Evaluation of New Field Test Methods for Base Number and Acid Number in Lubricating Fluids

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SUMMARY

Two new test methods have been developed to measure base number (TBN) and acid number (TAN) in lubricating fluids. The test kits, called Titra-Lube' TBN and Titra-Lube TAN, can be used in the field where laboratory equipment is not available. They eliminate the need for chlorinated solvents that present health and environmental hazards. The field tests use an aqueous-based extraction followed by a colorimetric titration in a plastic test tube. The aqueous titration provides a definitive end point that is much easier to read than traditional calorimetric methods that are titrated in the oil phase. The TBN kit shows excellent correlation with ASTM D-4739 and D-2896. The TAN kit compares well to ASTM D-664 and D-974.

INTRODUCTION

The accurate measurement of acid and reserve base in lubricating fluids is critical in determining when an oil is losing its ability to protect engine or pump components from corrosion. Preventative maintenance procedures dictate that acid or base number be measured on a regular basis, but because of the time and effort required to perform such testing, the procedure is often skipped or postponed. Samples must be sent to a laboratory where they often wait for days for the analysis to be performed and for results to be sent back to the field. Often, the information obtained by the operator is not seen as being worth the time and effort that must be invested to obtain results.

The easiest way to speed up the rate at which results are obtained is to perform the test in the field so that useful readings are available in a short time. A pair of field test kits have recently been developed that allow the user to obtain results in less than five minutes. Titra-Lube TBN and Titra-Lube TAN perform colorimetric determination of base number and acid number in the field without sending the samples to the lab. The kits work as follows:

Kit Mechanics

Each test kit consists of a sampling syringe, two polyethylene test tubes containing ampulized reagents, a filter, and a disposable titrating burette. The first step in running the kits is to take a sample of the fluid to be tested using the fixed volume-sampling syringe. The sample is then dispensed into the first test tube where

a glass "onion skin" ampule containing isooctane is broken releasing the isooctane to mix with the sample. A second ampule containing either isopropyl HCI (TBN) or isopropyl KOH (TAN) is broken and mixed well with the dissolved sample. Seven mL of an aqueous solution containing demulsifiers is poured out of the second tube into the first and the tube is capped and shaken well. The two phases are allowed to separate and five mL of the aqueous phase is filtered into tube 2. The titrating burette is screwed onto the top of the tube and an ampule containing a calorimetric pH indicator is broken and mixed with the solution. The titrating solution (KOH for TBN and HCI for TAN) is added dropwise and as soon as the solution changes color the titration is stopped and the test result is read off the side of the titration burette.

Traditional Methods

The tests differ from laboratory techniques such as ASTM D-664, D-2896, and D-4739 in several ways. One of the difficulties in performing a calorimetric test in used oils (D-974) is that dark oils often obscure the color change to such a degree that end points cannot be accurately determined. The test kits circumvent this problem by first reacting the oil sample with the base or acid and then extracting the excess reactant into the aqueous solution. In aqueous solution, the calorimetric titration provides an easy to discern end point that results in an accurate, repeatable result.

All of the established ASTM methods practiced in the laboratory use chlorinated solvents such as chlorobenzene or chloroform. Adverse health and environmental effects from these solvents mean that they are difficult to use and expensive to dispose of. These solvents are needed for most methods to solubulize dirty oils enough so that a pH titration can be performed in a mixed hydrocarbon/aqueous solution. The test kit methods enable the user to el' these solvents because the acid-base reaction takes place in the isopropanol/hydrocarbon phase first, and then the residual acid (base) is extracted into aqueous solution where it is easily titrated.

One of the reasons for the relatively poor reproducibility of ASTM methods D-664 (39%) and D-4739 (21%) is that individual operators are required to make, standardize and store several different reagents of limited stability. Any error due to making these reagents or from improper storage is directly realized in analytical results. The test kits use stable reagents that are pre-measured in glass ampules so that someone performing the test today will get the same result as someone else performing the test in six months. This eliminates one of the largest sources of interlaboratory error in TBN/TAN testing.

Although all TBN/TAN test methods report results in mg KOH/g sample, this does not mean that with different methods the results will be the same for a given sample. In fact, depending on the type of acid that is used to titrate a sample for TBN, results on a single sample may differ by more than 50%. This variation is

most evident when comparing results from D-4739 and D-2896. Although there are other variations, the main differences between these two methods are the acids that are used to titrate. D-2896 uses perchloric acid and D-4739 uses weaker hydrochloric acid. The stronger acid, perchloric, reacts with weaker bases than does the hydrochloric and therefore provides a higher TBN result. By reacting with weaker bases such as calcium and magnesium salts, method D-2896 (perchloric acid) is actually measuring compounds that indeed may act as bases but are not powerful enough to remove harmful acids from the oil. Therefore, it is believed that D-4739 provides a more realistic estimation of the *useful* residual base that remains in an oil. This is why in designing the TBN test kit it was decided that hydrochloric acid would be used. The chart below is an extension of one provided by J. R. Barnes in a paper titled "Importance of Railroad Diesel Engine Oil TBN and its Relevance to LMOA Generation 5 for Salicylate Oils" which was published in the September 1991 issue of Lubrication Engineering.

TBN Methods: What Do They Measure?[2]

	D-2896	D-664	D4739	Test Kit
ACID USED	Perchloric	Alcoholic HCI	Alcoholic HCI	Alcoholic HCI
SOLVENT	Chlorobenzene/ Acetic Acid	Toluene/IPA/ water	Toluene/IPA/ chloroform	Hydrocarbons
EXAMPLES FRESH OIL	All Detergent Base, All Dispersant Base	All Detergent Base, Most Dispersant Base	All Detergent Base, Most Dispersant Base	All Detergent Base, Most Dispersant Base
EXAMPLES USED OIL	Most Ca, Mg salts of degradation products	Very few Ca, Mg salts of degradation products	Some Ca, Mg salts of degradation products	Some Ca, Mg salts of degradation products

EVALUATION

To evaluate the two test kits, each was compared to corresponding ASTM methods. For TBN the kit was tested against D-4739 and D-2896. The TAN kit was compared to D-664.

TBN

The group of samples used in the evaluation for Titra-Lube TBN consisted of 50% new lube oils and 50% used lube oils. All of the oils were formulations that are used in diesel engines. Oil samples were limited to those with TBN values of less than 20 so that they would fall into the range of the test kit. Samples were chosen so that they would cover the entire range of the kit. Each sample was run in triplicate for each of the methods. The average result for each sample with each method is given below. All results are in units of mg KOH per gram of sample.

Table (except for test kit data) from J.R. Barnes. "Importance of Railroad Diesel Engine Oil TBN and its Relevance to LMOA Generation 5 for Salicylate Oils" Lubrication En2ineerinL, Vol. 47, 9, 713-722.

Comparison of Titra-Lube TBN Test Kit results to ASTM Methods D-4739 and D-2896.

SAMPLE	Oil Type	D-4739	D-2896	Test Kit
A	New	1.31	0.90	0.85
B	New	7.05	7.87	7.53
c	New	12.45	14.78	13.62
D	New	11.20	12.44	11.58
E	Used	3.79	6.79	5.42
F	Used	9.61	13.55	11.36
G	Used	4.64	6.37	5.26
H	Used	13.05	16.76	15.50

Precision for the TBN test kit was determined to be +/- 0.4 TBN units. It is important to note that the test kit does not resolve to .01 TBN units, but to . 1. The results shown here are an average of three runs. Used oils show a greater difference between samples than do new oils when comparing test methods. Test kit results

more closely match those of D-4739 than they do those of D-2896. This is what would be expected considering the same titration acids are used for both the test kit and D-4739. Method D-2896 reads consistently higher that do the other two techniques.

TAN

The Titra-Lube TAN kit was evaluated by comparing results obtained with the kit to those obtained with ASTM D-664 and D-974. Sample types that were tested included hydraulic fluids, cutting oils, pump oils, and compressor oils. Samples were limited to those exhibiting acid numbers between 0 and 2.0, the range of the test kit in the configuration tested. Each sample was run in triplicate for each method and the average result is given below. All results are in units of mg KOH per gram of sample.

TAN Test Kit vs. ASTM Methods D-664 and D-974

SAMPLE	0-664	0-974	Test Kit
A	.354	.337	.302
B	.657	.575	.393
C	.116	.098	.107
D	.078	.056	.045
E	1.66	1.78	1.42
F	.239	.150	.424
G	.430	.266	.399
H	1.18	1.30	1.39

Precision for the test kit method was determined to be +/- 0.02 TAN units. Test kit results can only be resolved to .05 TAN units. Reported results are averages of three runs.

Advantages of the Test Kit Methods

- No instrumentation is required
- Kits are portable and can be run on site
- Kits contain no hazardous solvents that are difficult to dispose of
- No calibration or standardization is required
- Titrations are performed in the aqueous phase
- Kits possess a long shelf life (one year)

° Kits measure actual base and acid numbers, not just specific additives

Disadvantages of the Test Kit Methods

o Samples are measured volumetrically, not by weight, so samples with a density different from 0. 9 g/mi will be biased high or low, depending on the oil's density.
o The range of the kits is limited to 0 to 20 TBN units and 0 to 2 TAN units. Samples outside these ranges need to be diluted.
o Sample results must be recorded manually.

CONCLUSION

Titra-Lube TBN and Titra-Lube TAN provide results in the field that are comparable to results obtained by traditional laboratory methods. Accuracy and precision are similar to that obtained by ASTM methods D-664, D-4739, D2896, and D-974. Titra-Lube TBN most closely mimics D-4739 and Titra-Lube TAN provides results that are similar to both D-664 and D-974. The test kits are most useful when quick answers in the field are desired or when laboratory instrumentation is not readily available. As the use of chlorinated solvents becomes more and more restricted. the test kit methods may become even more advantageous and replace the traditional methods in the laboratory.