Application Note #67 – Total Acid Number (TAN)

Updated December 2016

Introduction:

Acid Number or Total Acid Number (TAN) is used to test the quantity of acidic components in an oil sample. This test determines the amount of soluble or nearly soluble acids in a sample dissolved in a toluene and 2-propanol mixture. For example, compressor and turbine oils usually run at acid numbers of 0.01-0.25 mg KOH per gram of sample, gearbox and lube oil at 0.1-10 mg KOH per gram, and lubricant additives at 20-200 mg KOH per gram. Acidic characteristics are caused by numerous chemicals. These can include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents. These acidic constituents are usually present as additives or as degradation products formed during service, such as oxidation products[1]. In chemical terms, this method measures acids that have dissociation constants larger than 10^{-9} in water. Interference can be caused by salts with hydrolysis constants greater than 10^{-9}, but extremely weak acids with dissociation constants smaller than 10^{-9} do not interfere[2].

Acid number results are used as a guide in the quality control of lubricating oils. The rate of change of the acid number is more important than its absolute value. A rapid increase can be caused by many factors, including excessive degradation due to hotspots from dirty oil ways, top-up with different oil, or a change in fuel Sulphur content[3]. More commonly, a steady increase in acid number may be caused by oxidation over time or temperature effects. High operating temperatures can generate increasing levels of weak organic acids. Oils with a high acid number will form undesirable gums and lacquers on metal surfaces. High acid numbers are also associated with increased viscosity of pumping losses and system corrosion – especially in the presence of water[4]. A combination of compounds with a wide variety of corrosion properties contribute to the acid number. Therefore, this test cannot be used to predict the corrosiveness of oil being used under service conditions. There is no established link between acid number and the corrosive activity of oils toward metals[1], although acid number values are often used as a measure of lubricant degradation in service. Any limits must be manually established for the particular type of sample that is being analyzed[2].

The method described in this document is effective, accurate, and precise. It runs smoothly, can be equipped with fully automated solvent addition and extraction, and corresponds exactly to the ASTM method using a well-defined inflection point whenever possible. Please contact your local MANTECH sales representative to find out how this method can work for you.

Conforms to: ASTM D664

Sample: Oil samples

Concentration Range: 0.05 – 20 mg KOH/g sample

Apparatus:

1. pH Electrode
2. Electrode Cable
3. Interface
4. MANTECH Buret
5. Solvent Addition Pump
6. Solvent Extraction Pump
7. Autosampler
    a) AutoMax73, 30 sample locations from a 125mL cup
    b) AutoMax122, 47 sample locations from a 125mL cup
    c) AutoMax 197, 77 sample locations from a 125mL cup

Reagents:

1. 0.10 N Potassium Hydroxide (KOH) in 2-Propanol
2. Titration solvent: 5 mL Deionized water + 495 mL 2-Propanol + 500 mL Toluene
3. Three static rinse stations: a) Toluene b) Tap water c) 2-Propanol

Procedure:

Calibration:

1. Place approximately 40mL of pH 4, 7, and 11 buffers into the first three sample positions, and run a schedule to calibrate the pH probe. Ensure the pH electrode is filled with the appropriate fill solution, if applicable (i.e. 1M Lithium chloride in methanol).
2. The sampler will move to rinse position “R2” where the probe will be rinsed in the titration solvent to remove oil residue.
3. Next, the sampler will move to rinse position “R1” where the probe will be rehydrated in tap water.
4. The sampler will then move to rinse position “R3” where the probe will be rinsed in 2-Propanol to dry the electrode.
5. The sampler will move to the pH 4 buffer position where the pH of the solution is measured and recorded.
6. Steps 2 to 5 are repeated for the pH 7 and 11 buffer solutions.
7. The calibration curve is calculated and reported.

8. The mV reading for the pH 11 buffer is saved so that it may be used to determine the endpoint for the titration in cases where the graph is too noisy to detect an inflection endpoint. Often dirty oil samples have noisy curves and must rely on this saved mV value for endpoint determination.

Sample Analysis:

1. A blank is run as the first sample, titrating 60 mL of the unaccompanied solvent in the same manner as the sample titration. This blank value is recorded and subtracted from the sample value for accurate results.
2. The electrode is rinsed in toluene to remove oil residue (R2), rehydrated in tap water (R1) for at least 2 minutes, and rinsed again in 2-Propanol (R3) to dry the electrode after every sample.
3. 60 mL of titration solvent is pipetted into the sample.
4. The sample is stirred vigorously at a stirring rate of 60% for 45 seconds to ensure complete dissolution of the oil. The stirring time can be adjusted if necessary.
5. While stirring gently at a rate of 30%, the sample is titrated with standardized 0.1 N potassium hydroxide (KOH) in 2-propanol until the endpoint is detected.
6. Stirring is stopped and the solvent and sample mixture is pumped to a waste container.
7. The acid number of the sample is calculated and reported. If no endpoint is detected, the volume of titrant required to reach the mV equivalent to that of the basic pH 11 buffer solution is used. If a large endpoint is found at or near the value of the acidic pH 4 buffer solution, this should be reported separately as the Strong Acid Number.

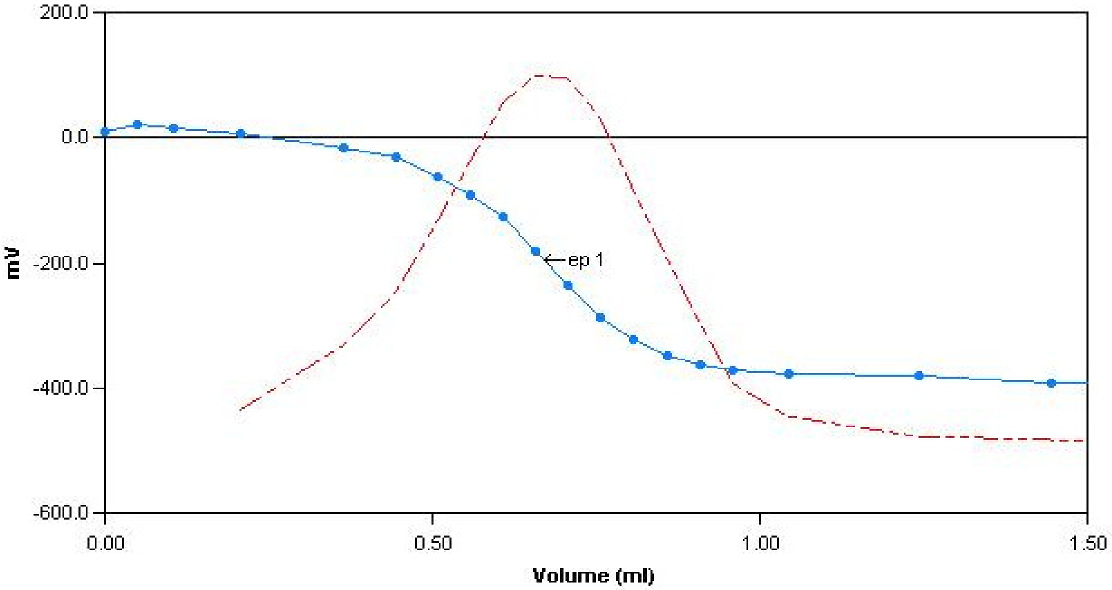

Figure 1: Titration Curve for a sample obtaining an Acid Number of 0.108mg KOH/g

Calculations:

Acid Number:

$$TAN = \frac{(ve1 - udv31)*tcon*56.1}{swght}$$

TAN = Total Acid Number reported as mg KOH/g sample
ve1 = volume of titrant added at the endpoint (mL)
udv31 = volume of titrant added at the endpoint of the blank titration (mL)
tcon = concentration of KOH in 2-propanol titrant (N)
swght = mass of sample analyzed (g)

Quality Control:

Replicates were run of standards made with propionic acid in mineral oil at levels of 0.05, 0.1, 0.2, and 0.65 mg KOH/g sample, with statistical data displayed below.

0.05 mg KOH/g sample:

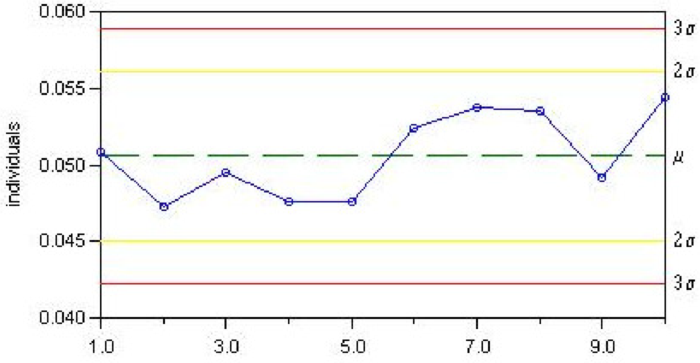

Figure 2: Control Limits plot for an Acid Number of 0.05g KOH/g sample

Control Limits – Individuals	95% Confidence Limits	99.7% Confidence Limits
μ= 0.051	μ - 2Θ = 0.045	μ - 3Θ = 0.042
Θ= 0.003	μ + 2Θ = 0.056	μ + 3Θ = 0.059
CV = 5.45%		

0.1 mg KOH/g sample:

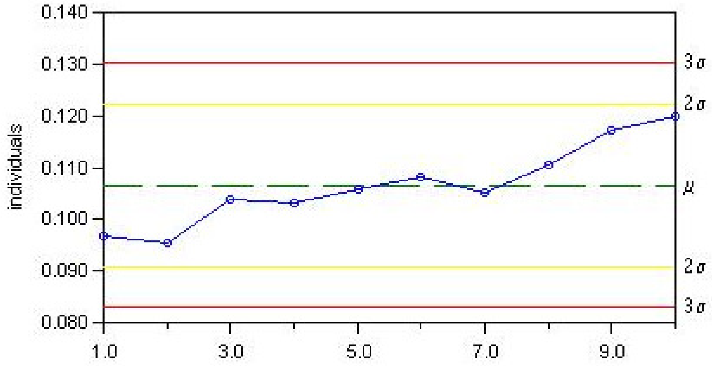

Figure 3: Control Limits plot for an Acid Number of 0.1g KOH/g sample

Control Limits – Individuals	95% Confidence Limits	99.7% Confidence Limits
μ= 0.107	μ - 2 Θ = 0.091	μ - 3 Θ = 0.083
Θ = 0.008	μ + 2 Θ = 0.122	μ + 3 Θ = 0.130
CV = 7.39%		

0.2 mg KOH/g sample:

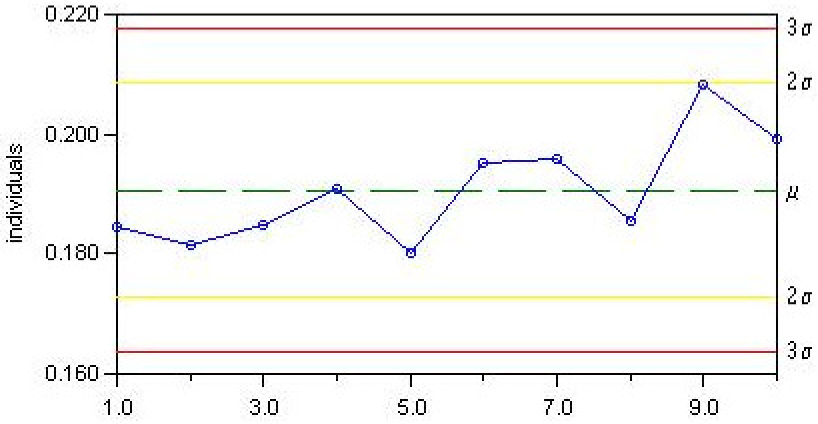

Figure 4: Control Limits plot for an Acid Number of 0.2g KOH/g sample

Control Limits – Individuals	95% Confidence Limits	99.7% Confidence Limits
μ= 0.191	μ - 2Θ = 0.173	μ - 3Θ = 0.164
Θ= 0.009	μ + 2 Θ = 0.209	μ + 3 Θ = 0.218
CV = 4.70%		

0.65 mg KOH/g sample:

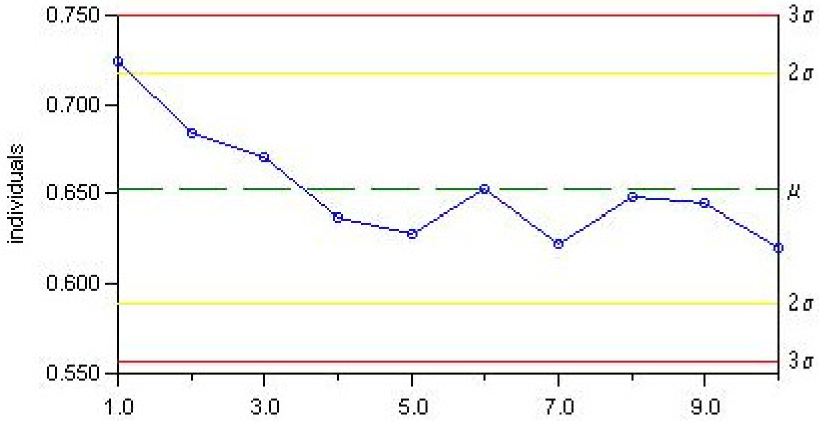

Figure 5: Control Limits plot for an Acid Number of 0.65g KOH/g sample

Control Limits – Individuals	95% Confidence Limits	99.7% Confidence Limits
µ= 0.653	µ - 2Θ = 0.589	µ - 3Θ = 0.557
Θ= 0.032	µ + 2Θ = 0.718	µ + 3Θ = 0.750
CV = 4.92%		

Hints/Suggestions:

1. Always ensure that when the titration solvent is freshly made, it is mixed thoroughly. Improper mixing will result in poor titrations and erroneous results due to solvent layering.

2. It is extremely important that the correct fill solution be used in the sleeve electrode; lithium chloride (LiCl) in methanol is the appropriate solution. Non-solvent based fill solution will not mix with the solvent-based samples correctly when the titration is taking place, which can seriously affect the results.

3. Tap water must be used as the second rinse, and the electrode must be allowed to soak for a minimum of 2 minutes in the tap water, although five minutes is the recommended soak time. This allows the electrode to be rehydrated between samples in order to function properly. Tap water is used because it has a higher ionic strength than deionized water and is therefore more effective in rehydrating the electrode.

4. The tightness of the sleeve on the electrode (if applicable) will greatly affect the flow rate of the fill solution and hence the results of the titrations performed. It is important that the sleeve is tightened in the same way each time for consistent results. New users will require some practice to accomplish consistent sleeve fits for a reproducible flow rate.

5. Extremely dirty, thick, or contaminated samples may require an increased volume of solvent, increased stirring to dissolve the sample, and/or increased rinse times. This will help to keep the electrode in a clean and consistent working state to ensure reliable and reproducible results. Otherwise, the electrode can become coated or contaminated and results will steadily deteriorate or run incorrectly. An extra static rinse can also be added if necessary. Manual cleaning after dirty samples must be done with care, particularly to minimize contact with the sensing element surface on the pH electrode bulb.

6. Automated solvent addition and extraction is highly recommended for this method. This eliminates the need for laboratory technicians to handle solvents for every sample, and reduces the amount of solvent available to evaporate and cause health concerns. This also enables the system to run completely unattended, allowing laboratory staff more time for other efforts.

7. An extended range is available if the sample size or titrant concentration is adjusted. A reduced sample size will enable the user to accurately measure high acid numbers. A reduced titrant concentration will enable the user to measure extremely low acid number values.

REFERECES

[1] Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants, Ed. by Nadkarni, R. A. Kishore, ASTM, Pennsylvania, 2000. p 12.

[2] Annual Book of ASTM Standards, Section Five: Petroleum Products, Lubricants, and Fossil Fuels, Volume 05.01, Petroleum Products and Lubricants (I): D 56-D 2596, ASTM, Pennsylvania, 2001. Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, p. 263-269.

[3] http://www.spectro-oil.com/industrysectors/industrial/analysistests.html

[4] http://www.kittiwake.com/products/product_pages/tan-elec.asp