CHALMERS

Total Acid Number (TAN) in Turbo Oil 2380; Comparison of thermometric and potentiometric titration and FTIR study of the degrading process for oils in use

Master's thesis

Olivia Stenman

Department of Chemistry and Chemical Engineering
Chalmers University of Technology
Gothenburg, Sweden, 2020

Total Acid Number (TAN) in Turbo Oil 2380; Comparison of thermometric and potentiometric titration and FTIR study of the degrading process for oils in use

OLIVIA STENMAN - oliste@student.chalmers.se

Examiner:
Gunnar Westman

Supervisor:
Bertil Sagnér

The department of chemistry and chemical engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone number +46 31 772 1000

Pictures without any reference are created by the author of this document.

Total Acid Number (TAN) in Turbo Oil 2380; Comparison of thermometric and potentiometric titration and FTIR study of the degrading process for oils in use

OLIVIA STENMAN

The department of chemistry and chemical engineering
Chalmers University of Technology

Abstract

Total acid number (TAN) determination is a useful tool in order to monitor degradation of oils used in e.g. aviation and aerospace industry. When an oil in service is being used over time additives used to enhance the properties of the oil will deplete and the oil will oxidize resulting in loss of important properties of the oil. By measuring TAN, which is expressed as mg KOH/g the increase of acidic components can be monitored and used as a quality control of the oil. Several techniques for TAN determination exist however the focus of the study was to investigate and compare TAN analysis using potentiometric and thermometric titration. FT-IR analysis were used as a complement in order to monitor the degradation of the oil. New and used samples of Eastman turbo oil 2380^{TM}, which is a synthetic lubricating oil has been analyzed with potentiometric titration based on test method ASTM D664 and thermometric titration based on test method ASTM D8045. TAN of new ETO 2380 determined with potentiometric titration in accordance with ASTM D664 resulted in values around 0.63 mg KOH/g. Optimization of the test method using 2-propanol as solvent instead of a toluene/2-propanol/water mixture and decreasing the rinsing/maintenance time of the electrode generated a TAN of 0.63 mg KOH/g as well. Regarding the thermometric titration in accordance with ASTM D8045 TAN values obtained for new ETO 2380 resulted in values around 0.20 mg KOH/g. However, using tetrabutylammonium hydroxid (TBAOH) as titrant instead of potassium hydroxid (KOH) resulted in similar values as those obtained for the potentiometric titration. By comparing results from analysis of ETO 2380 used in service, potentiometric titration using KOH and thermometric titration using TBAOH generated very similar values for both high and low TAN. Using KOH as titrant thermometric titration resulted in lower values compared to potentiometric titration for TAN below 1 mg KOH/g and higher values compared to potentiometric titration for samples with higher TAN. FTIR analysis showed increased amount of oxidation products and possible depletion of anti-oxidation additives for the oil samples used in service.

Keywords: TAN, potentiometric titration, thermometric titration, lubricating oil

Innehåll

1 Introduction

In order to reduce friction and wear between mechanical components a special class of oils referred as lubricating oils are used. In vehicles lubricating oils play a vital role since a properly lubricated engine will enhance the glide of the pistons in the engine leading to a decreased amount of fuel needed for the engine to operate. Over time the lubricating oil will reduce the wear and tear while in the same time enhance the efficiency. Besides the use of lubricating oils in vehicles lubricating oils can also be used in turbine engines. Usually two types of oils are used as turbine engine oils, High Performance Capable (HPC) and Standard Performance Capable (SPC) oils. When the demand of high thermal properties are not required SPC oils are used in engines and accessories and it has been used by airlines for several years. [1] Lubricating oils can also be divided into two classes based on the origin, mineral oils and synthetic oils. Mineral oils originates from natural occurring crude oils while synthetic oils are produced in manufacture ways.[2, 3] A well used synthetic SPC lubricating oil used in commercial aviation industry is Eastman Turbo oil 2380 ™ (ETO 230). The applications of ETO 2380 are within the field of aerospace and aviation turbine oil (ATO).[4]

When oils such as ETO 2380 are being stored or used in service for a longer period of time the oil starts to degrade, creating an increased amount of acidic constituents. The degradation of the oil while in service or stored is due to depletion of additives in the oil and the formation of oxidation products. Common compounds formed when the oil reacts with oxygen are carboxylic acids, ketones, aldehydes and esters.[5] If the amount of acidic spices in the oil increases to a certain limit it can cause severe damage to engines and accessories. To avoid such damage the amount of acidic species can be measured and monitored being expressed as the amount of potassium hydroxide (KOH) required to neutralize one gram of oil sample. Usually the measure of acidity in oils are referred to as the total acid number (TAN) or just acid number (AN). TAN can be measured in several ways, where different types of titration are very common. Both potentiometric titration and thermometric titration are methods used for determining TAN in oils.[6]

1.1 Background

GKN Aerospace Sweden is part of GKN Aerospace, where advanced components for engines for aircraft and space rockets are developed and manufactured. Beside the development and manufacture, engine maintenance are also preformed.[7]

At GKN Aerospace Sweden ETO 2380 is used as both lubricant and as fuel in order for the apparatus to operate. The internal demand of measuring the acidity in oils has increased and since the equipment currently used for measuring the TAN will be exchanged it is of high interest to perform an overview of analysis methods for measuring the acidity. TAN has previously being measured by using potentiometric titrtation based on ASTM D664.

1.2 Aim

The aim of the project was to investigate and compare the two titration methods, potentiometric and thermometric titration for analysis of total acid number in new and used samples of Eastman Turbo oil 2380^{TM}. The aim was also to use Fourier Transform Infrared (FT-IR) spectroscopy as a complement to the TAN measurements for monitoring the degradation process of the oil.

1.3 Limitations

Since the main focus of the project was to compare the two titration methods, most of the time was assigned to investigate and evaluate both methods. Regarding the optimization the main priory was to reduce or remove toxic chemicals that are currently being used for these methods. Existing methods used for TAN measurements other than potentiometric and thermometric titration will not be discussed.

Regarding the FT-IR analysis, spectra obtained were not analyzed in such way that every component and peak were assigned. The FT-IR was used as a tool for analyzing the differences between the spectra of new and used ETO 2380 samples.

2 Theory

Following sections will address the theory behind TAN and a more specific description of ETO 2380. Theory of potentiometric titration, thermometric titration and FT-IR spectroscopy will be addressed as well.

2.1 Total acid number determination

Acidic constituents in new and used oils, such as lubricants and petroleum products may occur as a result of degradation products formed during oxidation of the oil or depletion of additives present.[9] There are a variety of compounds that can contribute to the acidity such as carbonyl oxidation products, soot particles, nitration and sulfur oxidation products, fuel residues and water and glycol contamination. Depending on the additives present and the use of the oil, oxidation and depletion will generate different acidic species. By analyzing samples of the oil in service regularly the increase of acidic constituents can be monitored and rapid changes in TAN can be detected. TAN determination can therefore be used as a way to control the quality of the oil in service. [9, 10, 11]

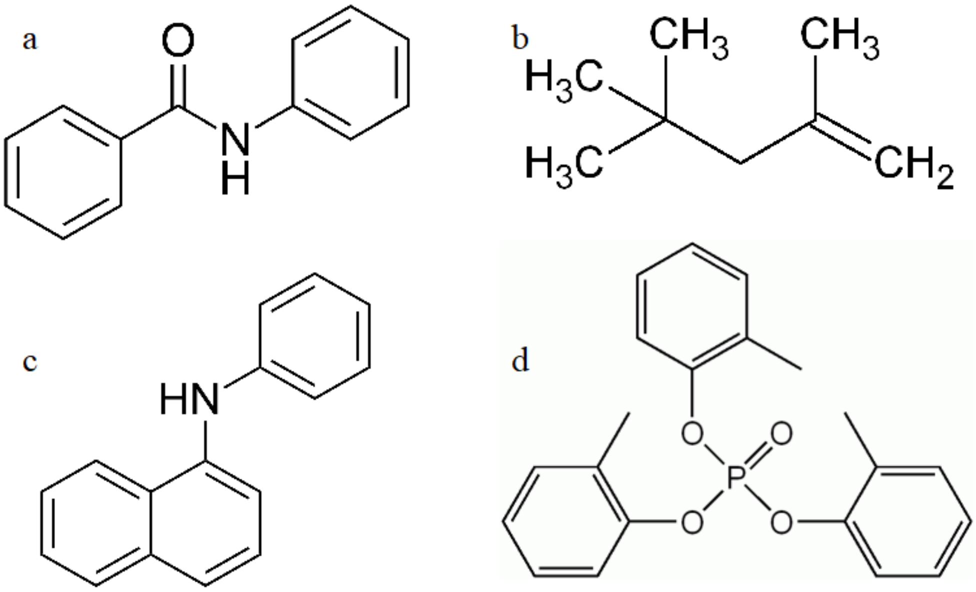
TAN can be measured in several ways depending on the type of oil and a number of analytical methods has been used over the years. A widely used technique for TAN determinations is potentiometric titration which has been used for the purpose of determining TAN in oils for many years.[9] More recently the use of thermometric titration for TAN determinations has increased. Both titration methods are preformed as non-aqueous acid-base titrations using a strong base, usually KOH, as titrant. The use of non-aqueous conditions is due to water is an amphiprotic solvent, can act as both an acid and a base. This means that very weak acidic constituents might not be detected using water as solvent since the titrant will react with the water molecules instead. A non-aqueous solvent will therefore give rise to the ability to detect a larger amount of acid constituents. It is also important that the solvent used for the titration is not introducing interfering side reactions.[12]

2.1.1 Lubricating oils

Usually lubricating oils consists of a base oil combined with additives appropriate for the specific purpose of the oil. Example of such additives are anti-oxidants which inhibits the oxidation process caused by radicals produced in the oil when exposed to e.g. heat or oxygen. The hydrocarbons i the oil react with oxygen resulting in the formation of carboxylic acids and depending on the temperature and amount of contamination the oxidation rate can vary significantly. Compounds that can act as anti-oxidants are e.g. aromatic amines and hindered phenols. Another type of additives are antiwear substances which function is to reduce the friction and wear. [13, 14] A common type of antiwear additives are phosphorus-based substances where tricresyl phosphate (TCP) has been used in aerospace systems for several decades. [15, 16]

Since additives consist of acidic components a new and unused oil has an initial TAN already before use. For an oil in service the additives will start to deplete after a certain period of time. This can lead to a decrease in TAN before it will increase due to oxidation products.[17] ETO 2380 has a predetermined value of 0,43 mg KOH/g. However, this value is determined in accordance with SAE ARP5088, which is an older version of total acidity determination by potentiometric titration. The test method is assigned to determining the TAN in polyester and diester gas turbine lubricants. [4, 18]

ETO 2380, which is a synthetic lubricating oil consists of N-Phenylbenzenamine, 2,4,4-Trimethyl-1-pentene, TCP, and N-Phenyl-1-naphthylamine, which can be seen in figure 2.1. Both N-Phenylbenzenamine, N-Phenyl-1-naphthylamine and 2,4,4-Trimethyl-1-pentene are used as ant-oxidants and TPC is used as antiwear agents. [19, 20, 21, 22] The remaining compounds in the oil are unknown.



Figur 2.1. Chemical structure of a) N-Phenylbenzenamine, b) 2,4,4-Trimethyl-1-pentene, C) N-Phenyl-1-naphthylamine och d) Tricresyl phosphate

The ETO 2380 samples to be analyzed are collected from three different test rigs with minor differences in temperature interval, which can be seen in table 2.1.

Tabell 2.1. Rigs and conditions

Name of rig	**Min. temp [C]**	**Max. temp [C]**
Rig 74	20	85
Rig 130	20	120
Rig 139	0	100

Samples of the oils are usually collected and analyzed every third month and the oils in each rig are exchanged every third year. In certain cases the oil can be refilled or exchanged within the three-year-period. This could for example be the case if the oil has been contaminated. Possible contamination are chip formation from engine components or appliance components or coked oil. If the oil exceeds the limit of 1.0 mg KOH/g the oil should be replaced as well. The oil in the three test rigs were last exchanged in January 2020.

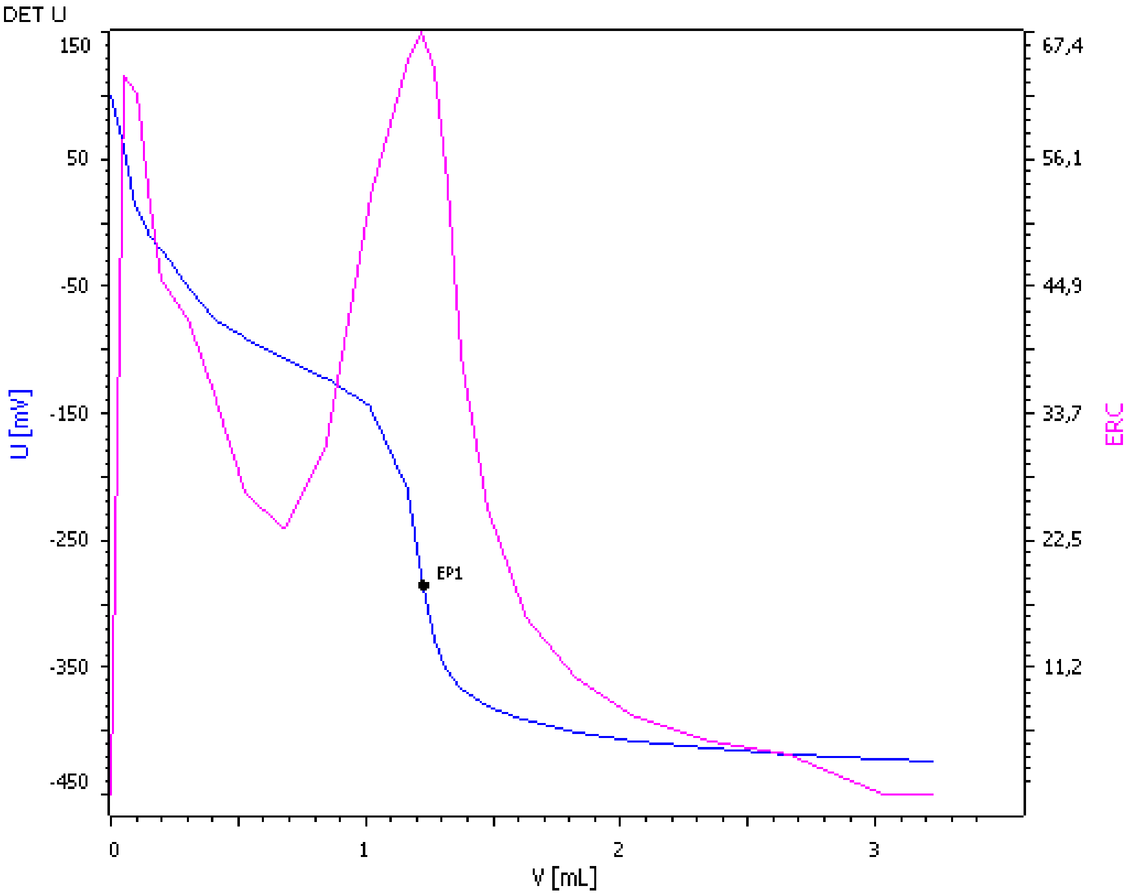
2.2 Potentiometric titration

Potentiometric titration is a very versatile tool for analytical measurements. It is a volumetric method which can be preformed either automatically or manually.[23] Potentiometric titration is based on changes in Gibbs free energy, equation 2.1, where the change in Gibbs free energy needs to be sufficient in order to generate a significant inflection.

$$\Delta G^o = -RTlnK \tag{2.1}$$

Where G^o is Gibbs free energy, R is the universal gas constant, T is the temperature (K) and K is the equilibrium constant at temperature T.

Potentiometric titration is often used in purpose of characterizing acids. This is proceeded by measuring the potential across the substance. The potential can for example be plotted against the amount of titrant (usually volume in mL) creating a potential curve similar to the curve in figure 2.2. The potential is then measured each time the titrant is added. [24]



Figur 2.2. Potentiometric titration curve where the potential is plotted against the volume.

2.2.1 ASTM D664

ASTM D664 is developed as a test method for determining TAN in lubricating oils, petroleum products, biodiesels and blends of biodielsels using potentiometric titration. For determining TAN in accordance with ASTM D664 a dissociation number larger than 10^{-9} for the acids in water is required, since weaker acids will not interfere. The range of TAN included in the precision statement is 0.1 mg KOH/g to 150 mg KOH/g. TAN is calculated using equation 2.2.

$$\text{TAN} = \frac{(V_{EP1} - Blk) * c(titrant) * M[KOH]}{W} \tag{2.2}$$

where V_{EP1} is the titrant consumption for the sample (mL), *Blk* ist the titrant consumption for the blank (mL), *c(titrant)* is the concentration of titrant (mol/l), M[KOH] is the formula mass of KOH 56.11 (g/mol) and W is the sample mass (g). According to ASTM D664 by ASTM International the sample amount needed are dependent on the TAN. Table 2.2 shows the correlation between the acidic number and the amount of sample required for the analysis. [9]

Tabell 2.2. Recommended size of test portion using 60 ml solvent [9]

Acid number	Mass of test portion	Accuracy of weighting
0.05 to <1.0	10.0 ± 1.0	0.10
1.0 to <5.0	2.5 ± 0.25	0.02
5 to <20	0.5 ± 0.05	0.005
20 to <100	0.25 ± 0.02	0.001
100 to <200	0.1 ± 0.01	0.0005

2.3 Thermometric titration

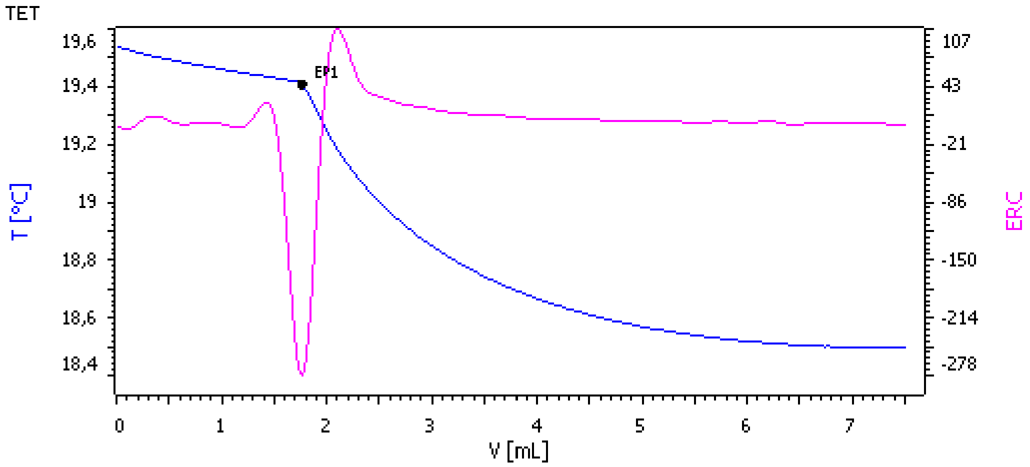
In thermometric titration the end-point measurements are based on changes in temperature instead of changes in potential. Whether the reaction is exothermic or endothermic the temperature change will create an inflection in the curve indicating the end-point of the titration. When thermometric titration is used the titrant is added at a constant predetermined rate to the analyte in order for the reaction to reach completion. Completion of the reaction creates a molar heat of the reaction, delta H, resulting in the change in temperature.

In thermometric titration the change in temperature is plotted against the volume of the titrant creating a titration curve. The inflection occurs when the reaction between analyte and titrant is complete and excess titrant is added to the analyte. Figure 2.3 depicts a conventional thermometric titration curve for a exothermic reaction. [25] In order to determine the inflection point when using automatic titration, the second derivative of the temperature curve is used. By applying a second derivative curve the intersect of the tangents pre and post the inflection point is being localized indicating the end point of the titration. In figure 2.3 an exothermic titration curve with an applied derivative curve can be seen.

A thermometric titration curve were the slope of the temperature change is very sharp and abrupt is desired since it indicates that the reaction has reached completion. For cases when the reactions is not complete near the end point the heat evolved per unit of reactant will be less, resulting in a more curved appearance of the titration curve at the endpoint. An increased curvature near the end point also results in a smaller value of the equilibrium constant. By preforming a tangential extrapolation from both sides, giving the non-equilibrium curve, the end point can be obtained at the intersection. [25]

Environmental influences creating gains and losses in heat will affect the titration resulting in a non-constant increase or decrease in temperature. Examples of environmental factors that can affect the temperature change are:

- Evaporating losses from the surface of the rapidly mixed fluid



Figur 2.3. Example of an exothermic titration curve with an applied derivative curve to localize the end-point.

- Heat gains or losses from outside the system via the vessel walls
- Differences in the temperature between the analyte and the titrant
- Heat of solution when the titrant solvent is mixed with the analyte solvent

A way to minimize the heat evolved due to the mixing between the solvent titrant and analyte solvent is to use the same solvent for both titrant and sample. The choice of solvent used for the sample is therefore very important and can be used as a way to determine a appropriate base for the titration.

Since the sensor used for measurements of thermometric titration requires to be sensitive in order to be able to measure small temperature changes, there is a risk of noise being registered as well. A sharper and more correct inflection point can be obtained by digitally smooth the curve. The digital smoothing is a parameter called filter factor that can be changed in the software prior to the titration. Depending on the sample to be analyzed different values of the filter factor is required. The filter factor is optimized by plotting the titrant consumption at different filter factors. By plotting the different volumes of titrant obtained against the filter factors the optimum filter factor is observed in the area where the titrant volume does not change with the change in filter factor.

The procedure for thermometric titration can vary depending on the acidity of the oil. If an oil with lower acidity is titrated in non-aqueous solvent the end-point can be difficult to obtain due to temperature changes can be rather small. A small change in temperature can lead to a decrease in accuracy since the end-point can be mistaken for e.g. the heat of the mixing of the titrant with the solvent and the solvent evaporation. In order to solve this problem an end-point indicator can be used. The function of the indicator is to react with the excess titrant producing an exothermic or endothermic reaction that creates a temperature change great enough for an accurate detection and determining of the end-point. It is of importance that the end-point indicator used will not interfere with the properties of the solvent.

2.3.1 ASTM D8045

ASTM D8045 is is a further development of ASTM D664, however more complicated products to dissolve, such as bitumen, waxes and asphalts can be analyzed. The test method uses thermometric titration and is applicable for crude oils and petroleum products that can be dissolved in a mixture of xylene and 2-propanol. As for the ASTM D664 the dissociation constant in water must must be lager than 10^{-9} or else the acidic constituents will not interfere. The rage of values of TAN that can be obtain lays in the interval of 0.1 mg KOH/g to 16 mg KOH/g.[26]

The titration method used in accordance with ASTM D 8045 is a catalyzed endpoint thermometric acid-base titration. The endpoint is detected by a fast responding, highly sensitive temperature sensor. In accordance with ASTM D8045 paraformaldehyde is used as an end-point indicator. Initially the titrant, KOH, will react with the acidic species in the sample. When the sample has been titrated until completion, excess of hydroxyl ions reacts with the paraformaldehyde. The reaction between the hydroxyl ions and paraformaldehyde will generate a depolymerization of the paraformaldehyde (to formaldehyde) causing a change in enthalpy which will be seen as a temperature decrease in the titration curve.

There are several advantages stated for using ASTM D8045 instead of ASTM D664. The thermoprobe used in ASTM D8045 requires no maintenance, conditioning or calibration compared to the solvotrode used in ASTM D664. Another advantage is the decreased amount of chemical waste generated from the decreased amount of solvent and reagent needed. A lower amount of solvent and reagent also leads to a lower cost per analysis.[6] In table 2.3. a comparison between ASTM D8045 and ASTM D644 can be seen.

Tabell 2.3. Parameters and settings for sample

Parameter	**D8045 thermometric titration**	**D664 potentiometric titration**
Electrode conditioning	Not necessary	3–5 min
Electrode storage	Dry	LiCl in ethanol
Volume of solvent required for analysis	30–35 mL	60 or 125 mL
Titration duration (averaged)	45–73 s	132–268 s
Method repeatability when measuring 1.0 mg KOH/g in crude oil	0.07 mg KOH/g	Not established
Method reproducibility when measuring 1.0 mg KOH/g in crude oil	0.31 mg KOH/g	Not established

As for the potentiometric titration the sample mass used are dependent on the assumed TAN of the sample. Recommended sample sizes dependent on the expected TAN according to ASTM D8045 can be seen in table 2.4.

Tabell 2.4. Recommended sample masses

Expected TAN (mg KOH/g	**Sample mass (g)**
0,05 - 0,99	10-20
1,00 - 4,99	5
5,00 - 15,00	1

When analyzing samples with thermometric titration in accordance with ASTM D8045, TAN can be calculated using equation 2.3.

$$TAN = \frac{(A)(M) * 56.11}{W} \tag{2.3}$$

where A is the volume of titrant at the end point (mL), M is the titrant concentration (mol/L) and W is the sample mass (g).

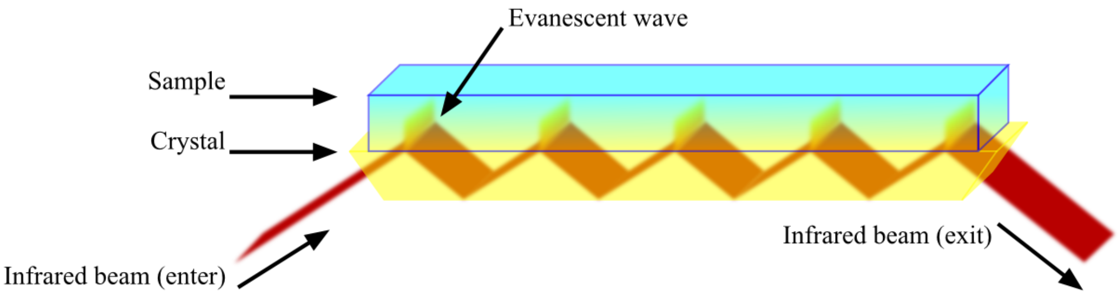
TAN measurements based on ASTM D8045 can differ depending on the source. Examples of differences obtained is sample mass required, software settings and if a blank determination is necessary or not. However, there are also different titrants used. KOH is in general the titrant used the most for both thermometric and potentiometric titration for the purpose of determining TAN. However some studies were preformed using tetrabutylammonium hydroxide (TBOH) as titrant, which is a quaternary ammonium salt. TBAOH is a larger and more bulky organic compound than KOH and is mainly used as a strong base. Most of the studies using TBAOH are assigned to potentiometric titration. Metler Toledo is suggesting the use of TBAOH as a possible titrant for determining TAN in petroleum oils using potentiometric titration. It was stated that the advantages of TBAOH compared to KOH was an increased reliability and evaluation of the equivalence point and an enhanced agreement with TAN. TBAOH generates a larger and steeper jump at the equivalence point and it was concluded that TBAOH compared to KOH resulted in an improvement of the TAN analysis. [27, 28] TBAOH has also been used as titrant for for determining TAN of pyrolysis bio-oils using potentiometric titration. This method is also based on ASTM D644 and it was stated that TBAOH was used in order to improve detection of the phenolic content, which is weak acidic species.[29]

2.4 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared, FT-IR, spectroscopy is an analysis technique used for determining functional groups in a sample. When infrared light interacts with the sample, absorption of the IR light will cause vibrations of the molecular bonds.

These vibrations will give rise to a specific wave number that can be obtained by a detector and transferred into a spectrum. FT-IR can be used in combination with multivariate data in order to determining TAN of an oil. However, it can also be used to monitor the degradation of the oil by comparing spectrum of a new oil with a spectrum of an oil used in service. Attenuated Total Reflectance (ATR) FT-IR and Transmission FT-IR are two well know techniques within the FT-IR field. Transmission FT-IR is a very widely used technique with the possibility of analyzing a wide range of samples. In transmission FT-IR the incident infrared radiation is passed through the sample to be analyzed and some of the incident radiation will be absorbed by the sample. Depending on the sample, light of characteristic wavelengths or frequencies will be absorbed. The light that is not absorbed by the sample will be transmitted through the sample and measured by a detector linked to a computer which will produce a spectrum in terms of frequency and intensity. When analyzing organic liquids with transmission FTIR a special transmission cell for liquids are used. The liquid cell has a fixed pathlength, which is the distance the infrared beam travels through the sample. Depending on the pathlength and the composition of the sample the intensities of the bands in the sample spectrum will differ. [30]

ATR is a more simple FT-IR technique to preform requiring little or no sample preparation. Compared to Transmission FTIR, ATR is based on internal reflection, see figure 2.4. The interaction between the sample and the infrared light is only occurring at the point where the infrared light is reflected. When using ATR FTIR it is of high importance that the sample is in contact with the ATR crystal, which can be made of several different materials depending on the sample to be analyzed. However, by using a diamond ATR crystal, all types of samples can be analyzed. Analysis of liquids requires no sample preparation and the sample can be pipetted directly on the crystal. In general the spectrum obtained with ATR FT-IR is very similar to the spectrum obtained with transmission FT-IR. However there are minor differences which can be corrected by using the ATR correction tool in the OMNIC ^{TM} software.[30, 31]



Figur 2.4. Schematic picture of ATR FT-IR. [34]

2.4.1 Lubricating oil analysis

Since a used lubricating oil can consist of several oxidation products and residues from additive depletion a FTIR spectrum of such an oil can be difficult to interpret due to its complexity. However, the different categories of oxidation and depletion products mentioned in the TAN section will have the corresponding peaks as table 2.5 is showing.[32, 33]

Tabell 2.5. Acidic components and their corresponding peaks in the FT-IR spectrum. [22, 33]

Acidic component	**wavelength [cm^{-1}]**
Carbonyl oxidation products	1730
Sulfuric oxidation products	1120-1180
Nitric oxidation products	1600-1800
Soot	2000
Additives	800-1000
Fule	800

If the different oxidation peaks becomes more intense for an oil that has been used in service compared to a new oil it indicates that oxidation has occurred. Compared to previously mentioned components soot has no specific frequency of absorption. However, the presence of soot will result in a shift in intensity of the baseline. To identify this shift the region around 2000 cm^{-1} are usually used since there are no other peaks in this region. Regarding the additive TCP changes in concentration of TCP can be observed in the region around 940 cm^{-1}. [14, 22]

3 Method

All analysis were preformed on ETO 2380 and by the same operator. The software used for both methods was Tiamo ^{TM}. Method investigation and optimization of each titration method were preformed with new unused ETO 2380. Samples of ETO 2380 used in service from rig 74, 130 and 139 were also analyzed. The samples of oils in service were collected from the rigs during the last year, see table 3.1. The dates of collection will be referred as specific sample numbers in tables and text. Note that the oil in each rig was exchanged after sample number 3. Sample number 1-3 will therefore have much higher TAN then sample number 4-6.

Tabell 3.1. Dates of collected samples converted into sample numbers

Sample number	**Date of collection**
1	2019-09-24
2	2019-12-11
3	2020-01-03
4	2020-03-19
5	2020-06-11
6	2020-09-10

Since the samples of the oils in service were collected during the last year the sample amount was very limited. Due to this all analysis could not be preformed for every sample number of each rig. Absent analysis will be marked with -.

3.1 Potentiometric titration

The investigation of potentiometric titration were divided into four parts. The first part included analysis of new ETO 2380 with parameters and settings in accordance with ASTM D664. The method was then optimized in two steps resulting in a final method used for analyzing ETO 2380 samples used in service. Each series for the first three parts included a duplicate of blanks and 8 samples of new unused ETO 2380. The fourth part contained duplicates of blanks and duplicates of every oil of each sample number. The first series to be analyzed each new day also included a duplicate of Acid Number standard (TAN standard) used as a reference sample. The TAN standard had a predetermined TAN of 0.5 mg KOH/g. Blanks used for each sample series consisted of the solvent used for the samples analyzed. The titrant used for all analysis was KOH in 2-propanol [0.1 M].

3.1.1 Reagents

Total Acid Number (AN) standard: 0.5 mg KOH/g in Hydrocarbon oil, 2-propanol >=99.8%, toluene >=99,8% and potassium hydroxide (KOH) were of reagent-grade quality. The new and used ETO 2380 were commercial bought.

3.1.2 Apparatus

Solvotrode easyClean 6.0229.010, 855 Robotic titrosampler, 800 Dosino 10 mL.

3.1.3 Procedure in accordance with ASTM D664

Apparatus settings in accordance with the ASTM D664 standard and can be seen in table 3.2 and 3.3. However, in order to minimize the wast of titrant and analysis time stop conditions were set to stop after 2 ml of titrant added after the last equivalence.

Tabell 3.2. Settings for blank analysis

Parameter	**Setting**
Mode	DET U
Meas. point density	4
Min. increment	10 μL
Max. increment	50 μL
Signal drift	60 mv/min
Max. waiting time	60s
EP criterion	5
EP recognition	All

Tabell 3.3. Settings for sample analysis

Parameter	**Setting**
Mode	DET U
Meas. point density	4
Min. increment	50 μL
Max. increment	0.5 mL
Signal drift	60 mv/min
Max. waiting time	60s
Stop EP	off
EP criterion	5
EP recognition	Last

For the potentiometric titration measurements a Solvotrode easyClean was used. It is a combined pH electrode for non-aqueous acid/base titrations. The electrolyte used for the electrode was LiCl in ethanol with a concentration of 2 M. The electrolyte was prepared by dissolving LiCl in ethanol. While the electrode was not in use it was stored in LiCl in ethanol [2M]. The electrode was calibrated every day before use with pH 4 and pH 7. The electrode potential in pH 4 and pH 10 was also measured and the potential difference between the two buffer solutions was required to differ at least 200 mV.

Preparation of solvent was performed by mixing 2-propanol, water and toluene. 5 ml deionized water was added to a 1000 ml volumetric flask in addition with 495 ml 2-propanol. 500 ml of toluene was added to the solvent mixture. The solvent mixture was well mixed before transferred to a storage bottle. 10 mg of new ETO 2380 was weighted in a 125 ml beaker and 60 ml solvent was added. Reference samples of TAN standard were prepared in the same way as the ETO 2380 samples.

The titration method for both blank and oil samples consisted of five rinsing/-maintenance steps of the electrode. These steps were preformed before the initial titration and between each sample and after the final sample had been titrated. Stirring time used for every step can be seen in table 3.4.

Tabell 3.4. Stirring time for each rinsing step

Liquid	**Stirring time [s]**
Solvent mixture	10
Toluene	45
2-propanol	30
Deionized water	240
2-propanol	30

For calculations of TAN (mg KOH/g) according to equation 2.1 a mean value of the two blank samples were used. If the values of the blanks exceeded 0.1 mL each, two new blank samples were analyzed. [9]

3.1.4 Optimization 1

The potentiometric titration method was first optimized by changing the solvent and blank samples used from the mixture of toluene, 2-propanol and water to 2-propanol only. The remaining parameters and settings were remained unchanged. 10 sample series were analyzed.

3.1.5 Optimization 2

Further optimization was proceeded by decreasing the stirring time. The reduced stirring times can be seen in table 3.5. The remaining settings were in accordance with ASTM D664 and 2-propanol was used as blank and solvent.

Tabell 3.5. Parameters and settings for blank

Liquid	**Stirring time [s]**	**Optimized stirring time [s]**
Solvent	10	10
Toluene	45	30
2-Propanol	30	10
Deionized water	240	60
2-Propanol	30	10

Analysis of ETO 2380 samples from rig 74, 130 and 139 were preformed in accordance with parameters and settings for optimization 2. Sample masses used were 10 g for assumed TAN below 1 and 2.5 g for assumed TAN above 1.

3.2 Thermometric titration

In order to measure TAN with thermometric titration the method based on ASTM D8045 was optimized to be appropriate for ETO 2380 samples in order to generate accurate values similar to those obtained for potentiometric titration. The procedure for the investigation of thermometric titration can be divided into three larger parts. Optimization of ASTM D8045, test series analysis of new ETO 2380 and analysis of used ETO 2380 from rig 74, 130 and 139.

3.2.1 Reagents

Potassium hydroxide (KOH) in 2-propanol and xylene were commercially produced and of Analytical reagent grad and laboratory reagent grade respectively. Other reagents used were 2-propanol (isoproyl alcohol, anhydrous, >99% purity), toluene (pre-dissolution solvent) ans tetrabutylammonium hydroxide (TBAOH) in 2-propanol.

3.2.2 Apparatus

Thermoprobe 6.9011.020, 869 Titrotherm, 800 Dosino 10mL and 20mL.

3.2.3 Procedure for optimization of ASTM D8045

The solvent was prepared by adding 250 ml 2-propanol into a 1000 ml flask. In addition, 750 ml isomeric xylene was added. The solvent mixture was well mixed and transferred to a storage bottle where 17 g of paraformaldehyde was added. To ensure that the paraformaldehyde was dissolved in the solvent mixture the storage bottle was well shaken before every use. 10 g sample was weighted into the titration vessel and 30 ml solvent was added. The sample mixture was then titrated with KOH in 2-propanol [0.1 mol/L)] until the endpoint was reached. Between each sample and after every sample series the thermoprobe was immersed in two different titration vessels containing 2-propanol. The stirring times were 15 and 10 s respectively.

Settings in accordance with Metrohms version of ASTM D8045 can be seen in table 3.6. Settings for parameters marked with * remained unchanged throughout the whole investigation of thermometric titration. Stop volume was changed dependent on the assumed titrant consumption.

Tabell 3.6. Parameters and settings for thermometric titration in accordance with ASTM D8045.

Parameter	**Setting**
* Mode	DET U
*Pause	30 s
*Stirrer rate	15
Dosing rate	2 mL/min
* Filter factor	60
* Damping until	0,2 mL
* Stop slope	Off
Stop volume	2,5 mL
* Added volume after stop	0,5 mL
* Evolution start	0,0 mL
* End points	Ex (exothermic)
* EP criterion	-5

Parameters changed in attempt to generate accurate TAN values were:

- Titrant
- Titrant concentration
- Sample mass
- Dosing rate
- Solvent composition
- Solvent volume
- Amount of paraformaldehyde
- Pause

In table 3.7 different parameter and setting combinations tested can be seen. Parameters and settings not stated in table 3.7 were in accordance with ASTM D8045. KOH was used as titrant for every analysis.

Tabell 3.7. Values of TAN obtained for ETO 2380 when different parameters and settings were tested using KOH as titrant

Test	Sample mass [g]	Amount of paraformaldehyde [g]	Solvent volume [mL]	Dosing rate [mL/min]	Titrant conc. [M]	Paus [s]
1	10	0.5	30	2	0.1	30
2	20	0.5	30	2	0.1	30
3	20	1.0	60	2	0.1	30
4	20	1.0	30	2	0.1	30
5	20	1.0	30	0.2	0.1	30
6	20	-	30	2	0.1	30
7	-	0.5	30	2	0. 1	30
8	20	0.5	30	2.5	0.1	30
9	20	0.5	30	2	0.1	30
10	20	0.5	30	1	0.1	30
11	10	0.5	30	1	0.01	30
12	10	0.5	30	2	0.01	30
13	20	0.5	30	1	0.1	60
14	20	0.5	50	1	0.1	60
15	20	0.5	50	1	0.1	30

Combinations of solvent and titrant tested in addition to the one specified in ASTM D8045 can be seen in table 3.8. Remaining parameters and settings were in accordance with ASTM D8045.

Tabell 3.8. Values of TAN obtained for ETO 2380 when different parameters and settings were tested using KOH as titrant

Test	Sample mass [g]
KOH	Toluene/2-propanol (3:1)
TBAOH	Toluene/2-propanol (3:1)
TBAOH	2-propanol

3.2.4 Procedure for test series of new ETO 2380

Final parameters and settings for the analysis of test series of new ETO 2380 can be seen in table 3.9. Eight series were analyzed with ten oil samples in each series. A doublet of TAN standard were analyzed before the analysis every new day. The thermoprobe was rinsed in 2-propanol between every sample.

Tabell 3.9. Final parameters an settings for the test series of new ETO 2380

Titrant	TBAOH [0.1 M]
Titrant concentration	0.1 M
Sample mass	10 mL
Dosing rate	2.5 mL/min
Solvent composition	2-propanol
Solvent volume	30mL
Pause	30s

3.2.5 Procedure for used ETO 2380

Regarding the procedure for used ETO 2380 the samples were titrated with both KOH [0.1 M] and TBAOH [0.1 M]. The mass used for samples with an assumed TAN below 1 mg KOH/g was 10g and the mass used for samples with assumed TAN above 1 mg KOH/g was 5g. Dosing rate, solvent volume and pause were in accordance with table 3.9.

3.3 Fourier Transform Infrared Spectroscopy

Both ATR FT-IR and transmission FT-IR were used in order to analyze the samples of the new and used oils. A background spectrum was collected for each FT-IR technique before sample analysis. The background spectrum used for respectively technique used the same settings as for the sample analysis. A new background spectrum were collected every second hour.

3.3.1 Attenuated Total Reflectance Infrared Spectroscopy

Since ATR-FTIR requires no sample preparation the sample was pipetted directly on the crystal. The crystal was cleaned with ethanol and Kleenex® before and after every sample. The sample to be analyzed were shaken in the storage container before pipetted onto the crystal.

3.3.2 Apparatus and settings

The settings used for the ATR FT-IR measurements were in accordance with the settings appropriate for liquids recommended by the OMNIC ™ software.

Tabell 3.10. Apparatus and settings for ATR FT-IR

Parameter	**Settings**
Detector	DTGS KBr
Beamsplitter	KBr
Crystal	Dimond
Accessory	Smart OMNI-ATR
Range	4000-625 cm^{-1}
Resolution	4 cm^{-1}
Number of scans	32
Cleaning agent for diamond	Ethanol

3.3.3 Transmission FT-IR

For the Transmission FT-IR a SmartSeal liquid cell with Teflon stoppers was used. The liquid transmission cell used had a pathlength of 0.025 mm and a volume of 0.012 ml. Before the samples were collected a background was collected. The background was then collected once each 120 minutes. The background spectrum was collected by placing the liquid transmission cell without sample and Teflon stoppers in the instrument.

The sample was injected in the liquid cell with two glass syringes with a volume of 2 mL. One of the syringes was filled with sample while the remaining one was kept empty. The empty syringe was placed in the left luer lock connector and the syringe with the sample was placed in the right one. After both syringes were attached to the liquid cell the cell was tilted 45^o. The sample was then transferred into the liquid cell by pulling the empty syringe creating a vacuum. The liquid cell was sealed with the teflon stoppers and then placed in the FT-IR transmission sample holder. Settings for transmission FT-IR measurements can be seen in table 3.11.

Tabell 3.11. Apparatus and settings for Transmission FT-IR

Parameter	**Settings**
Detector	DTGS KBr
Beamsplitter	KBr
Window	NaCl
Accessory	Smart OMNI-Transmission
Range	4000-625 cm^-1
Resolution	4 cm^-1
Number of scans	32
Recommended cleaning agent for NaCl	Anhydrous solvent

4 Results and discussion

Following section will contain the results obtained for test series of new and used ETO 2380 samples for both potentiometric and thermometric titration. It will also contain an evaluation and comparison of both titration methods. Results and discussion of the FT-IR analysis will be preformed as well.

4.1 Potentiometric titration

The results for all sample series preformed can be sen in Appendix A. Obtained values of TAN standard were for all analysis within the specified limits. The results for TAN values when parameters and settings were in accordance with ASTM D664 varied between 0.60 mg KOH/g to 0.66 mg KOH/g for all 10 test series. Compared to 0.43 mg KOH/g this is relatively high. However, the predetermined TAN was determined in accordance with another ASTM standard which can be the reason for the difference in TAN. The highest ant the lowest obtained TAN only differed 0.06 mg KOH/g indicating a robust and reliable method. In table 4.1 mean values and standard deviation of each series can be seen.

Tabell 4.1. Mean values of TAN for each series in accordance with parameters and settings for ASTM D664.

Series number	**Mean value TAN [mg KOH/g]**	**Standard deviation**
1	0,63	0,018
2	0,65	0,005
3	0,62	0,004
4	0,63	0,005
5	0,63	0,007
6	0,68	0,053
7	0,64	0,006
8	0,64	0,011
9	0,64	0,036
10	0,63	0,005

TAN values obtained for the 10 test series using parameters and setting in accordance with optimization 1 were also obtained in the range between 0.6-0.66 mg KOH/g indicating that 2-propanol can be used as solvent instead of the toluene/2-propanol/water mixture. In table 4.2. the mean value of TAN and standard deviation of each series can be seen.

Tabell 4.2. Mean values of TAN for each series, optimization 1

Series number	**Mean value TAN [mg KOH/g]**	**Standard deviation**
1	0,62	0,018
2	0,	0,005
3	0,63	0,004
4	0,64	0,005
5	0,65	0,007
6	0,62	0,053
7	0,63	0,006
8	0,64	0,011
9	0,63	0,036
10	0,62	0,005

Regarding optimization 2 the results received were very similar to previously received results. Mean values and standard deviation for each series and mean standard deviation can be seen in table 4.3.

Tabell 4.3. Mean values of TAN for each series, optimization 2

Series number	**Mean value TAN [mg KOH/g]**	**Standard deviation**
1	0,63	0,018
2	0,63	0,005
3	0,63	0,004
4	0,65	0,005
5	0,65	0,007
6	0,63	0,053
7	0,62	0,006
8	0,59	0,011
9	0,59	0,036
10	0,60	0,005

Except for some outliars the the values obtained for all sample series preformed with potentiometric titration showed results with low standard deviation for each series indicating good repeatability. Depending on the amount of KOH that is consumed for the blank the result will generate minor differences in TAN. In table 4.4. There is a demonstration of what happens if the volume of titrant is remaining the same while the blank value varying from 0.04 to 0.1.

Tabell 4.4. Variation of TAN depening on blank value

Blank [ml]	TAN [mg KOH/g]
0,040	0,651
0,045	0,648
0,050	0,645
0,055	0,642
0,060	0,640
0,065	0,637
0,070	0,634
0,075	0,631
0,080	0,628
0,085	0,626
0,090	0,623
0,095	0,620
0,100	0,617

The results for the mean value of TAN obtained for rig 74, 130 and 139 can be seen in table 4.5.

Tabell 4.5. Values of TAN obtained for rig 74, 130 and 139 analyzed with potentiometric titration

Rig	Sample number	TAN (mg KOH/g)
74	1	7,15
74	2	7,28
74	3	7,73
74	4	0,76
74	5	-
74	6	0,84
130	1	8,30
130	2	-
130	3	-
130	4	0,93
130	5	0,93
130	6	0,82
139	1	4,17
139	2	4,04
139	3	4,35
139	4	0,77
139	5	0,79
139	6	0,76

4.2 Thermometric titration

Before the start of thermometric titration the values of TAN were predicted to be similar to the values obtained by the potentiometric titration. ASTM D8045 by ASTM International is developed for complex oils to dissolve however it is also written for analysis preformed manually. Analysis in this report were preformed automatically only, leading to apparatus settings were based on Metrohms version of ASTM D8045. The thermometric titration were originally supposed to be preformed in accordance with ASTM D8045 as a first step, however the method needed to be modified at the very beginning in order to achieve accurate values. Compared to potentiometric titration the thermometric titration required several tests and modifications of parameters before test series of new ETO 2380 could be preformed.

According to ASTM D8045 by ASTM International, no blank determination is required if less than the recommended sample mass is used. However, when following ASTM D8045 according to Methrom, there is no indication that a blank determination would not be required. Since Methroms version of D8045 is assigned to automatic titration and the sample mass recommend is 3-9 g instead of 10-20g the decreased sample mass used in Metrohms version of ASTM D8045 could be a possible explanation for requiring a blank determination. The sample mass used for all analysis were within the recommended interval according to ASTM D8045 by ASTM International and no blank determination was preformed.

4.2.1 Acid Number Standard (AN) determination

Several different sample masses were tested for the analysis of the Acid number standard. Both 3g and 6g resulted in very low TAN and titration curves without inflections points indicating an increase in sample mass was required. The sample mass interval recommended by Methroms version of ASTM D8045 could not be used. Since the sample mass in ASTM D8045 by ASTM International is 10-20 g for TAN below 1 mg KOH/g, 20 g sample was tested. When the sample mass was increased from 10 g to 20 g a titrant volume of 1.76 mL was consumed resulting in 0.49 mg KOH/g, which is in the 0.5 mg KOH/g ± 0.07 interval. The sample mass was decreased to 10 g as an attempt to minimize chemical waste resulting in a TAN within the accepted interval for the TAN standard. The sample mass used for the TAN standard analysis was therefore 10 g for the remaining tests.

4.2.2 Optimization of D8045 for ETO 2380

In table 4.6 a list of parameters and settings changed in order to receive similar values to potentiometric titration can be seen and the TAN they resulted in. When the parameters and settings were in accordance with ASTM D8045 from ASTM International, test 1. the value obtained was much lower compared to those obtained for the potentiometric titration. It was also significantly lower than the predetermined value, 43 mg KOH/g. Since the sample mass tested was the lowest required according to ASTM D8045 by ASTM International the sample mass was increased to 20 g, resulting in almost the same value as for 10 g of sample, test 2.

Since ASTM D8045 originally is developed for different kinds of oils than lubricating oils it was discussed if the amount of paraformaldehyde could affect the results. However, the the increase in amount of paraformaldehyde did not increase the TAN, test 4. It was also discussed if the dosing rate of the titrant could affect the result. A dosing rate of 0.2 mL/min was tested, test 5 and a dosing rate of 2.5 mL/min, test 8. No increase in TAN was observed. Since the low TAN could not be explained the remaining changes in parameters and setting in table x. were preformed as an attempt to achieve values closer to those obtained with potentiometric titration.

Tabell 4.6. Values of TAN obtained for ETO 2380 when different parameters and settings were tested using KOH as titrant

Test	**Sample mass [g]**	**Amount of paraformaldehyde [g]**	**Solvent volume [mL]**	**Dosing rate [mL/-min]**	**Titrant conc. [M]**	**Paus [s]**	**TAN [mg KOH/g]**
1	10	0.5	30	2	0.1	30	0.25
2	20	0.5	30	2	0.1	30	0.29
3	20	1.0	60	2	0.1	30	0.24
4	20	1.0	30	2	0.1	30	0.22
5	20	1.0	30	0.2	0.1	30	0.03
6	20	-	30	2	0.1	30	invalid
7	-	0.5	30	2	0. 1	30	0.12
8	20	0.5	30	2.5	0.1	30	0.15
9	20	0.5	30	2	0.1	30	0.23
10	20	0.5	30	1	0.1	30	0.20
11	10	0.5	30	1	0.01	30	0.16
12	10	0.5	30	2	0.01	30	0.18
13	20	0.5	30	1	0.1	60	0.21
14	20	0.5	50	1	0.1	60	0.18
15	20	0.5	50	1	0.1	30	0.19

Almost all tests resulted in a TAN around 0.2 mg KOH/g independent of the parameters and settings changed. This was assumed to be non-accurate values since it is a much lower value than both the predetermined value (0.43 mg KOH/g) and the values obtained using the potentiometric titration. Since all changes of parameters and settings resulted in lower values than expected it was assumed that either the solvent or the titrant were the problem. The exchange of solvent mixture from xylene/2-propanol to toluene/2-propanol using KOH as titrant resulted in 0.25 mg KOH/g. However, when changing the titrant to TBAOH the TAN received was 0.64 mg KOH/g. Changing the solvent to 2-propanol instead of toluene/2-propanol resulted in a similar value. Test series of new ETO 2380 with TBAOH as titrant and 2-propanol as solvent were therefore preformed. The dosing rate were also increased from 2 mL/min to 2.5 mL/min in order to decrease the analysis time.

4.2.3 Test series of new ETO 2380

The results for all sample series of new ETO 2380 using thermometric titration can be seen in Appendix B. In table 4.7 the mean value of TAN for each series can be seen together with the standard deviation for each series. All series except for one resulted in a mean TAN of 0.63 mg KOH/g, which is in agreement with the results for potentiometric titration.

Tabell 4.7. Mean values of TAN and standard deviation of each series of new ETO 2380

Series number	**Mean value TAN [mg KOH/g]**	**Standard deviation**
1	0,63	0,000
2	0,64	0,014
3	0,63	0,003
4	0,63	0,006
5	0,63	0,000
6	0,63	0,000
7	0,63	0,004
8	0,63	0,005

4.2.4 Thermometric titration of used ETO 2380

According to ASTM D8045 by ASTM International the sample mass used for predicted TAN of 5 mg KOH/g and higher are 1g. Since the sample mass used for the test series of pure oil was 10 g a test series of oil samples with a much higher TAN, rig 130 (sample number 1), were analyzed using a sample mass of 1 g. The results can be seen in table 4.8.

Tabell 4.8. ETO 2380 samples from rig 130 (sample numer 1) where 1g of sample was used.

Test	**TAN [mg KOH/g]**
1	8,81
2	8,65
3	8,67
4	8,74
5	8,70
6	8,69
7	8,84
8	8,69
9	8,81
10	8,69
11	8,79
Standard deviation	0,066

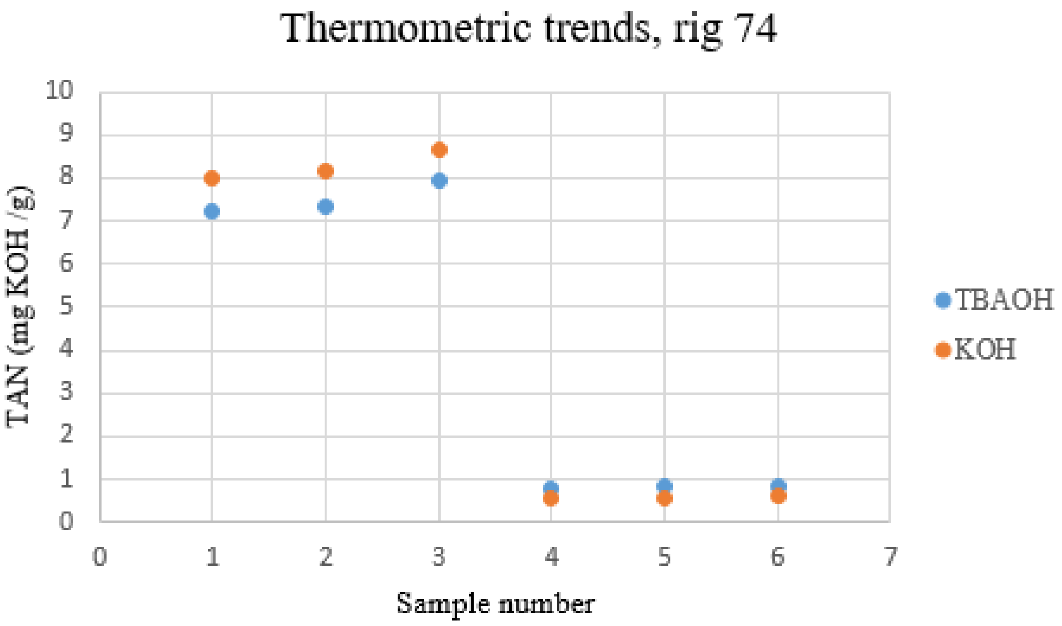
The standard deviation obtained were higher than for all series in table 4.7. Since it is known that more similar values can be obtained for oils with lower TAN the sample mass for predicted TAN of 5.0 mg KOH/g were increased to 5g.

In table 4.9 the results from the analysis of the oil samples from rig 74, 130 and 139 can be seen. The table contains the result for when both TBAOH and KOH were used as titrant. Even if it was previously stated that KOH generates lower TAN than expected the analysis preformed in order to investigate if more similar values could be obtained for oils with higher TAN. The sample mass used for TAN below 1 mg KOH/g was 10 g while the sample mass used for TAN above 1 mg KOH/g was 5g. Note that each value is a mean value for every sample number and the extended table can be seen in table B.9 in Appendix B.

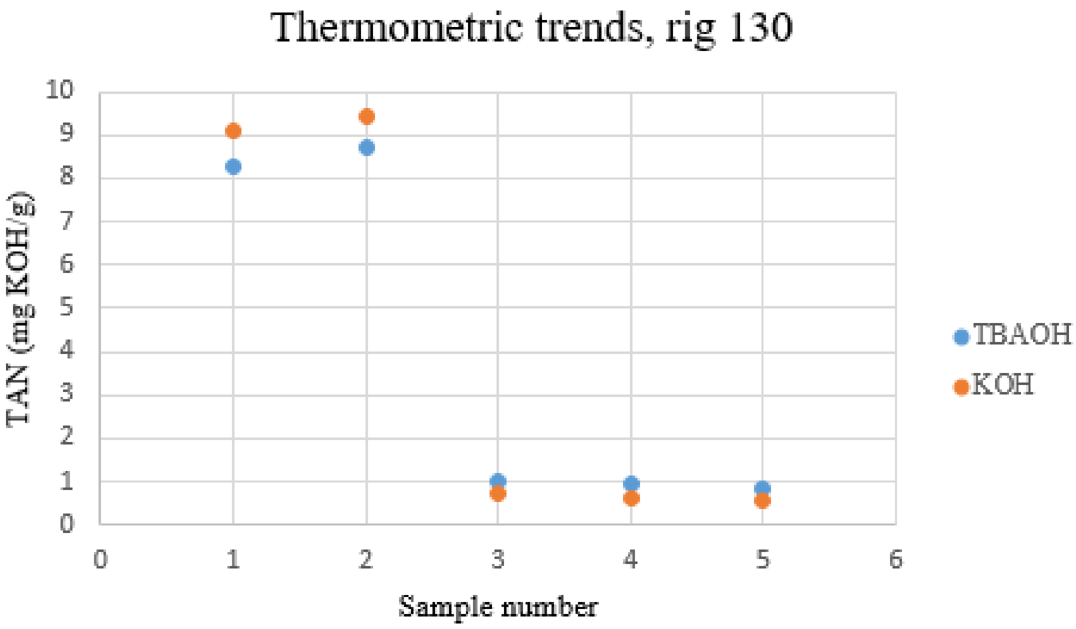
Tabell 4.9. Values of TAN obtained for rig 74, 130 and 139 analyzed with both TBAOH and KOH as titrant

Rig	Sample number	TAN, TBAOH [mg KOH/g]	TAN, KOH [mg KOH/g]
74	1	7,230	7,993
74	2	7,363	8,177
74	3	7,955	8,675
74	4	0,770	0,545
74	5	0,84	-
74	6	0,815	0,605
130	1	8,277	9,213
130	2	8,72	9,42
130	4	0,99	0,745
130	5	0,935	-
130	6	0,830	0,550
139	1	4,300	4,727
139	2	4,140	4,59
139	4	0,785	0,555
139	5	0,795	-
139	6	0,755	0,540

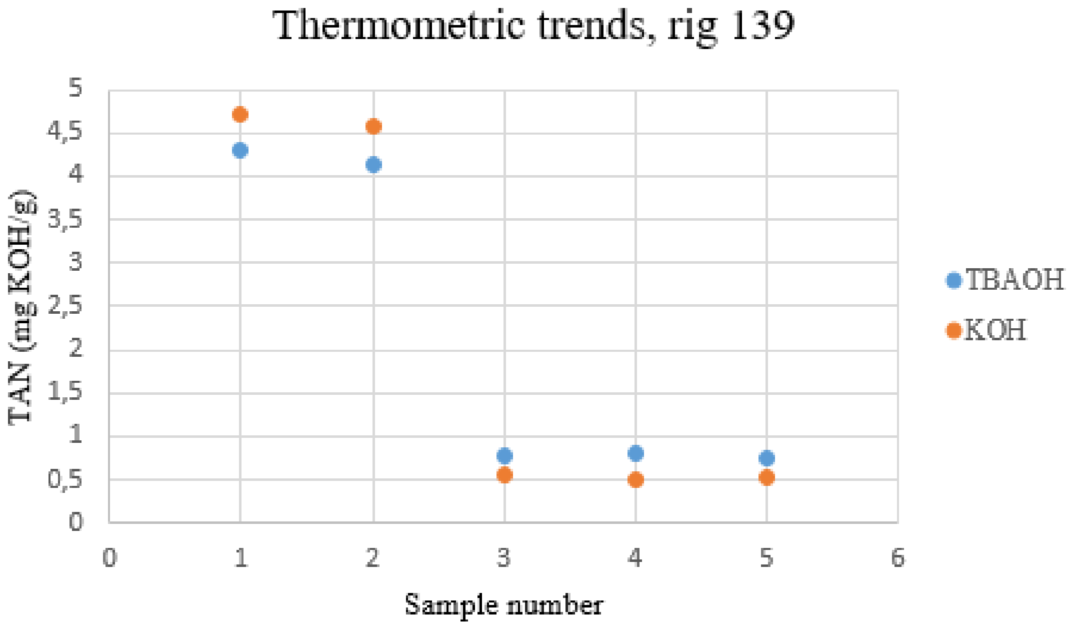
When comparing the results from using different titrants especially two trends were obtained. For high TAN, over 1 mg KOH/g, the values received using TBA-OH as titrant were lower compared to the values obtained when KOH was used. However, for lower TAN, below 1 mg/KOH, values obtained using TBAOH were higher than for titration with KOH. These trends were obtained for all three rigs and can be seen in figure 4.1, 4.2 and 4.3.



Figur 4.1. Thermometric trends obtained for rig 74 comparing TBAOH and KOH



Figur 4.2. Thermometric trends obtained for rig 130 comparing TBAOH and KOH



Figur 4.3. Thermometric trends obtained for rig 139 comparing TBAOH and KOH

A possible explanation for these trends can be that some acidic species cannot be detected using KOH as titrant if the concentration of these species is to low. Note that since most of the samples have a TAN below 1 mg KOH/g or around 7 mg KOH/g it is impossible to predict in which TAN KOH will result in higher values than TBAOH.

For rig 130 and 139 TAN decreases with time for sample number 4, 5 and 6. This might indicate a depletion of the additives which will decrease the initial TAN before the oil starts to oxidize. However, the oils with sample number 1-4 has been stored for several months before analyzed which could have affected the TAN. To be able to investigate these trends in a more accurate way further analysis of samples from the the three rigs are required. These samples need to be analyzed immediately after collection and over a longer period of time in order to rule out possible errors and deviations due to storage.

4.3 Potentiometric versus thermometric titration

The comparison between potentiometric and thermometric titration will be preformed with respect to the latest optimization of each method. The methods will therefor not be compared fully in accordance with their respectively ASTM standard. Using potentiometric titration in order to determining TAN based on ASTM D644 is method that is well tested over the years. ASTM D664 is also developed for lubricating oils among others compared to ASTM which is developed for crude oils, waxes and bitumen. With this in mind the TAN obtained with potentiometric titration (around 0.63 mg KOH/g) were assumed to be more correct than TAN obtained using KOH as titrant with thermometric titration (around 0.2 mg KOH/g).

Thermometric titration is a more complex titration method than potentiometric titration and minor changes in parameters and settings will affect the outcome of the result in higher extent compare to potentiometric titration.

Comparing the results from the test series of new ETO 2380 both methods generated values around 0.63 mg KOH/g with a low standard deviation. However, the values obtained for thermometric titration resulted in general in a lower standard deviation for each series. A possible a explanation for this can be the effect of the blank determination for potentiometric titration. The comparison of the results received from the analysis of the oils from the different rigs can be seen in table 4.10.

Tabell 4.10. TAN obtained for rig 74, 130 and 139 analyzed with thermometric titration (TET) and potentiometric titration (POT)

Rig	**Sample number**	TET (TBAOH)	TET (KOH)	POT (TBAOH)
74	1	7,23	7,99	7,15
74	2	7,36	8,18	7,28
74	3	7,955	8,66	7,73
74	4	0,77	0,545	0,76
74	5	0,84	-	-
74	6	0,81	0,55	0,84
130	1	8,28	9,21	8,30
130	2	8,72	9,41	-
130	3	-	-	-
130	4	0,99	0,754	0,93
130	5	0,935		0,931
130	6	0,830	0,550	0,819
139	1	4,30	4,73	4,17
139	2	4,14	4,59	4,04
139	3	-	5,0	4,35
139	4	0,785	0,555	0,77
139	5	0,795	-	0,788
139	6	0,755	0,540	0,757

By comparing the values obtained from thermometric titration using TBAOH with the values obtained from potentiometric titration almost all values are very similar. Regarding the values obtained from thermometric titration using KOH they were either significantly higher or lower compared to the potentiometric values. Since the thermometric values using TBAOH were so similar to the potentiometric values it was assumed that these values were more accurate than the thermometric values using KOH.

From table 4.10 it can also be seen TAN values for both thermometric and potentiometric titration are decreased for sample number 6 compared to sample number

5. This could possible be the start of additive depletion decreasing the TAN. However, further investigations of samples collected over time are required in order to confirm this hypothesis.

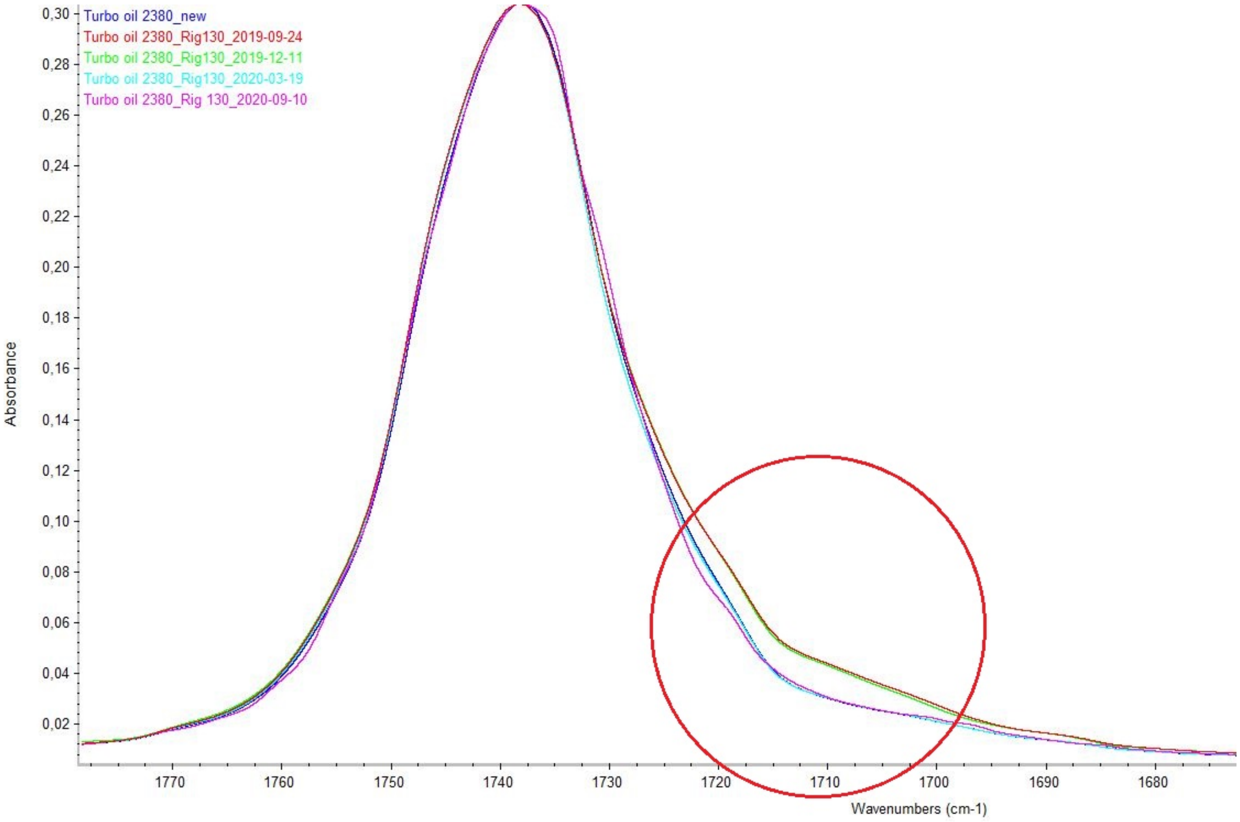
Regarding the sample preparation for potentiometric titration using only 2-propanol as solvent is very convenient since the sample preparation of thermometric titration possesses several drawbacks. The reduced amount of toxic chemicals required for the potentiometric titration is a huge advantage both in therms of human and environmental health. Since the use of an indicator is necessary in thermometric titration of oils containing weak acidic spices the use of toxic chemicals cannot be reduce as much as wanted. Further optimization potentiometric titration can also probably result in decreased amount of toluene in the rinsing/maintains steps of the pH-electrode. It is possible that potentiometric titration can be used fully without toluene making KOH and 2-propanol the only chemicals used. The decreased amount of harmful chemicals is the strongest advantage of using potentiometric titration compared to thermometric titration. However, since thermometric titration offers less preparation of the thermoprobe and a huge decrease in analysis time there is a trade-off between using a method completely or partially without chemicals compared to a method requiring almost no time to preform. Except for the weighing of the samples thermometric analysis takes only a few minutes to preform, while it takes almost over an hour to prepare the electrode and analyze blanks and TAN standard samples for potentiometric titration.

4.4 FT-IR analysis

ATR analysis were preformed as a first step due to its simple sample preparation. However, since transmission FT-IR is better for qualitatively analysis all sample were measured with transmission FT-IR as well. There were no comparison between the spectrum produces by ATR and transmission FT-IR however it was investigated if transmission FT-IR could give more information about the degradation of the oils than ATR.

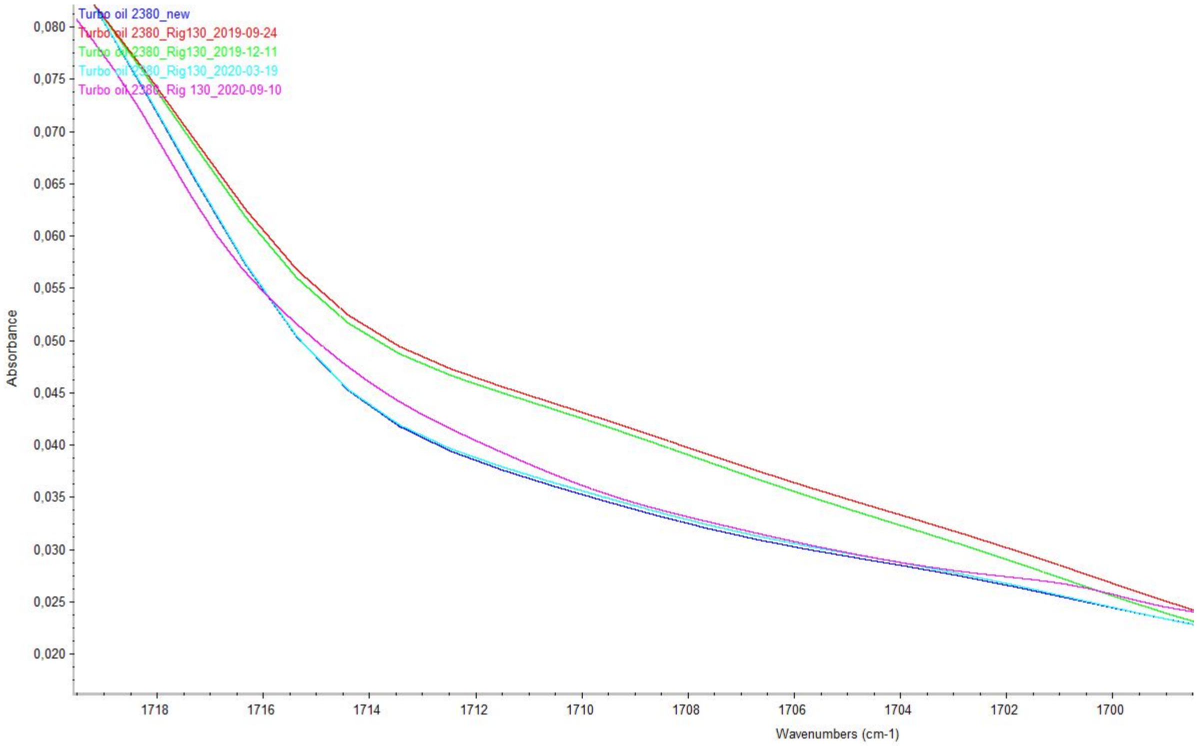
4.4.1 ATR FT-IR

In Appendix C spectrum of each sample number from respectively rig measured with ATR FT-IR can be seen. In order to see any changes in oxidation products or depletion of additives all spectrum from the same rig including the spectrum of new ETO 2380 were stacked. Since degradation of oil in general should contain oxidation of carbonyl the the area around 1700 cm^{-1} was first investigated. In figure 4.4 spectra of oils from rig 130 can be seen for the region around 1700 cm^{-1}. The green and the red spectra are oils of high TAN which are expected to contain a higher amount of carbonyl oxidation products then the oils with lower TAN. The difference in intensity between the red and green spectra and the remaining spectra is a possible indication of an increased amount of carbonyl oxidation products. This trend were observed for all three rigs. In figure 4.5 a close up of the area marked with the red ring in figure 4.4 can be seen. In figure 4.5 it can also be seen that the latest collected oil sample (sample number 6), the pink spectrum, has higher intensity than the two blue colored spectra which are the new ETO 2380 and the sample number 4. Since the oil generating the pink spectrum has been in the rig for several additional months than the oil of the light blue spectrum it is possible that carbonyl oxidation products has started to form.



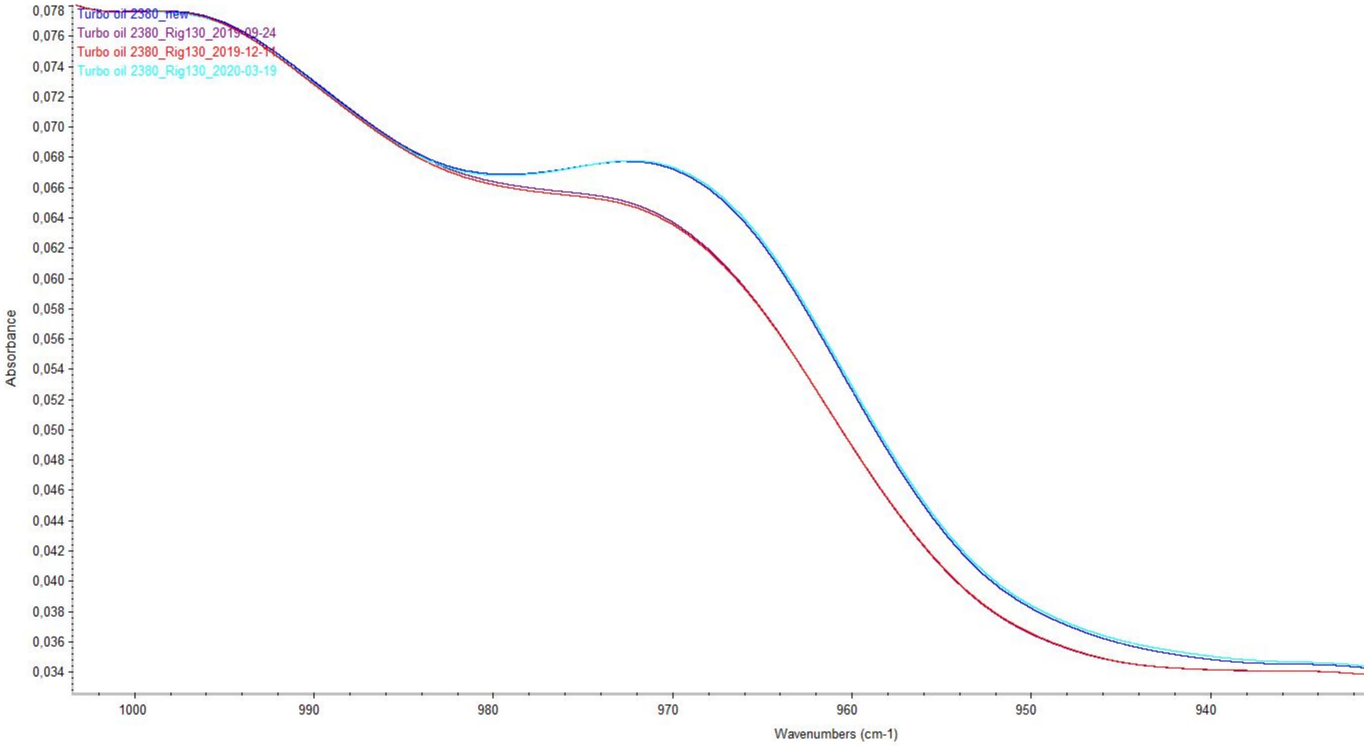
Figur 4.4. Spectra of samples from Rig 130

By observing the area around 940 cm^{-}1 where the depletion of the additive TCP should occur the red and the green spectra are below the remaining spectra, see figure 4.6. This is a possible indication of additive depletion that has occurred over time. Same trend was observed for test rig 74 and 139. Depletion of the remaining additives requires further analysis of the spectra.



Figur 4.5. Spectra of samples from Rig 130 measured with ATR FT-IR

Further investigation was proceeded by subtracting spectrum of pure Turbo oil 2380 from some of the oil samples, sample number 1,2 and 4. The remaining spectra were then searched through a library of already analyzed compounds within the software. The results of the search can be seen in table 4.11. Since the database of compounds are based on samples/compounds that have been analyzed before there is a possibility that there exists compounds outside the database that fits the results better. The library search was only used to get an indication of possible compounds.



Figur 4.6. Spectra of samples from Rig 130 measured with ATR FT-IR

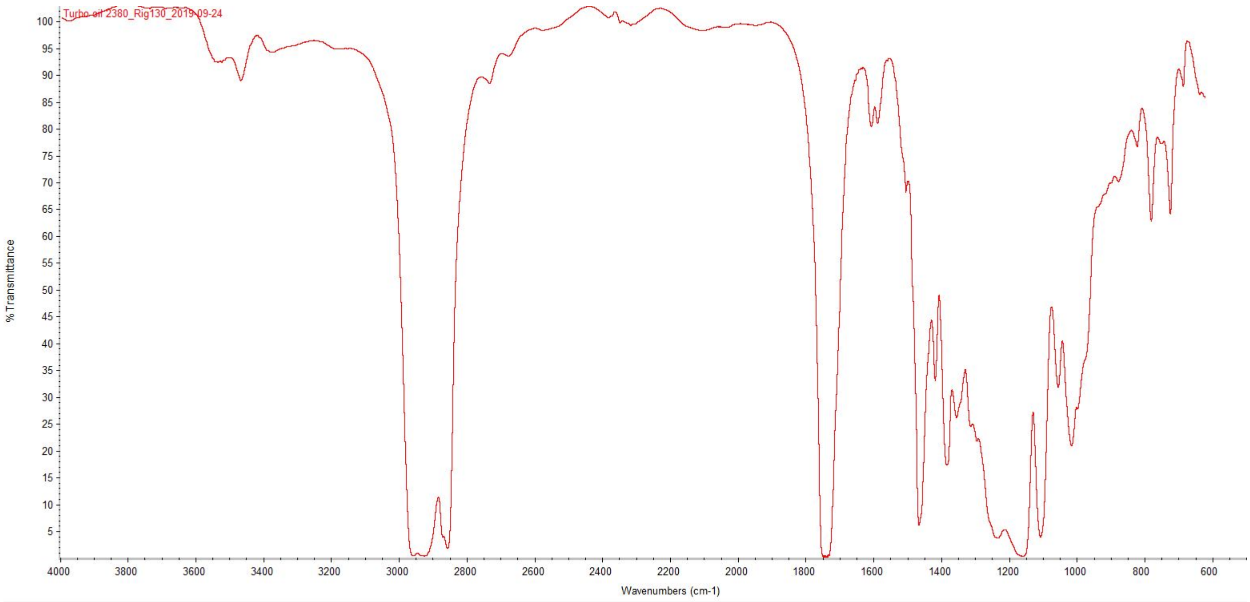
Tabell 4.11. Remaining compounds after subtraction of pure Turbo oil 2380 spectrum

Rig	Sample number	Compound
74	1	Octanoic acid
74	2	Octanoic acid
74	4	Methyl laurate
130	1	Octanoic acid
130	2	Octanoic acid
130	4	Methyl laurate
139	1	Syntehtic Motor oil
139	2	CO_2
139	4	Methyl laurate

The results for rig 74 and 130 showed the exact same compounds. By analyzing the composition of octanoic acid ($C_8H_{16}O_2$) compared to methyl laurate ($C_{13}H_{26}O_2$) the two compounds have a very similar structure. Both compounds consists of a long carbon chain, however octanoic acid contains a carboxylic group and methyl laurate contains an ester group. Both the ester group and the carboxylic group are mentioned as oxidation products of degradation of lubricating oils. It is difficult to relate the two compounds to each other with respect to degradation of the oil since these compound matches are based only based on pre-analyzed compounds. It is also difficult to draw any conclusions about the results for sample number 1 and 2 for rig 139.

4.4.2 Transmission FT-IR

The results from the Transmission FT-IR analysis of pure ETO 2380 and the ETO 2380 samples from the different test rigs gave no further information about the degradation process or the change in TAN. In figure 4.7 an example of the spectrum obtained using Transmission FT-IR can be seen. The broad flattered peak around 2900 cm $^{-1}$ indicates that the path length is to small.



Figur 4.7. Spectrum of sample number 1 from Rig 130 measured with transmission FT-IR

5 Future prospects

Further work should include optimization of thermometric titration since it is a simple and fast analysis technique. It should be prioritized to investigate if paraformaldehyde could be exchanged to another less harmful indicator.

Since the comparison of the potentiometric and thermometric titration was the main focus less time was assigned to the FT-IR analysis. Further analysis of the spactra and the depletion of the remaining additives should be preformed. FT-IR analysis of oil samples from the test rigs should also be preformed over a longer period of time for further monitoring of the degradation process. Since the the limitation for ETO 2380 is 1.0 mg KOH/g it would be interesting to analyze oil samples with a TAN close to 1 mg KOH/g, both below and above.

6 Conclusion

Both potentiometric and thermometric titration can be used in order to measure TAN in new and used samples of ETO 2380. The use of potentiometric titration generated very similar values both in accordance with ASTM D664 and for the optimizations preformed. The decrease in use of toxic chemicals is a huge advantage for the use of potentiometric titration. However, the preparation of the electrode required and the analysis time is a major drawback. Regrading the thermometric titration KOH and TBAOH generated different TAN where the TAN received using TBAOH were almost the same as those obtained for potentiometric titration.

The results from the FT-IR analysis indicated an increase of carbonyl oxidation products and a possible depletion of the additive TCP. The use of transmission FT-IR gained no further information compared to ATR FT-IR. In order to be able to monitor the degradation of the oil using FT-IR further analysis of oil samples from the rigs are required.

Referenser

[1] Aviation Pros. Advancements In Turbine Engine Oils. [online] Available at: https://www.aviationpros.com/engines-components/aircraft-engines/turbine-engines-parts/article/12196059/advancements-in-turbine-engine-oils.

[2] Energyeducation.ca. Lubricating Oil - Energy Education. [online] Available at: https://energyeducation.ca/encyclopedia/$Lubricating_oil.

[3] Eastman.com. Turbo Oils | High Performance Capability | Eastman. [online] Available at: https://www.eastman.com/Markets/Energy/Lubricants/Pages/High-Performance-Capability.aspx.

[4] Eastman.com. Eastman | Turbo Oil 2380. [online] Available at: https://www.eastman.com/Pages/ProductHome.aspx?product=71097793.

[5] Standards.globalspec.com. 2018. ASTM - D7414 - Standard Test Method For Condition Monitoring Of Oxidation In In-Service Petroleum And Hydrocarbon Based Lubricants By Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry | Engineering360. [online] Available at: https://standards.globalspec.com/std/10285507/ASTM%20D7414.

[6] ASTM D8045: New, superior method for Acid Number determination in crude oil and petroleum products | Metrohm [Internet]. Metrohm.com. 2020 [cited 12 May 2020]. Available from: https://www.metrohm.com/en/company/news/news-acid-number-thermometric-titration-astm-d8045/

[7] GKN. n.d. GKN Aerospace I Sverige. [online] Available at: https://www.gknaerospace.com/en/about-gkn-aerospace/locations/gkn-aerospace-in-europe/gkn-aerospace-in-sweden/.

[8] Turbo Oil 2380 Aircraft-type gas turbine lubricant [Internet]. Msdspds.bp.com. 2020 [cited 8 May 2020]. Available from: https://msdspds.bp.com/bpglis/FusionPDS.nsf/Files/802577040037FB4B80257AD800035A64/$File/BPXE-92RGEV.pdf

[9] Astm.org. n.d. ASTM D664 - 18E2 Standard Test Method For Acid Number Of Petroleum Products By Potentiometric Titration.

[10] MANTECH-INK.com. 2016. Application Note 67 – Total Acid Number (TAN). [online] Available at: https://mantech-inc.com/wp-content/uploads/2016/07/67-Total-Acid-Number-TAN.pdfochStandard.

[11] Garry, M. and Bowman, J., 2007. FT-IR Analysis Of Used Lubricating Oils – General Considerations. [online] Tools.thermofisher.com. Available at: http://tools.thermofisher.com/content/sfs/brochures/AN-50731-FT-IR-Analysis-of-Used-Lubricating-Oils-General-Considerations.pdf.

[12] SPARKS R. NON-AQUEOUS POTENTIOMETRIC TITRATIONS OF WEAK ACID [Internet]. Ttu-ir.tdl.org. 1969. Available from: https://ttu-ir.tdl.org/bitstream/handle/2346/17311/31295015504672.pdf;sequence=1

[13] Nguele R, Said Al-Salim H, Mohammad K. Modeling and Forecasting of Depletion of Additives in Car Engine Oils Using Attenuated Total Reflectance Fast Transform Infrared Spectroscopy [Internet]. www.mdpi.com/journal/lubricants. 2014. Available from: https://www.researchgate.net/publication/307682089_Modeling_and_Forecasting_of_Depletion_of_Additives_in_Car_Engine_Oils_Using_Attenuated_Total_Reflectance_Fast_Transform_Infrared_Spectroscopy

[14] Guide to Measuring Oil Chemistry: Nitration, Oxidation and Sulfation [Internet]. Spectrosci.com. 2017. Available from: https://www.spectrosci.com/resource-center/lubrication-analysis/literature/e-guides/guide-to-measuring-oxidation-nitration-and-sulfation-in-oil/

[15] Luiz, J.F., Spikes, H. Tribofilm Formation, Friction and Wear-Reducing Properties of Some Phosphorus-Containing Antiwear Additives. Tribol Lett 68, 75 (2020). https://doi.org/10.1007/s11249-020-01315-8

[16] Osei-Agyemang, E., Berkebile, S. Martini, A. Decomposition Mechanisms of Anti-wear Lubricant Additive Tricresyl Phosphate on Iron Surfaces Using DFT and Atomistic Thermodynamic Studies. Tribol Lett 66, 48 (2018). https://doi.org/10.1007/s11249-018-0998-x

[17] Acid Number: A Comprehensive Guide. Machinerylubrication.com. Available from: https://www.machinerylubrication.com/Read/1052/acid-number-test

[18] ARP5088: Test Method for the Determination of Total Acidity in Polyol Ester and Dieseter Gas Turbine Lubricants by Automatic Potentiometric Titration - SAE International. Sae.org. Available from: https://www.sae.org/standards/content/arp5088/

[19] 2,4,4-Trimethyl-1-pentene. Pubchem.ncbi.nlm.nih.gov. Available from: https://pubchem.ncbi.nlm.nih.gov/compound/2_4_4-Trimethyl-1-pentene#section=Uses

[20] N-Phenyl-1-naphthylamine. Pubchem.ncbi.nlm.nih.gov. Available from: https://pubchem.ncbi.nlm.nih.gov/compound/7013#section=Uses

[21] Diphenylamine. Pubchem.ncbi.nlm.nih.gov. 2020 [cited 18 November 2020]. Available from: https://pubchem.ncbi.nlm.nih.gov/compound/11487#section=Uses

[22] Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry. ASTM INTERNATIONAL. 2018.

[23] Hulanicki A, Głąb S. Potentiometric. Sciencedirect.com. 2005. Available from: https://www.sciencedirect.com/sdfe/pdf/download/eid/3-s2.0-B0123693977006269/first-page-pdf

[24] Potentiometric Titration - Principle, Formula, Procedure, Types and Application [Internet]. Vedantu.com. Available from: https://www.vedantu.com/chemistry/potentiometric-titration

[25] Vaughan G. Thermometric and enthalpimetric titrimetry [by] G.A. Vaughan. London: Van Nostrand-Reinhold; 1973.

[26] 17e1 A. ASTM D8045 - 17e1 Standard Test Method for Acid Number of Crude Oils and Petroleum Products by Catalytic Thermometric Titration. Astm.org. 2018. Available from: https://www.astm.org/Standards/D8045.htm

[27] Determination of the Acid Number (TAN) Tips and Tricks. Mt.com. Available from: https://www.mt.com/dam/LabDiv/Campaigns/Chemistry2013/petrochemistry/downloads/4_determination_acid_number_EN.pdf

[28] Tetrabutylammonium Hydroxide | TBAH | CAS 2052-49-5. SACHEM, Inc. Available from: https://www.sacheminc.com/chemicals-by-category/tetrabutylammonium-hydroxide-tbah/

[29] Christensen E, Ferrell J, Olarte M, Padmaperuma A, Lemmon T. Acid Number Determination of Pyrolysis Bio-oils using Potentiometric Titration. Nrel.gov. Available from: https://www.nrel.gov/docs/fy16osti/65890.pdf

[30] Omnic Specta Software. Thermo Fisher Scientific.

[31] FT-IR Spectroscopy Basics. Bruker.com. Available from: https://www.bruker.com/products/infrared-near-infrared-and-raman-spectroscopy/ftir-basics.html

[32] Borin A, Poppi R. Multivariate quality control of lubricating oils using Fourier transform infrared spectroscopy. Scielo. 2004. Available from: https://www.scielo.br/scielo.php?pid=S0103-50532004000400020&script=sci_arttext&tlng=en

[33] FTIR Analysis of In-Service Lubricating Oil [Internet]. AZO MATERIALS. 2019. Available from: https://www.azom.com/article.aspx?ArticleID=18316

[34] File:ATR path-en.svg - Wikimedia Commons [Internet]. Commons.wikimedia.org. 2020 [cited 5 May 2020]. Available from: https://commons.wikimedia.org/wiki/File:ATR_path-en.svg

[35] Bradley M. Pathlength Considerations With ATR Sampling in FTIR [Internet]. Labcompare.com. 2020 [cited 5 May 2020]. Available from: https://www.labcompare.com/10-Featured-Articles/352695-Pathlength-Considerations-With-ATR-Sampling-in-FTIR/

A Appendix

Table A.1-A.10 show the result of potentiometric titration of Turbo oil 2380 in accordance with ASTM D664. Table A.1 shows the blank values measured for each sample series used for calculating the TAN values. All samples of Turbo oil 2380 are from the same batch.

Tabell A.1. Samples of Turbo oil 2380 analyzed 2020-05-07

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.22	0.62
2	1.23	0.63
3	1.19	0.61
4	1.20	0.61
5	1.26	0.64
6	1.24	0.63
7	1.26	0.65
8	1.29	0.66

Tabell A.2. Samples of Turbo oil 2380 analyzed 2020-05-11

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1,24	0,65
2	1,24	0.65
3	1,25	0.65
4	1.24	0.65
5	1.25	0.65
6	1.25	0.65
7	1.26	0.66
8	1.26	0.66

Tabell A.3. Samples of Turbo oil 2380 analyzed 2020-05-12

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1,19	0,62
2	1,19	0.62
3	1,19	0.62
4	1.21	0.63
5	1.20	0.63
6	1.19	0.62
7	1.20	0.63
8	1.20	0.63

Tabell A.4. Samples of Turbo oil 2380 analyzed 2020-05-13

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1,21	0,63
2	1,20	0.63
3	1,21	0.63
4	1.21	0.63
5	1.20	0.63
6	1.22	0.64
7	1.22	0.64
8	1.22	0.64

Tabell A.5. Samples of Turbo oil 2380 analyzed 2020-05-13

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1,19	0,63
2	1,20	0.64
3	1,19	0.63
4	1.18	0.63
5	1.21	0.64
6	1.18	0.63
7	1.21	0.64
8	1.19	0.63

Tabell A.6. Samples of Turbo oil 2380 analyzed 2020-05-14

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1,21	0,63
2	1,20	0.63
3	1,21	0.63
4	1.21	0.63
5	1.20	0.63
6	1.22	0.64
7	1.22	0.64
8	1.22	0.64

Tabell A.7. Samples of Turbo oil 2380 analyzed 2020-05-14

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1,19	0,63
2	1,21	0.64
3	1,20	0.63
4	1.21	0.63
5	1.21	0.64
6	1.19	0.63
7	1.22	0.64
8	1.21	0.63

Tabell A.8. Samples of Turbo oil 2380 analyzed 2020-05-15

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1,24	0,63
2	1,23	0.63
3	1,25	0.64
4	1.24	0.63
5	1.26	0.64
6	1.27	0.65
7	1.27	0.65
8	1.29	0.66

Tabell A.9. Samples of Turbo oil 2380 analyzed 2020-05-18

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1.39	0.71
2	1.20	0.60
3	1.20	0.60
4	1.31	0.66
5	1.22	0.61
6	1.25	0.63
7	1.26	0.64
8	1.23	0.62

Tabell A.10. Samples of Turbo oil 2380 analyzed 2020-05-19

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1.21	0.63
2	1.21	0.63
3	1.20	0.62
4	1.21	0.63
5	1.21	0.63
6	1.22	0.63
7	1.22	0.63
8	1.23	0.64

A.1 Optimization 1

Table A.11-A.20 shows the result for the analysis using only 2-propanol as solvent. Apparatus settings, amount of sample/solvent and rinsing steps remain the same as for previous analysis.

Tabell A.11. Samples of Turbo oil 2380 analyzed 2020-05-25

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1.18	0.61
2	1.18	0.61
3	1.20	0.62
4	1.20	0.62
5	1.20	0.62
6	1.21	0.63
7	1.20	0.62
8	1.20	0.62

Tabell A.12. Samples of Turbo oil 2380 analyzed 2020-05-25

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	0,90	0.46
2	0,91	0.47
3	1.25	0.66
4	1.21	0.64
5	1.21	0.64
6	1.25	0.66
7	1.24	0.65
8	1.24	0.65

Tabell A.13. Samples of Turbo oil 2380 analyzed 2020-05-27

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.20	0.66
2	1.21	0.64
3	1.20	0.64
4	1.20	0.66
5	1.20	0.65
6	1.21	0.65
7	1.24	0.65
8	1.22	0.65

Tabell A.14. Samples of Turbo oil 2380 analyzed 2020-05-27

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.20	0.62
2	1.22	0.63
3	1.25	0.65
4	1.23	0.64
5	1.24	0.64
6	1.26	0.65
7	1.27	0.66
8	1.28	0.66

Tabell A.15. Samples of Turbo oil 2380 analyzed 2020-05-28

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.20	0.66
2	1.21	0.64
3	1.20	0.64
4	1.20	0.66
5	1.20	0.65
6	1.21	0.65
7	1.24	0.65
8	1.22	0.65

Tabell A.16. Samples of Turbo oil 2380 analyzed 2020-05-28

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.17	0.61
2	1.18	0.61
3	1.19	0.62
4	1.20	0.63
5	1.21	0.63
6	1.19	0.62
7	1.19	0.62
8	1.19	0.62

Tabell A.17. Samples of Turbo oil 2380 analyzed 2020-06-01

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
3	1.18	0.61
4	1.18	0.61
5	1.20	0.62
6	1.20	0.62
7	1.20	0.62
5	1.21	0.63
6	1.20	0.62
7	1.20	0.62

Tabell A.18. Samples of Turbo oil 2380 analyzed 2020-06-02

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
3	1.18	0.61
4	1.18	0.61
5	1.20	0.62
6	1.20	0.62
7	1.20	0.62
5	1.21	0.63
6	1.20	0.62
7	1.20	0.62

Tabell A.19. Samples of Turbo oil 2380 analyzed 2020-05-02

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.17	0.61
2	1.18	0.61
3	1.19	0.62
4	1.20	0.63
5	1.21	0.63
6	1.19	0.62
7	1.19	0.62
8	1.19	0.62

Tabell A.20. Samples of Turbo oil 2380 analyzed 2020-06-03

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
3	1.19	0.63
4	1.18	0.62
5	1.19	0.63
6	1.18	0.62
7	1.18	0.62
5	1.18	0.62
6	1.18	0.62
7	1.18	0.62

A.2 Optimization 2

The results obtained in table A.21-A.30 are samples analyzed with 2-propanol as solvent. The time to rinse/maintain the electrode has been decreased.

Tabell A.21. Samples of Turbo oil 2380 analyzed 2020-06-03

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.19	0.64
2	1.18	0.63
3	1.18	0.63
4	1.18	0.63
5	1.18	0.63
6	1.18	0.63
7	1.18	0.63
8	1.17	0.63

Tabell A.22. Samples of Turbo oil 2380 analyzed 2020-06-04

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.19	0.63
2	1.19	0.63
3	1.22	0.65
4	1.20	0.64
5	1.17	0.62
6	1.19	0.63
7	1.19	0.63
8	1.19	0.63

Tabell A.23. Samples of Turbo oil 2380 analyzed 2020-06-04

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.17	0.62
2	1.18	0.63
3	1.20	0.64
4	1.20	0.64
5	1.18	0.63
6	1.20	0.64
7	1.20	0.64
8	1.19	0.63

Tabell A.24. Samples of Turbo oil 2380 analyzed 2020-06-05?

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.19	0.64
2	1.18	0.63
3	1.18	0.63
4	1.18	0.63
5	1.18	0.63
6	1.18	0.63
7	1.18	0.63
8	1.17	0.63

Tabell A.25. Samples of Turbo oil 2380 analyzed 2020-06-11

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1.19	0.64
2	1.18	0.63
3	1.19	0.64
4	1.19	0.64
5	1.29	0.70
6	1.19	0.64
7	1.19	0.64
8	1.19	0.64

Tabell A.26. Samples of Turbo oil 2380 analyzed 2020-06-12

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1.19	0.63
2	1.18	0.63
3	1.19	0.63
4	1.19	0.63
5	1.19	0.63
6	1.19	0.63
7	1.19	0.63
8	1.19	0.63

Tabell A.27. Samples of Turbo oil 2380 analyzed 2020-06-16

Sample ID	**Volume of KOH (ml)**	**TAN mg KOH/mg**
1	1.19	0.63
2	1.20	0.63
3	1.20	0.63
4	1.19	0.63
5	1.19	0.63
6	1.20	0.63
7	1.20	0.63
8	1.19	0.63

Tabell A.28. Samples of Turbo oil 2380 analyzed 2020-06-17

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.14	0.59
2	1.14	0.59
3	1.13	0.58
4	1.14	0.59
5	1.14	0.59
6	1.14	0.59
7	1.14	0.59
8	1.14	0.59

Tabell A.29. Samples of Turbo oil 2380 analyzed 2020-06-18

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.13	0.59
2	1.13	0.59
3	1.13	0.59
4	1.13	0.59
5	1.13	0.59
6	1.13	0.59
7	1.13	0.59
8	1.13	0.59

Tabell A.30. Samples of Turbo oil 2380 analyzed 2020-06-18

Sample ID	Volume of KOH (ml)	TAN mg KOH/mg
1	1.11	0.59
2	1.13	0.61
3	1.11	0.59
4	1.14	0.61
5	1.11	0.59
6	1.11	0.59
7	1.14	0.61
8	1.13	0.61

B Appendix

Table B.1-B.10 show the result of thermometric titration of Turbo oil 2380 in accordance with a modified version of ASTM D8045.

Tabell B.1. Samples of Turbo oil 2380 analyzed 2020-05-25

Sample ID	**Volume of TBAOH (ml)**	**TAN mg KOH/mg**
1	1.18	0.63
2	1.18	0.63
3	1.20	0.63
4	1.20	0.63
5	1.20	0.63
6	1.21	0.63
7	1.20	0.63
8	1.20	0.63

Tabell B.2. Samples of Turbo oil 2380 analyzed 2020-09-28

Sample ID	**Volume of TBAOH (ml)**	**TAN mg KOH/mg**
1	1.16	0.65
2	1.12	0.63
3	1.18	0.66
4	1.10	0.61
5	1.14	0.64
6	1.13	0.64
7	1.13	0.63
8	1.14	0.64
9	1.15	0.65
10	1.14	0.64

Tabell B.3. Samples of Turbo oil 2380 analyzed 2020-09-29

Sample ID	**Volume of TBAOH (ml)**	**TAN mg KOH/mg**
1	1.13	0.63
2	1.12	0.63
3	1.12	0.63
4	1.12	0.63
5	1.12	0.63
6	1.13	0.63
7	1.12	0.63
8	1.12	0.63
9	1.12	0.63
10	1.11	0.62

Tabell B.4. Samples of Turbo oil 2380 analyzed 2020-10-01

Sample ID	Volume of TBAOH (ml)	TAN mg KOH/mg
1	1.12	0.62
2	1.12	0.63
3	1.14	0.63
4	1.12	0.63
5	1.14	0.64
6	1.11	0.63
7	1.12	0.63
8	1.12	0.64
9	1.12	0.63
10	1.14	0.64

Tabell B.5. Samples of Turbo oil 2380 analyzed 2020-10-02

Sample ID	Volume of TBAOH (ml)	TAN mg KOH/mg
1	1.18	0.63
2	1.18	0.63
3	1.20	0.63
4	1.20	0.63
5	1.20	0.63
6	1.21	0.63
7	1.20	0.63
8	1.20	0.63

Tabell B.6. Samples of Turbo oil 2380 analyzed 2020-10-02

Sample ID	Volume of TBAOH (ml)	TAN mg KOH/mg
1	1.18	0.63
2	1.18	0.63
3	1.20	0.63
4	1.20	0.63
5	1.20	0.63
6	1.21	0.63
7	1.20	0.63
8	1.20	0.63
9	1.20	0.63
10	1.20	0.63

Tabell B.7. Samples of Turbo oil 2380 analyzed 2020-10-06

Sample ID	**Volume of KOH (ml)**	**TAN mg TBAOH/mg**
1	1.12	0.63
2	1.12	0.63
3	1.12	0.63
4	1.12	0.63
5	1.12	0.63
6	1.11	0.62
7	1.11	0.62
8	1.12	0.63
9	1.11	0.62
10	1.12	0.63

Tabell B.8. Samples of Turbo oil 2380 analyzed 2020-10-08

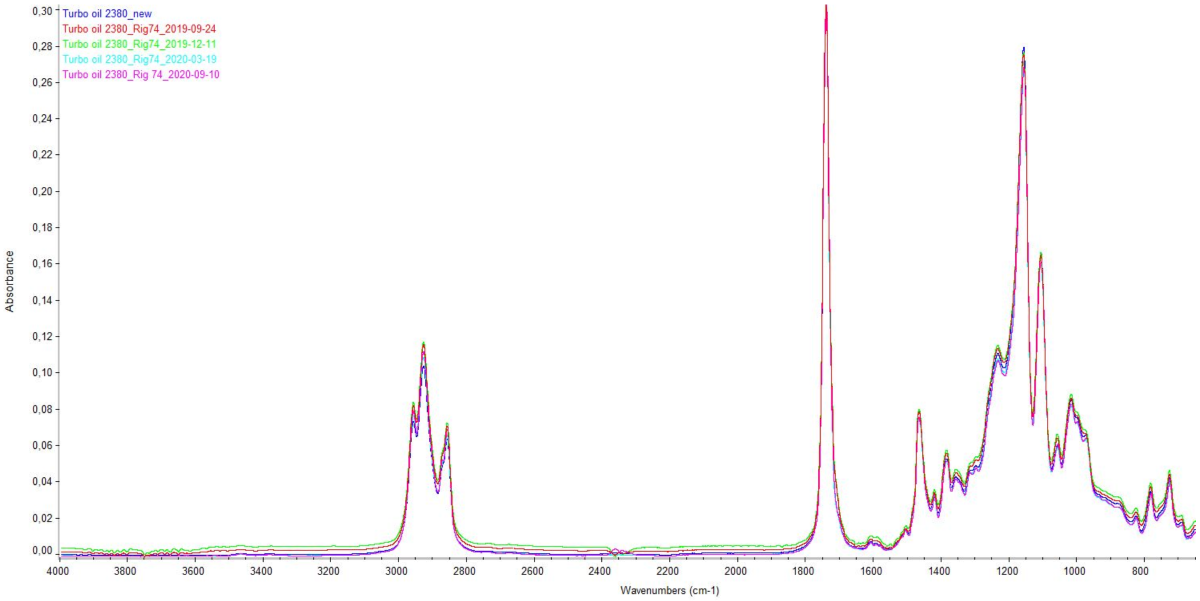
Sample ID	**Volume of TBAOH (ml)**	**TAN mg KOH/mg**
1	1.12	0.63
2	1.12	0.63
3	1.12	0.63
4	1.12	0.63
5	1.12	0.63
6	1.11	0.62
7	1.11	0.62
8	1.12	0.63
9	1.11	0.62
10	1.12	0.63

Tabell B.9. Values of TAN obtained for rig 74, 130 and 139 analyzed with thermometric titration with TBAOH and KOH

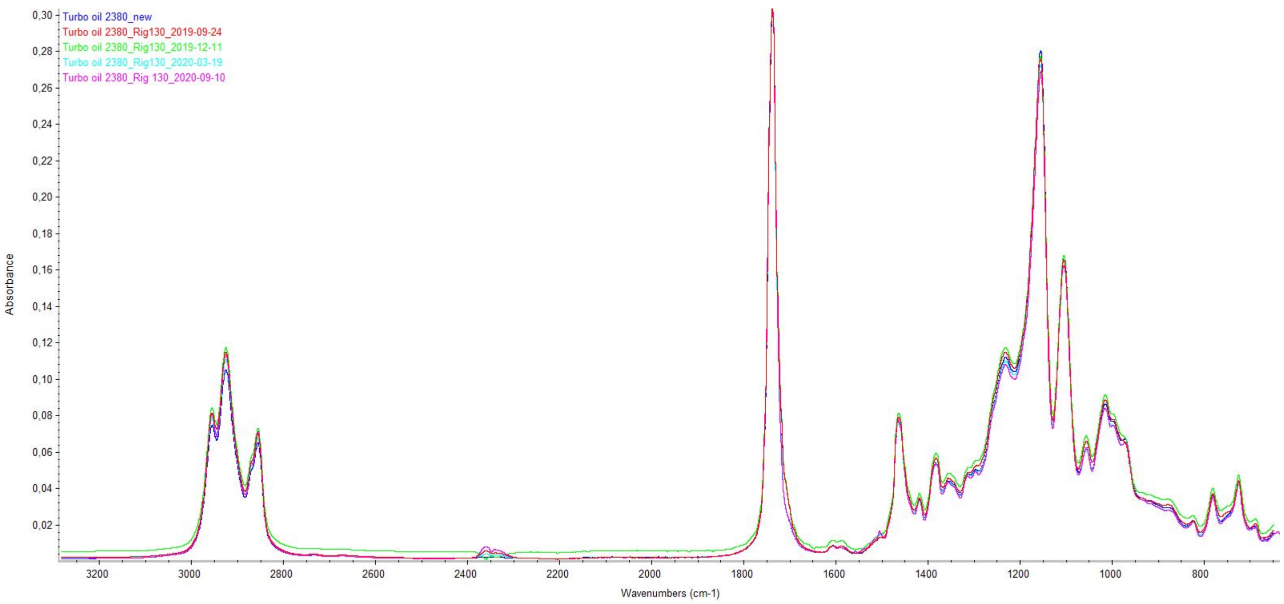
Rig	**Date**	**TAN [mg KOH/g](TBAOH)**	**TAN [mg KOH/g](KOH)**
74	2019-09-24	7,24	7,99
74	2019-09-24	7,23	8,00
74	2019-12-11	7,37	8,20
74	2019-12-11	7,38	8,18
74	2020-01-03	7,96	8,67
74	2020-01-03	7,95	8,68
74	2020-03-19	0,77	0,54
74	2020-03-19	0,77	0,55
74	2020-06-11	0,84	-
74	2020-06-11	0,84	-
74	2020-09-10	0,81	0,63
74	2020-09-10	0,82	0,58
130	2019-09-24	8,28	9,25
130	2019-09-24	8,29	9,21
130	2019-12-11	8,72	9,43
130	2019-12-11	8,72	9,41
130	2020-03-19	1,00	0,75
130	2020-03-19	0,98	0,74
130	2020-06-11	0,93	-
130	2020-06-11	0,94	-
130	2020-09-10	0,83	0,55
130	2020-09-10	0,83	0,55
139	2019-09-24	4,31	4,74
139	2019-09-24	4,29	4,72
139	2019-12-11	4,15	4,60
139	2019-12-11	4,14	4,59
139	2020-01-03		4,94
139	2020-01-03		5,02
139	2020-03-19	0,79	0,55
139	2020-03-19	0,78	0,56
139	2020-06-11	0,79	-
139	2020-06-11	0,80	-
139	2020-09-10	0,76	0,57
139	2020-09-10	0,75	0,55

C Appendix

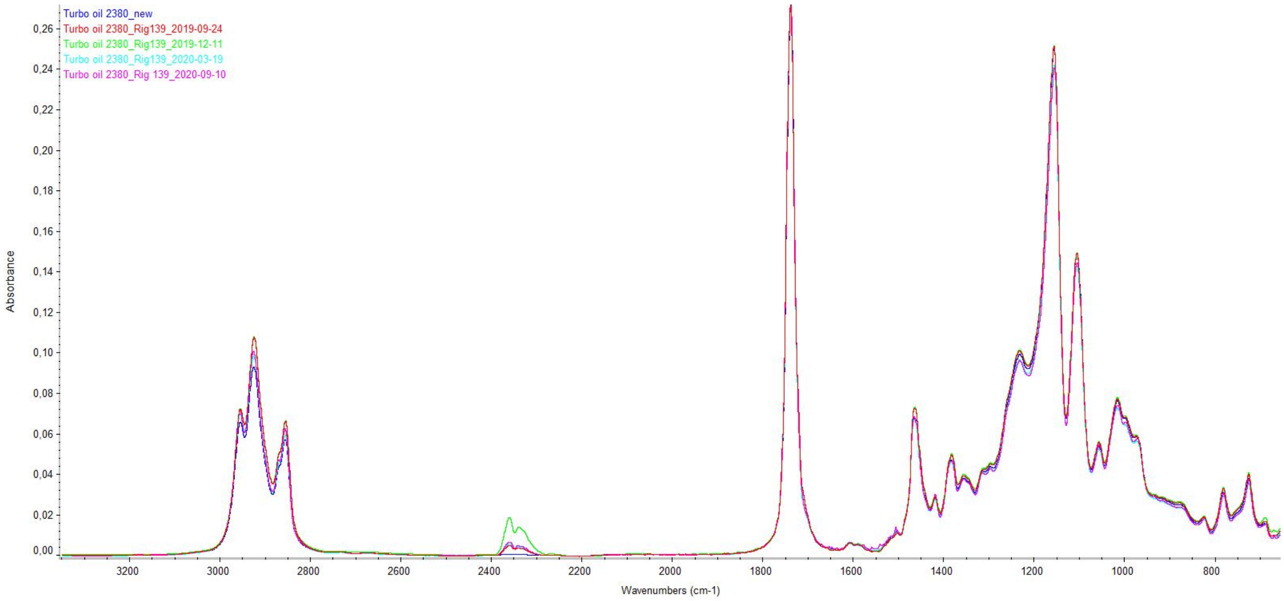
Figure C.1, C.2 and C.3 shows the result from ATR-FTIR measurements of oil sample from rig 74, 130 and 139.



Figur C.1. Spectra of samples from Rig 130 measured with ATR FT-IR



Figur C.2. Spectra of samples from Rig 130 measured with ATR FT-IR



Figur C.3. Spectra of samples from Rig 130 measured with ATR FT-IR