow some differentiation between category B2 from the remaining categories. Overall, samples B2 display lower contents of these elements. Surface tension, FTIR, water, aluminium and zinc content did not allow a segregation of samples based on their coagulation categories. It was not possible to identify one property that allows coagulation phenomena anticipation, however TAN and IS are general good indicators. Given the so many different origins and formulations lubricant oils can have, as well as the distinct conditions and routes it may follow, it was not possible to narrow down to one explanation for the coagulation phenomenon. Nevertheless, results suggest a strong probability of the additives package formulation used in virgin lubricant oils to be a key factor to understand the coagulation phenomenon.

Efforts in finding a solution that can overcome this problem should be continued. Used oil regeneration is an expensive technology, and without the aid of government subsidies in many cases it is not even profitable. This might be overcome if more studies were to be made in order to avoid unnecessary rejection of oil samples.

Minimizing waste and natural resources exploitation combined with giving a new life to what previously was considered waste are the guidelines to follow in order to achieve a developed

society in harmony with the environment it depends on. Efforts to achieve that are never futile, regardless of the results.

Future work:

Science is a constant developing field, with more resources to be exploited every day. So, there is always some other techniques to be explored until an answer is finally achieved.

For a further research on the matter of this dissertation, it is suggested to explore other chemical analysis techniques such as gas chromatography - mass spectrometry (GC-MS), given that in the literature were found good results using this technique.

The influence of specific additives in oil coagulation behaviour should be further investigated, since they seem to be assume a relevant factor in the coagulation phenomena observed in oil samples.

Overall having more samples from positive coagulation categories (B2 and C), could help to have more robust and conclusive statistical results.

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ANNEXES

Annexe A- Experimental Results

In this annex all experimental results for characterizing used oil properties are presented, including some statistical results. Samples identified with “OU” are samples whose characterization was made in the previous project CONUR I.

Table A.1 - Coagulation test results for all used oils samples

Used oil sample	Coagulation test result	Used oil sample	Coagulation test result	Used oil sample	Coagulation test result	Used oil sample	Coagulation test result
S1	A	S35	A	S68	C	S101	B2
S2	A	S36	A	S69	C	S102	B2
S3	A	S37	A	S70	C	S103	C
S4	B1	S38	A	S71	B1	S104	C
S5	B1	S39	A	S72	A	S105	C
S6	B1	S40	B1	S73	C	S106	C
S7	A	S41	B2	S74	B1	S107	C
S8	A	S42	A	S75	A	S108	C
S9	A	S43	A	S76	C	S109	C
S10	A	S44	A	S77	A	S110	C
S11	A	S45	A	S78	B1	S111	C
S12	A	S46	A	S79	C	S112	C
S13	C	S47	A	S80	B2	S113	C
S14	A	S48	A	S81	B2	S114	C
S15	A	S49	B1	S82	A	S115	C
S16	B1	S50	A	S83	A	S116	C
S17	A	S51	A	S84	B2	S117	C
S18	A	S52	A	S85	B2	S118	C
S19	B2	S53	A	S86	B2	S119	A
S20	A	S54	A	S87	B2	S120	B2
S21	A	S55	A	S88	A	S121	C
S22	A	S56	A	S89	B2	S122	A
S23	B1	S57	B1	S90	B2	S123	C
S24	A	S58	A	S91	B2	S124	C
S25	A	S59	A	S92	C	S125	A
S26	A	S60	C	S93	C	S126	C
S27	C	S61	A	S94	B2	S127	A
S28	B1	S62	A	S95	B2	S128	C
S29	B1	S63	A	S96	B2	S129	C
S30	A	S64	A	S97	C	S130	C
S31	A	S65	A	S98	B2	S131	A
S32	A	S66	A	S99	B2	S132	B1
S33	A	S67	A	S100	C	S133	C
S34	A						

Table A.2 - Superficial tension results

Coagulation test result	Sample	Superficial tension (mN/m)	Coagulation test result	Sample	Superficial tension (mN/m)	Coagulation test result	Sample	Superficial tension (mN/m)
C	S13	23.35	C	S117	24.53	B2	S101	25.88
C	S27	28.64	C	S118	25.71	B2	S102	23.36
C	S60	30.89	C	S121	22.93	B2	S120	24.44
C	S68	27.04	C	S123	24.75	B2	OU36	27.64
C	S69	29.85	C	S124	28.19	B2	OU57	27.49
C	S70	27.96	C	S126	23.70	B2	OU60	30.06
C	S73	29.12	C	S128	28.74	B1	S4	26.38
C	S76	28.01	C	S129	25.49	B1	S5	27.33
C	S79	24.30	C	S130	27.91	B1	S6	26.92
C	S92	25.56	C	S133	24.94	B1	S16	27.53
C	S93	23.53	B2	S19	27.28	B1	S23	27.09
C	S97	23.56	B2	S41	29.89	B1	S28	25.05
C	S100	25.79	B2	S80	25.55	B1	S29	24.38
C	S103	25.92	B2	S81	24.42	B1	S40	27.25
C	S104	22.70	B2	S84	25.48	B1	S49	24.48
C	S105	23.20	B2	S85	28.04	B1	S57	28.16
C	S106	26.64	B2	S86	28.47	B1	S71	28.02
C	S107	25.97	B2	S87	26.13	B1	S74	24.88
C	S108	26.74	B2	S89	28.57	B1	S78	28.99
C	S109	29.22	B2	S90	28.52	B1	S132	27.80
C	S110	30.51	B2	S91	28.04	B1	OU18	25.43
C	S111	24.19	B2	S94	23.83	B1	OU31	27.01
C	S112	25.20	B2	S95	25.33	B1	OU35	26.98
C	S113	28.23	B2	S96	22.81	A	OU7	25.28
C	S114	24.51	B2	S98	25.41	A	OU40	28.90
C	S115	26.05	B2	S99	27.71	A	OU63	25.79
C	S116	25.39						

Table A.3 - Ordered Differences Report for Superficial Tension

Category	Category	Standard Error Deviation	p-Value
B1	C	0.60	0.41
A	C	1.22	0.70
B2	C	0.55	0.50
B1	B2	0.66	0.85
A	B2	1.25	0.94
B1	A	1.27	0.98

Table A.4 - Kinematic Viscosity results for categories C, B2 and B1

Coagulation test result	Sample	Kinematic Viscosity 40 °C (cSt)	Coagulation test result	Sample	Kinematic Viscosity 40 °C (cSt)	Coagulation test result	Sample	Kinematic Viscosity 40 °C (cSt)
C	S13	42.1	C	S124	13.3	B1	OU56	145.9
C	S27	9.5	C	S126	48.1	B1	OU58	7.1
C	S60	9.1	C	S128	35.7	B1	OU59	65.8
C	S68	9.3	C	S129	65.1	B1	OU65	90.6
C	S69	9.8	C	S130	82.0	B1	OU68	98.7
C	S73	9.4	C	S133	85.0	B1	OU70	48.3
C	S76	10.7	B1	S4	74.0	B1	OU72	97.2
C	S79	7.2	B1	S5	70.6	B1	OU75	67.0
C	S92	6.6	B1	S6	79.0	B1	OU76	93.5
C	S93	11.9	B1	S23	96.3	B2	S19	118.5
C	S97	11.9	B1	S28	7.9	B2	S41	68.2
C	S100	60.2	B1	S29	77.7	B2	S80	115.2
C	S103	78.9	B1	S40	60.4	B2	S81	79.8
C	S104	63.8	B1	S57	77.6	B2	S84	80.1
C	S105	59.7	B1	S71	92.7	B2	S85	74.1
C	S106	67.1	B1	S74	52.5	B2	S86	77.9
C	S107	110.6	B1	S78	79.7	B2	S87	15.1
C	S108	114.4	B1	S132	68.3	B2	S89	64.6
C	S109	75.2	B1	OU18	68.1	B2	S90	7.6
C	S110	57.7	B1	OU24	50.6	B2	S91	9.3
C	S111	115.4	B1	OU27	78.4	B2	S94	10.9
C	S112	67.9	B1	OU31	75.3	B2	S95	8.4
C	S113	78.2	B1	OU33	84.2	B2	S96	9.2
C	S114	89.0	B1	OU35	92.6	B2	S98	9.2
C	S115	71.9	B1	OU37	69.0	B2	S99	8.3
C	S116	68.2	B1	OU43	85.2	B2	S101	8.3
C	S117	16.5	B1	OU51	76.8	B2	S102	9.4
C	S118	49.2	B1	OU52	65.6	B2	S120	10.5
C	S121	46.7	B1	OU53	63.1	B2	OU36	15
C	S123	124.6	B1	OU55	89.4	B2	OU77	35

Table A.5 - Ordered Differences Report for Kinematic Viscosity

Coagulation Category	Coagulation Category	Standard Error Difference	p-Value
A	B2	9.16	<.001
A	C	7.94	<.001
B1	B2	9.05	<.001
B1	C	7.81	0.006
A	B1	8.11	0.01
C	B2	8.90	0.16

Table A.6 - Kinematic Viscosity results for category A

Coagulation test result	Sample	Kinematic Viscosity 40 °C (cSt)
A	OU6	146.1
A	OU7	111.0
A	OU8	86.0
A	OU9	96.8
A	OU11	114.0
A	OU12	97.6
A	OU13	109.6
A	OU14	116.3
A	OU16	86.8
A	OU17	69.7
A	OU19	67.5
A	OU26	67.5
A	OU28	133.2
A	OU29	57.6
A	OU30	71.7
A	OU32	92.1
A	OU34	140.7
A	OU38	85.7
A	OU39	74.9
A	OU40	89.1
A	OU41	105.7
A	OU42	108.2
A	OU54	94.3
A	OU61	205.7
A	OU62	79.2
A	OU63	77.4
A	OU64	65.0
A	OU67	68.4
A	OU71	77.5
A	OU73	62.7
A	OU74	80.1

Table A.7 - Total acid number results for categories C, B2 and B1

Coagulation test result	Sample	TAN (mg KOH/g)	Coagulation test result	Sample	TAN (mg KOH/g)	Coagulation test result	Sample	TAN (mg KOH/g)
C	S13	0.89	C	S126	1.26	B1	S23	2.742
C	S27	1.22	C	S128	1.45	B1	S28	1.703
C	S60	1.85	C	S129	1.20	B1	S29	2.593
C	S68	3.03	C	S130	1.74	B1	S40	2.359
C	S69	9.11	C	S133	2.46	B1	S49	2.538
C	S70	3.02	B2	S19	< L.Q.	B1	S57	3.024
C	S73	1.25	B2	S41	0.44	B1	S71	0.183
C	S76	1.06	B2	S80	< L.Q.	B1	S74	3.049
C	S79	1.11	B2	S81	< L.Q.	B1	S78	2.028
C	S92	0.58	B2	S84	< L.Q.	B1	S132	2.328
C	S93	1.81	B2	S85	< L.Q.	B1	OU18	1.75
C	S97	0.44	B2	S86	0.40	B1	OU24	1.778
C	S100	1.52	B2	S87	0.19	B1	OU27	0.859
C	S103	1.10	B2	S89	0.13	B1	OU31	2.7
C	S104	1.94	B2	S90	< L.Q.	B1	OU33	2.83
C	S105	1.69	B2	S91	< L.Q.	B1	OU35	2.276
C	S106	3.09	B2	S94	< L.Q.	B1	OU37	3.436
C	S107	1.77	B2	S95	< L.Q.	B1	OU43	2.133
C	S108	1.92	B2	S96	0.20	B1	OU51	2.732
C	S109	2.92	B2	S98	0.23	B1	OU52	1.123
C	S110	2.12	B2	S99	0.18	B1	OU53	1.257
C	S111	2.55	B2	S101	1.49	B1	OU55	2.53
C	S112	2.86	B2	S102	0.26	B1	OU56	2.028
C	S113	1.10	B2	S120	0.78	B1	OU58	2.513
C	S114	1.59	B2	OU36	0.33	B1	OU59	3.156
C	S115	0.52	B2	OU57	2.19	B1	OU65	0.263
C	S116	2.87	B2	OU60	0.33	B1	OU68	3.406
C	S117	2.13	B2	OU77	0.42	B1	OU70	1.024
C	S118	2.16	B1	S4	2.997	B1	OU72	2.597
C	S121	2.00	B1	S5	2.475	B1	OU75	2.77
C	S123	0.87	B1	S6	2.453	B1	OU76	3.594
C	S124	0.93	B1	S16	3.04			

Table A.8 - Ordered Differences Report for Total Acid Number

Coagulation Category	Coagulation Category	Standard Error Difference	p-Value
A	B2	0.26	<.001
B1	B2	0.26	<.001
C	B2	0.25	<.001
A	C	0.20	<.001
B1	C	0.19	<.001
A	B1	0.20	0.20

Table A.9 - Total acid number results for category A

Coagulation test result	Sample	TAN (mg KOH/g)
A	OU6	2.32
A	OU7	3.97
A	OU8	2.28
A	OU9	2.99
A	OU11	3.35
A	OU12	3.56
A	OU13	2.73
A	OU14	2.63
A	OU15	4.60
A	OU16	0.43
A	OU17	2.49
A	OU19	1.44
A	OU26	1.20
A	OU28	1.19
A	OU29	1.97
A	OU30	2.28
A	OU32	3.00
A	OU34	2.86
A	OU38	2.44
A	OU39	2.83
A	OU40	2.44
A	OU41	3.08
A	OU42	3.48
A	OU54	2.65
A	OU61	2.17
A	OU62	1.81
A	OU63	2.94
A	OU64	2.02
A	OU67	3.41
A	OU71	2.79
A	OU73	0.95
A	OU74	3.22

Table A.10 - Water content results for categories C, B2 and B1

coagulation test result	Sample	water content (%)	coagulation test result	Sample	water content (%)	coagulation test result	Sample	water content (%)
C	S27	1.3	C	S123	14.6	B1	40	7.0
C	S60	8.4	C	S124	3.6	B1	49	1.8
C	S68	0.4	C	S126	5.5	B1	57	0.5
C	S69	2.9	C	S128	2.8	B1	71	3.1
C	S70	2.1	C	S129	6.0	B1	74	2.6
C	S73	3.0	C	S130	6.0	B1	78	3.4
C	S76	9.8	C	S133	12.2	B1	132	11.8
C	S79	8.9	B2	S41	2.1	B1	OU18	4.0
C	S92	19.2	B2	S80	0.0	B1	OU24	1.1
C	S93	8.4	B2	S81	0.0	B1	OU27	0.8
C	S97	9.4	B2	S84	0.0	B1	OU31	2.1
C	S100	5.7	B2	S85	0.1	B1	OU33	12.3
C	S103	6.6	B2	S86	0.0	B1	OU35	2.7
C	S104	4.2	B2	S87	0.1	B1	OU37	4.2
C	S105	2.6	B2	S89	0.1	B1	OU43	10.5
C	S106	1.8	B2	S90	1.4	B1	OU51	2.1
C	S107	3.0	B2	S91	0.3	B1	OU52	0.7
C	S108	4.6	B2	S94	0.0	B1	OU53	1.6
C	S109	9.2	B2	S95	0.4	B1	OU55	3.9
C	S110	5.7	B2	S96	0.7	B1	OU58	2.0
C	S111	8.6	B2	S98	0.7	B1	OU59	2.4
C	S112	1.1	B2	S99	1.4	B1	OU65	1.4
C	S113	1.8	B2	S101	10.3	B1	OU68	0.3
C	S114	3.6	B2	S102	3.4	B1	OU70	4.5
C	S115	2.0	B2	S120	2.3	B1	OU72	11.3
C	S116	11.5	B2	OU36	19.5	B1	OU75	1.3
C	S117	4.2	B2	OU77	1.5	B1	OU76	7.4
C	S118	2.1	B1	29	3.3			

Table A.11 - Ordered Differences Report of Water Content

Coagulation Category	Coagulation Category	Standard Error Difference	p-Value
C	B2	1.42	0.01
A	B2	1.46	0.02
C	B1	1.28	0.15
A	B1	1.33	0.18
B1	B2	1.48	0.25
C	A	1.26	0.95

Table A.12 - Water content results for categories C, B2 and B1

coagulation test result	Sample	water content (%)
A	OU6	23.6
A	OU7	9.1
A	OU8	1.3
A	OU9	1.5
A	OU11	5.0
A	OU12	0.8
A	OU13	0.6
A	OU14	0.8
A	OU16	0.1
A	OU17	7.3
A	OU19	5.8
A	OU26	0.9
A	OU28	22.8
A	OU29	1.3
A	OU30	1.9
A	OU32	10.4
A	OU34	22.5
A	OU38	7.8
A	OU39	2.3
A	OU40	3.3
A	OU41	6.5
A	OU42	14.7
A	OU54	12.6
A	OU62	1.3
A	OU63	0.7
A	OU64	2.8
A	OU67	0.6
A	OU71	0.8
A	OU73	1.5
A	OU74	1.1

Table A.13 - Saponification number results for categories C, B2 and B1

Coagulation test result	Sample	Saponification Number (mg KOH/g)	Coagulation test result	Sample	Saponification Number (mg KOH/g)	Coagulation test result	Sample	Saponification Number (mg KOH/g)
C	S13	40.5	C	S126	26.5	B1	S23	14.5
C	S27	76.0	C	S128	104.0	B1	S28	5.5
C	S60	42.0	C	S129	13.0	B1	S29	15.0
C	S68	16.5	C	S130	18.0	B1	S40	14.5
C	S69	21.5	C	S133	17.0	B1	S49	16.0
C	S70	18.0	B2	S19	60.0	B1	S57	17.5
C	S73	44.0	B2	S41	5.5	B1	S71	13.0
C	S76	7.0	B2	S80	0.0	B1	S74	10.5
C	S79	39.0	B2	S81	0.5	B1	S78	8.0
C	S92	8.0	B2	S84	0.5	B1	S132	15.0
C	S93	10.0	B2	S85	1.0	B1	OU18	13.4
C	S97	86.0	B2	S86	< L.Q.	B1	OU24	11.1
C	S100	43.0	B2	S87	0.5	B1	OU27	4.9
C	S103	69.0	B2	S89	0.5	B1	OU31	9.9
C	S104	24.0	B2	S90	0.5	B1	OU33	13.5
C	S105	72.0	B2	S91	0.5	B1	OU35	12.5
C	S106	16.5	B2	S94	0.0	B1	OU37	14.8
C	S107	11.5	B2	S95	0.5	B1	OU43	11.7
C	S108	24.5	B2	S96	0.5	B1	OU51	13.2
C	S109	45.0	B2	S98	1.5	B1	OU52	9.3
C	S110	55.0	B2	S99	4.0	B1	OU53	7.8
C	S111	12.5	B2	S101	60.0	B1	OU55	11.4
C	S112	27.5	B2	S102	89.0	B1	OU56	8.5
C	S113	9.5	B2	S120	6.0	B1	OU58	10.7
C	S114	11.0	B2	OU36	2.1	B1	OU59	17.7
C	S115	46.5	B2	OU57	6.0	B1	OU65	20.1
C	S116	17.0	B2	OU60	2.8	B1	OU68	12.5
C	S117	37.5	B2	OU77	2.9	B1	OU70	8.0
C	S118	19.0	B1	S4	16.0	B1	OU72	11.4
C	S121	24.0	B1	S5	12.0	B1	OU75	11.9
C	S123	52.0	B1	S6	18.5	B1	OU76	11.3
C	S124	16.0	B1	S16	13.0			

Table A.14 - Ordered Differences Report for Saponification Number

Coagulation Category	Coagulation Category	Standard Error Difference	p-Value
C	B2	3.80	<.001
C	A	3.25	<.001
C	B1	3.18	<.001
B1	B2	3.84	0.007
A	B2	3.90	0.03
B1	A	3.29	0.55

Table A.15 - Saponification number results for category A

Coagulation test result	Sample	Saponification Number (mg KOH/g)
A	OU6	6.3
A	OU7	13.8
A	OU8	14.0
A	OU9	13.0
A	OU11	13.9
A	OU12	14.6
A	OU13	11.1
A	OU14	11.4
A	OU15	5.2
A	OU16	2.4
A	OU17	10.8
A	OU19	8.5
A	OU26	5.1
A	OU28	6.0
A	OU29	10.8
A	OU30	12.3
A	OU32	11.1
A	OU34	10.6
A	OU38	12.3
A	OU39	12.2
A	OU40	9.5
A	OU41	14.5
A	OU42	14.4
A	OU54	11.2
A	OU61	7.0
A	OU62	5.0
A	OU63	10.4
A	OU64	14.9
A	OU67	15.7
A	OU71	10.7
A	OU73	3.4
A	OU74	12.0

Table A.16 - EDXRF results from samples S1 to sample S95

Sample	Coagulation test result	Element Analysed													
		Mg	Al	Si	P	S	Cl	Ca	Cr	Fe	Cu	Zn	Na	Mn	Pb
S1	A	<L.Q	53.9	11.9	978	9190	137	2800	8.6	167	22.4	1470	<L.Q	<L.Q	<L.Q
S4	B1	<L.Q	49.3	9.0	777	5710	151	2460	8.2	147	24.7	1100	7.0	<L.Q	8.8
S5	B1	<L.Q	47	8.3	864	8360	116	2560	6.6	128	30.2	1240	<L.Q	<L.Q	7.8
S6	B1	<L.Q	56.8	12.3	977	12300	705	2400	5.5	147	21.7	1400	3.4	<L.Q	<L.Q
S13	C	<L.Q	234	234.0	172	17600	131	161	1.5	92.7	<L.Q	103	<L.Q	<L.Q	<L.Q
S16	B1	<L.Q	41.5	9.7	656	2960	40.8	1890	7.9	124	12.3	921	<L.Q	<L.Q	<L.Q
S19	B2	<L.Q	25.7	34.5	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	41.7	9.56	<L.Q	<L.Q	<L.Q
S23	B1	<L.Q	52.8	10.5	808	7870	116	2330	9.5	178	33.4	1100	<L.Q	<L.Q	<L.Q
S27	C	<L.Q	56.5	68.1	213	1200	130	337	3.1	44.1	8.13	293	<L.Q	<L.Q	<L.Q
S28	B1	<L.Q	137	172	331	1340	70.4	652	2.6	122	<L.Q	279	<L.Q	<L.Q	<L.Q
S29	B1	<L.Q	66.6	23.2	759	7310	66.8	2360	8.1	157	26.2	1080	<L.Q	<L.Q	<L.Q
S40	B1	<L.Q	60.8	40.5	742	6040	74.7	2370	7.3	134	16.8	1020	<L.Q	<L.Q	<L.Q
S41	B2	<L.Q	48.1	29.3	300	7310	28	138	<L.Q	23.4	<L.Q	477	<L.Q	<L.Q	<L.Q
S49	B1	<L.Q	42.5	9.3	866	8430	117	2480	6.7	117	27.5	1290	<L.Q	<L.Q	<L.Q
S57	B1	<L.Q	45.8	7.5	623	4930	27.7	1650	6.3	124	25.2	903	<L.Q	<L.Q	<L.Q
S58	A	<L.Q	167	18.6	580	14700	30500	1090	<L.Q	10.9	14.4	737	<L.Q	<L.Q	<L.Q
S60	C	<L.Q	269	97.1	1240	4960	38.1	47.6	3.3	99.9	11.5	48.6	<L.Q	<L.Q	<L.Q
S68	C	<L.Q	40.9	8.2	818	6800	82.5	2380	8.1	151	18	1230	<L.Q	<L.Q	5.74
S69	C	<L.Q	174	516	305	16300	208	644	<L.Q	473	45.8	170	<L.Q	<L.Q	<L.Q
S70	C	<L.Q	91.3	61	765	22200	188	1670	9.0	268	32.2	772	<L.Q	<L.Q	17.8
S71	B1	<L.Q	73.4	25.1	805	9030	86.3	2340	9.2	177	25	1160	5.87	<L.Q	63.6
S73	C	<L.Q	90.8	34.5	351	7160	7890	277	<L.Q	86.9	51.2	209	132	<L.Q	<L.Q
S74	B1	<L.Q	79.2	105	795	5680	67.2	2430	7.8	173	28.5	1120	<L.Q	<L.Q	<L.Q
S76	C	<L.Q	129	388	284	<L.Q	36	622	144	3910	6.61	306	<L.Q	18.6	<L.Q
S78	B1	<L.Q	136	136	765	14200	118	2530	3.9	107	58.8	1060	<L.Q	<L.Q	16.7
S79	C	52.6	251	389	346	<L.Q	56.8	1350	13.7	75.8	6.39	162	<L.Q	<L.Q	2.2
S80	B2	<L.Q	31.6	50.1	<L.Q	451	14.8	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S81	B2	<L.Q	41.5	62.7	<L.Q	3000	56.4	18.4	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S84	B2	17.1	29.8	64	<L.Q	<L.Q	4.6	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S85	B2	23.5	32.2	63.6	<L.Q	49.7	6.4	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S86	B2	31.2	33.7	112	<L.Q	674	<L.Q	<L.Q	<L.Q	38.5	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S87	B2	<L.Q	28.9	45.5	<L.Q	<L.Q	3.9	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S89	B2	<L.Q	33.9	46.5	<L.Q	4250	11.6	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S90	B2	25.3	29.7	63.2	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S91	B2	23.7	26.9	63.2	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S92	C	41.6	257	271	1280	537	1120	1010	33.9	394	40.5	345	64.2	4.39	8.5
S93	C	20.7	140	218	394	1640	69	455	16.3	425	<L.Q	133	<L.Q	<L.Q	<L.Q
S94	B2	30.9	32.6	68	<L.Q	<L.Q	2.8	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q	<L.Q
S95	B2	32.9	54	112	<L.Q	380	45.3	32.1	<L.Q	<L.Q	<L.Q	2.5	<L.Q	<L.Q	<L.Q

Table A.17 - EDXRF results from samples S96 to sample S133

Sample	Coagulation test result	Element Analysed													
		Mg	Al	Si	P	S	Cl	Ca	Cr	Fe	Cu	Zn	Na	Mn	Pb
S96	B2	54.4	74.8	106.0	75.3	<L.Q	1550	79.5	3.0	145	<L.Q	79.7	68.2	<L.Q	<L.Q
S97	C	<L.Q	102	1010.0	7190	<L.Q	24	2890	26.0	32	<L.Q	313	63.7	<L.Q	<L.Q
S98	B2	<L.Q	40.9	62.5	14.7	1390	30.7	81.4	8.2	148	<L.Q	14.1	<L.Q	<L.Q	<L.Q
S99	B2	20.4	44.4	53.1	160	1150	51.2	294	<L.Q	15.3	<L.Q	54.7	<L.Q	<L.Q	<L.Q
S100	C	45.0	292	397.0	1250	587	105	2240	7.7	103	5.6	612	<L.Q	<L.Q	<L.Q
S101	B2	40.0	80.5	190.0	298	<L.Q	114	923	11.8	346	3.95	178	<L.Q	<L.Q	<L.Q
S102	B2	15.0	109	91.9	77.5	<L.Q	37.3	71.2	12.6	27.9	<L.Q	9.07	<L.Q	<L.Q	<L.Q
S103	C	39.8	198	280.0	982	<L.Q	103	1370	25.7	165	15	304	<L.Q	<L.Q	3.7
S104	C	<L.Q	68.7	81.6	628	4280	151	1250	7.3	130	23	701	<L.Q	<L.Q	6.1
S105	C	<L.Q	76.4	59.5	792	5890	69.2	1390	4.7	137	15.2	706	<L.Q	<L.Q	4.1
S106	C	<L.Q	98.7	92.3	786	6640	82.9	2200	8.4	197	31.5	1060	<L.Q	<L.Q	6.9
S107	C	<L.Q	150	183	669	9710	130	2070	11.5	212	23.3	888	<L.Q	<L.Q	<L.Q
S108	C	<L.Q	87.5	101	626	8330	174	1550	6.8	150	24.0	769	<L.Q	<L.Q	5.0
S109	C	<L.Q	147	117	582	34900	174	2510	10.2	397	23.9	854	<L.Q	9.5	2.9
S110	C	<L.Q	253	236	889	97900	267	4800	15.3	993	<L.Q	1540	<L.Q	38.2	<L.Q
S111	C	<L.Q	88.4	58.5	570	4110	104	1490	8.8	143	24.6	725	<L.Q	<L.Q	4.1
S112	C	4.4	47.4	29.9	706	3840	52	2030	10.3	180	23.2	995	<L.Q	3.6	3.7
S113	C	<L.Q	54.4	48.3	431	6260	77.9	1410	5.6	261	12.4	552	<L.Q	<L.Q	2.44
S114	C	19.0	79.6	67	731	6660	428	1980	7.1	155	29.1	936	<L.Q	<L.Q	8.2
S115	C	<L.Q	281	55.6	396	13100	209	395	72.2	46.8	69.8	447	<L.Q	5.8	10
S116	C	<L.Q	44	32	407	<L.Q	47.1	1190	5.5	140	22.1	598	<L.Q	11.3	<L.Q
S117	C	<L.Q	135	140	841	6460	391	2840	6.5	239	21.6	1100	<L.Q	<L.Q	5.9
S118	C	<L.Q	55.9	28	759	6250	100	2150	11.2	154	20	1050	<L.Q	<L.Q	8.8
S119	A	<L.Q	54.1	49.3	434	<L.Q	275	1030	4.37	83.9	14.9	454	<L.Q	<L.Q	4.0
S120	B2	47.0	70.9	43.8	162	<L.Q	3630	657	1.7	24	5.12	172	<L.Q	<L.Q	<L.Q
S121	C	30.6	81.6	72.9	899	8710	174.0	1950	10.2	278	44.1	962	<L.Q	<L.Q	7.5
S122	A	<L.Q	59.7	34.4	796	12400	130.0	2280	6.1	174	30.1	1030	<L.Q	<L.Q	7.6
S123	C	40.5	88.7	148	294	552	1660.0	629	34.8	138	8.7	308	<L.Q	<L.Q	2.4
S124	C	<L.Q	161	274	440	18400	244.0	2510	60.7	979	12.7	453	<L.Q	68.9	<L.Q
S125	A	<L.Q	130	1610	168	142	58.9	491	<L.Q	83.4	5.6	177	<L.Q	<L.Q	<L.Q
S126	C	<L.Q	90.3	147	484	459	71.8	1070	7.6	89.9	22.4	504	<L.Q	<L.Q	2.8
S127	A	<L.Q	61.5	310	286	1410	40.8	691	4.1	58.7	9.9	329	<L.Q	<L.Q	<L.Q
S128	C	<L.Q	66.2	74.2	1080	6420	356	1980	3.7	96.3	31.0	846	<L.Q	<L.Q	4.6
S129	C	<L.Q	123	238	509	1960	106.0	1740	6.9	204	12.1	627	<L.Q	<L.Q	2.4
S130	C	<L.Q	213	450	671	3090	153.0	2150	4.6	249	38.1	969	<L.Q	<L.Q	5.4
S131	A	<L.Q	115	153	342	8340	311	2640	3.5	571	7.73	475	<L.Q	<L.Q	<L.Q
S132	B1	<L.Q	44.3	50.7	356	1220	27.7	514	2.07	67.8	12.4	424	<L.Q	<L.Q	<L.Q
S133	C	<L.Q	58.1	72.7	441	1660	37.3	713	<L.Q	87.8	10.9	542	<L.Q	5.0	9.7

Table A.18 - Ordered Differences Report for magnesium content analysis

Category	Category	Standard Error Difference	p-Value
B2	A	6.28	0.003
B2	B1	5.01	<.001
B2	C	4.01	0.01
C	A	5.86	0.18
C	B1	4.46	0.08
B1	A	6.58	1.00

Table A.19 - Ordered Differences Report for aluminium content analysis

Category	Category	Standard Error Difference	p-Value
C	B2	16.39	<.001
C	B1	18.22	<.001
A	B2	25.67	0.08
C	A	23.93	0.10
A	B1	26.88	0.36
B1	B2	20.45	0.31

Table A.20 - Ordered Differences Report for phosphorus content analysis

Category	Category	Standard Error Difference	p-Value
B1	B2	84.46	<.001
C	B2	68.00	<.001
A	B2	106.02	<.001
B1	A	111.00	0.06
C	A	99.05	0.20
B1	C	75.53	0.27

Table A.21 - Ordered differences report for sulphur content analysis

Category	Category	Standard Error Difference	p-Value
B1	B2	2043.74	0.01
A	B2	2565.49	0.03
C	B2	1645.37	<.001
B1	C	1827.59	0.90
B1	A	2686.00	0.94
A	C	2396.86	0.99

Table A.22 - Ordered differences report for calcium content analysis

Category	Category	Standard Error Difference	p-Value
B1	B2	245.71	<.001
A	B2	308.44	<.001
C	B2	197.82	<.001
B1	C	219.72	<.008
B1	A	322.93	0.13
A	C	288.17	0.70

Table A.23 - Ordered differences report for zinc content analysis

Category	Category	Standard Error Difference	p-Value
B1	B2	115.86	<.001
A	B2	144.17	<.001
C	B2	94.06	<.001
B1	C	100.73	<.001
B1	A	148.61	0.03
A	C	132.32	0.75