

TBN ANALYSIS OF LUBRICANTS USING NON-HAZARDOUS SOLVENTS

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ABSTRACT

Traditional methods of analyzing lubricants for base number use various solvents that function both as solvents for the oil sample and as media for a potentiometric titration using a pH electrode. These chlorinated solvents, specifically chlorobenzene and chloroform, have recently come under fire because of environmental and health concerns. In many industries they are being phased out. A new laboratory method has been developed that eliminates the use of these restricted solvents and still provides a precise, accurate result that is reproducible between laboratories. The method uses isooctane and isopropyl HCl combined with an aqueous extractant to eliminate the need for a solvent that can both solvate an oil and support an acid/base titration. Initial studies show good correlation between the new method and ASTM method D-2896.

INTRODUCTION

For years, base number analysis in used lubricants has been performed most often by either ASTM method D-2896 or D-4739 (revised D-664), both of which determine base number by means of potentiometric titration. Both techniques have provided consistent results that can be reproduced by different laboratories, but recently, alternatives for these methods have been sought because of the use of chlorinated solvents in both of these methods. Chloroform (D-4739) and chlorobenzene (D-2896) are considered to be health hazards and are expensive to dispose of because of the difficulty in burning them without violating EPA regulations. Chloroform and toluene, used in method D 4739, are both on the Department of Defense's list of Haztox solvents and ASTM has been asked to remove them from any methods practiced by the DOD. ASTM has looked at alternative solvents for these methods

and has recently balloted a proposal to substitute mixed xylenes for chlorobenzene in method D-2896, but this substitution resulted in worse precision than when using the original solvent, and xylenes are also considered a haztox solvent by the DOD.

Dexsil Corporation has recently developed a method for TBN analysis that eliminates the use of chlorinated solvents and supplies results comparable to those obtained with methods D-4739 and D-2896. The technique uses a high flash point hydrocarbon solvent in combination with alcoholic HCl to solvate the oil and react with the basic components of the lubricant. The reaction step is followed by an extraction into an aqueous based solution where the residual base can be easily detected and quantified. The new method, based on Titra Lube™ chemistry, eliminates the use of chlorinated solvents and reduces both the analysis cost and the time required to perform the test.

BACKGROUND

Within the past several years Dexsil has introduced the Titra-Lube™ TBN and Titra-Lube™ TAN test kits for testing lubricants for residual base and acid in the field. These kits have proven to be reliable and accurate, but many laboratories require methods that are automated and produce hard copy results. The new laboratory method discussed here used the chemistry of the portable test kits, but incorporates several changes that allow an automated analysis to be performed in the laboratory on samples with TBN ranging from 0 to 400 mg KOH/g sample. The method eliminates the use of chlorinated solvents and reduces the total amount of solvent used by a factor of 20. Preparation time is greatly reduced and actual titration time is much less than conventional methods.

THE METHOD

The Titra-Lube laboratory method is run as follows:

1. A sample of the lubricant to be tested is weighed out into a disposable test tube. The amount of sample used in grams is determined by dividing 16 by the expected TBN value of the sample. The maximum amount of sample to be used is 2 grams.
2. The tube is filled to a 5 mL line with a high flash point hydrocarbon based solvent and the tube is capped and shaken until the sample is totally dissolved.
3. 3.1.5 mL of 0.40 M isopropyl HCl is added to the tube and it is shaken for 30 seconds.
4. 12 mL of aqueous extract solution is added and the mixture shaken for 30 seconds.
5. The two phases are allowed to separate for 3 minutes.
6. The aqueous layer is decanted off and 10 mL is transferred to a titration beaker.
7. 12 mL of additional aqueous extract solution (clean) is added to the beaker and the solution is titrated with 0.0425 N NaOH to the inflection point. The titration can be done manually or with an automatic titrator.
8. TBN is calculated as follows:
$$\text{TBN} = 3.20 (V_{bl} - V_s) / W_s$$
where V_{bl} is the amount of titrant used to titrate a 0 TBN blank sample, V_s is the volume of titrant needed to titrate the sample being analyzed, and W_s is the weight of the sample used in the procedure.

RESULTS

A series of new and used oils (and additive packages) was run using both the Titra-Lube laboratory method and ASTM method D-2896. The results comparing the two techniques are shown below. Results between both methods show good correlation exhibiting an R^2 of .997, and the Titra-Lube laboratory method shows a standard deviation of

less than 2% on most samples. Sample W, and additive package, could not be run on the Titra-Lube laboratory method because the two phases emulsified and could not be separated. This was the only sample for which the method did not obtain a result.

HOW THE METHOD WORKS

Traditional TBN methods D-2896 and D-4739 require that a non aqueous hydrocarbon sample be dissolved in a solution capable of facilitating an acid-base reaction and titration. This requirement limits the method to using a limited number of powerful solvents, usually chlorinated ones. More polar solvents could not dissolve the oils and less polar ones would not permit a potentiometric titration to take place. The Titra-Lube laboratory method circumvents this problem by performing the test in two steps. In the first step, the oil is dissolved in a non-polar solvent and reacted with an isopropyl HCl solution which also easily dissolves in the solvent. The solution is then mixed with an aqueous extractant which removes any excess acid from the non-polar solvent and isolates it in the aqueous phase. This aqueous phase is then physically separated from the oil and placed into the titration beaker. The acid/base titration then proceeds much more quickly than in other methods because the titration is taking place in a strictly aqueous medium. The titration itself takes about 3 minutes where previously it would take up to 30 minutes because of the time necessary for the electrode to stabilize in the non-aqueous solution.

STANDARDIZATION OF REAGENTS

Much of the oil analyst's time is spent making up and standardizing reagents for the analysis of base and acid numbers. Alcoholic HCl and alcoholic KOH solutions are tedious to make, require standardization, and have a shelf life of a matter of days before they need to be restandardized. This means that much of the analyst's time is used preparing reagents rather than running tests. The Titra-Lube laboratory method requires no standardization or production of reagents because each of the critical

components is sealed in a glass ampule providing a shelf life of one year without a variation in reagent concentration. This means that a given laboratory can run a sample whenever it becomes available and does not have to wait for a large number of samples to make the exercise worthwhile. Whatever time is available to the analyst can be spent running samples, not preparing reagents.

SUMMARY

The Titra-Lube laboratory method provides a new alternative to analysts who are looking for a TBN testing method that does not require the use of chlorinated solvents. The technique is easy to run, requires no preparation, can be used on a wide range of samples and provides results that correlate well with ASTM methods D-2896 and D-4739.

TABLE 1

Comparison of Base Number Results for Dexsil Laboratory Method and ASTM D-2896

Oil	D-2896 Result (mg KOH/g)	Titra-Lube Laboratory Method				
		Trial 1 (mg KOH/g)	Trial 2 (mg KOH/g)	Trial 3 (mg KOH/g)	Ave (mg KOH/g)	SD (mg KOH/g)
A	0.37	-0.220	0.267	NA	0.024	0.244
B	0.89	-0.572	-0.547	NA	-0.560	0.013
C	3.3	3.40	3.44	3.45	3.43	0.022
D	5.0	4.17	4.33	4.05	4.18	0.115
E	6.2	7.88	7.89	7.75	7.84	0.064
G	7.8	7.77	9.21	NA	8.49	0.720
H	10	12.1	12.1	NA	12.1	0.000
F	11	11.7	11.8	12.3	11.9	0.262
I	15	16.0	15.7	15.6	15.8	0.170
K	17	14.4	13.1	NA	13.8	0.650
J	22	21.5	21.7	21.3	21.5	0.163
O	26	25.2	25.4	25.2	25.3	0.094
M	28	27.8	28.1	27.8	27.9	0.141
L	42	43.3	43.7	43.7	43.6	0.189
N	71	69.7	69.4	70.5	69.9	0.464
Q	94	104	106	NA	105	1.000
T	130	122	122	123	122	0.471
R	160	173	175	176	175	1.247
X	260	256	253	250	253	2.449
S	300	297	300	301	299	1.700
W	410	387	NA	NA	NA	NA