Determination of Total Base Number of Used Lubricating Oils From Marine Engines by Potentiometric Titration

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A modification of the IP 276-83–ASTM D2896-92 standardized method for the determination of the total base number of petroleum products is described. This method allows this determination in used lubricating oils from marine engines, which was not possible with the standardized procedure. It shows a better precision, shorter voltage stabilizing time and in many instances avoids back titration. It can be suggested as an alternative to ASTM-IP methods.

Keywords: Total base number determination; lubricating oils; marine engines; potentiometric titration

Introduction

The degradation of lubricating oils by oxidation can lead to the development of corrosive organic acids. Further, the residual fuels used in marine internal combustion engines frequently contain sulfur, which is oxidized during combustion and H_2SO_4 is formed. Basicity is therefore an important property of lubricating oils, as bases neutralize acidity and therefore offset corrosion. The basicity of an oil is produced by additives (auxiliary materials added to liquid lubricants to enhance their properties), nitrogen compounds and salts of weak acids.

The total base number (TBN) of an oil is defined as the amount of acid, expressed in milligrams of potassium hydroxide, that is needed to neutralize all basic constituents present in 1 g of sample.[1–4] The TBN initial value of an unused lubricating oil, decreases after several hundred hours of working (until a re-equilibrium value is reached). This implies an increase in metal wear in the oil. The change depends on several factors, such as sulfur content of fuel, motor refrigerating temperature and quality and consumption of lubricating oil.

The determination of TBN by a simple, precise and reproducible method is of great technological interest. Most of the methods described for this determination are based on acid–base reactions using a chromogenic indicator[5–7] or potentiometry[1–4] to detect the end-point. A flow injection potentiometric method[8] and a high-frequency microtitration method[9,10] have also been described. A method consisting of measuring the gas pressure at the end of the acid–base reaction has been proposed.[11]

The ASTM D664-58 and IP 177/64 methods[1,2] for measuring TBN involve the potentiometric titration of a solution of the oil in toluene–propan-2-ol with a standardized solution of hydrochloric acid in propan-2-ol, but the graph obtained does not always show a satisfactory end-point, particularly with used oils. The IP 276-83 and ASTM D2896-92 methods[3,4] using chlorobenzene as a solvent for oil and perchloric acid in acetic acid as titration reagent, is more widely accepted, but it often requires a back titration and with used marine oils the detection of the end-point is not always possible.

This paper describes a modification of the IP 276-83–ASTM D2896-92 method in order to be able to determine the TBN of used lubricating oils from marine engines. Different solvents were tested to increase the sensitivity of the TBN determination and shorten the voltage stabilization time. The results were compared with those obtained by the IP 276-83–ASTM D2896-92 method.

Experimental

Apparatus

A Crison 2.000 pH meter with a glass–calomel combined electrode for non-aqueous media was used for normal determinations. A Mettler DL20 pH meter was used for automatic determinations.

Reagents

All chemicals were of analytical-reagent grade. Potassium hydrogenphthalate and 60% perchloric acid were obtained from Merck. Propan-2-ol, xylene and glacial acetic acid were purchased from Panreac.

Sampling

Thirty-one samples of used lubricating oils of several tradenames with different TBN values were taken from different ship engines. They were collected with the engine hot and running to provide a homogeneous and representative sample; they were stored in poly(propylene) bottles.

Procedure

Standardize the perchloric acid as follows. Heat an amount of potassium hydrogenphthalate in an oven at 120 °C for 2 h and allow it to cool. Take 0.1–0.2 g of the potassium hydrogenphthalate and dissolve it in 40 ml of warm glacial acetic acid. Add 80 ml of xylene, cool and titrate with 0.1 mol l^{-1} perchloric acid in acetic acid using the electrode system and procedures given for TBN determination.

Carry out a blank titration on 40 ml of glacial acetic acid plus 80 ml of xylene.

Sample Titration

Shake the used oil thoroughly to ensure homogeneity before sampling. Calculate the amount of sample required from the TBN expected:

Approximate mass of sample (g) = 28/expected TBN

Add 120 ml of xylene–glacial acetic acid (2 + 1) by volume and stir the solution until the sample has dissolved. Position the electrodes immersed in the solution. Continue the stirring throughout the determination. Adjust the meter so that it reads in the upper part of the millivolt scale. Fill the burette with 0.1 mol l^{-1} perchloric acid in glacial acetic acid and record the initial cell potential reading.

For manual titration, add suitable small portions of titrant and, after waiting until a constant potential has been established, record the burette and meter readings.

For automatic titration, adjust the instrument in accordance with the manufacturer's instructions and set the titration speed at 1.0 ml min^{-1} maximum.

For each set of samples make a blank titration on 120 ml of xylene–glacial acetic acid (2 + 1).

Calculate the total base number as follows:

$$\text{TBN (mg g}^{-1}\text{ KOH)} = \frac{(V - V')\,M \times 56.1}{g}$$

where V = volume of perchloric acid (ml) used to titrate the sample to the inflection point on the titration curve, V' = volume (ml) corresponding to V for the blank titration, M = $HClO_4$ concentration (mol l^{-1}) and g = amount of sample (g).

Results and Discussion

Previous Tests

The determination of the TBN of used lubricating oils from marine engines following the IP–ASTM method was tested, but for this type of sample the repeatability was poor, the voltage stabilization was very slow and often the end-point was hardly detected. Several attempts were made to improve this method.

It was taken into account that the solvent used as the medium for the titration of weak bases in petroleum products must dissolve the sample completely, enhance the basicity of the species to be titrated and have a low solvating power for cations.[10]

Different solvents for both titrant and sample were tested and the other reagents were maintained as specified in the IP–ASTM method. Perchloric acid in dioxane as titrant reagent was tested, but no end-point was detected and the potential readings were very unstable. The use of xylene–propan-2-ol (9 + 1) as the sample solvent improved the voltage readings but there was no clear end-point detection (probably the weak bases to be titrated need an acidic solvent to enhance their basic properties).

Subsequently, several mixed solvents were tried, always containing acetic acid: toluene–acetic acid (2 + 1), toluene–propan-2-ol–acetic acid (9 + 1 + 5) and xylene–propan-2-ol–acetic acid (9 + 1 + 5). We thought that a ternary mixture solvent would be suitable owing to the complexity of the samples. In all three instances the voltage values were unstable and no sharp breaks at the end-point were detected. The addition of acetic anhydride to the samples to avoid problems due to the water content was also tested but the results were the same as described above.

Further trials were made, replacing the monochlorobenzene, used in the standardized method, with xylene. The solubility of the oils in this solvent was acceptable, the voltage stabilization was very rapid and the end-point could be detected very clearly owing to the high potential increments at the end-point. Some improvements were also observed when the perchloric acid was titrated with the standardized method but replacing the chlorobenzene–acetic acid used to dissolve phthalate with xylene–acetic acid. The time of analysis was shortened and sharper breaks at the end-point were observed.

Repeatability

The criteria used for judging repeatability results (95% confidence) with the IP–ASTM standard method of test for TBN of petroleum products by potentiometric perchloric acid titration when applied to used oils are 5% when forward titration is employed and 24% when back titration is required. During the development of this method the complete range of TBN was not covered. It was believed that reasonable interpolation and extrapolation from the ranges used would not introduce serious errors. The TBN range studied was 2.9–11 for used oils (TBN of 5.5–13 for fresh oils and 60–99 for additive concentrates were also studied).

The repeatability of the proposed method was evaluated by determining the TBN of 11 aliquots of the same sample following the procedure. A sample with a high TBN was chosen because it is very representative of the oils used in marine trunk engines. The results were mean = 26.63, standard deviation = 0.143, relative standard deviation =

Table 1 Potential increments at the end-point in the titration of different samples and TBN results obtained by both methods

	IP 276-83–ASTM D2896-92		Proposed method	
Sample No.	Potential increment/ mV ml^{-1}	TBN	Potential increment/ mV ml^{-1}	TBN
1	220	2.84	220	2.99
2	240	2.89	270	2.87
3	210	2.49	260	2.73
4	170	19.75	200	19.67
5	160	19.63	180	19.34
6	190	17.70	200	17.87
7*	130	21.43	210	21.42
8*	130	23.76	240	23.85
9	160	23.17	180	22.97
10	150	25.05	180	24.65
11	150	22.92	170	22.94
12	150	21.29	180	23.74
13	200	18.57	210	18.05
14	140	18.13	180	18.08
15	160	25.12	220	25.04
16	150	23.26	190	23.36
17	170	23.58	220	23.63
18	180	32.43	230	32.20
19	130	24.45	160	23.91
20*	140	26.65	190	26.62
21	130	30.11	190	30.17
22	140	30.11	180	30.02
23	150	28.39	220	28.51
94	140	27.41	210	27.90
25*	120	26.63	180	26.66
26	140	27.25	190	26.66
27	130	23.05	160	23.27
28	130	27.90	160	27.43
29	140	23.05	170	23.07
30	140	22.07	200	22.50
31*	130	26.36	150	25.45

* Samples requiring back titration in the IP–ASTM method.

0.043% and error = 0.36%. This percentage error is far better than that obtained by the standardized method (5% for forward titration or 24% for back titration).

Accuracy

The results obtained as described under Experimental were compared with those obtained by the IP–ASTM method for 31 samples of used oils of several tradenames taken from different ship engines. The TBN values obtained by both methods are given in Table 1. The Youden graph obtained showed that the correlation is very good (slope = 1, r = 0.997). The results obtained by the proposed method are considered to be more accurate because they show a better repeatability. The TBN of the unused oil was around 30 (very common in the crankcase of marine trunk engines). Used lubricating oil samples in this TBN range are not mentioned in the description of the IP–ASTM method. The TBN values obtained were lower than that of the unused oil, as expected.

Voltage Increases at the End-point

Comparison of the titration curves obtained by the two methods are shown in Fig. 1 for $HClO_4$ titration and in Fig. 2 for a sample titration.

The sample shown in Fig. 2(*b*) could not be titrated following the direct standardized method and required a back titration; however, it is easily titrated following the proposed direct method. As can be observed, the IP–ASTM method is not adequate for this application but TBN determination is possible when the modified method is used. This is not an exceptional case and it always occurs when the used oil results from many working hours.

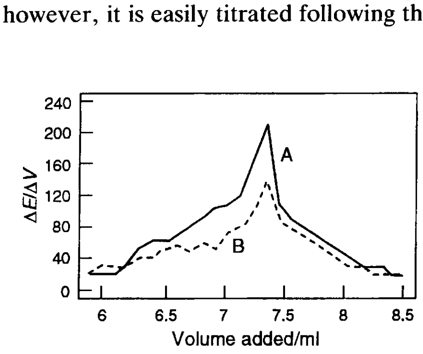

Fig. 1 Comparison of the $HClO_4$ titration curves obtained by A, the xylene and B, chlorobenzene methods.

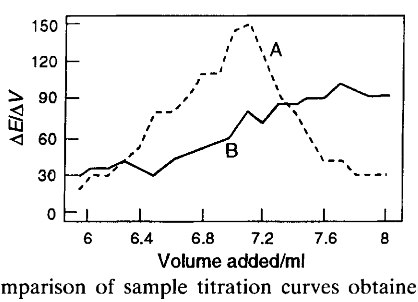

Fig. 2 Comparison of sample titration curves obtained by A, the xylene and B, the chlorobenzene methods.

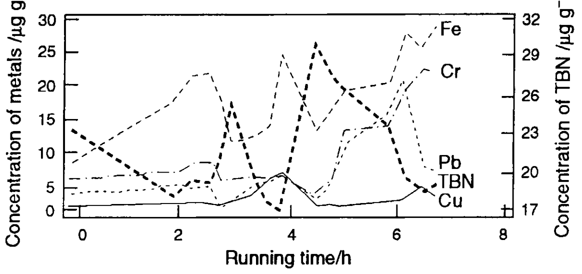

Fig. 3 Correlation between TBN values and wear metals.

The voltage increases at the end-point were compared. It is higher when the proposed method is used, mainly when the initial TBN is high. Also, the $HClO_4$ titration in both methods showed that the voltage increase at the end-point is higher for the proposed method.

Table 1 shows the voltage increase at the end-point for the titration of the 31 samples described above for both methods.

The voltage stabilization time after each addition of titrant is shortened when the proposed method is used. This is another advantage of the proposed method over the standardized method.

Correlation Between TBN Values and Wear Metals

The TBN value of a used oil decreases with increased engine working time. It has also been found that there is a correlation between TBN decrease and wear metal increase with time.

To verify this correlation, several samples were taken from the same engine (with the engine running) at fortnightly intervals. Iron, Cr, Cu and Pb wear metals were measured by atomic absorption spectrometry following a procedure developed previously.[12] The TBN was determined by the procedure proposed in this paper. The results are shown in Fig. 3.

As it can be seen, when the TBN decreases the wear metal concentration increases. Therefore, there is a direct relationship between TBN value and engine wear.

The peaks show the addition of new oil and therefore a TBN increase and wear metal decrease, but in spite of this a tendency for the TBN to decrease and the wear metal concentration to increase can be seen.

On some occasions, apart from the corrosive wear, it is necessary to take into account the abrasive wear, and in this event the correlation between wear and TBN is not so clear. However, in any case a decrease in the TBN values implies higher wear and the possibility of engine failure.

Conclusions

The control of quality-related parameters in marine internal combustion engines is of great importance because the oil is not usually changed. In spite of this, there is no accepted and reliable method for the analysis of used lubricating oil samples from marine engines with many working hours. A very simple modification of the standardized IP–2ASTM method suitable for used oils from marine engines has been proposed. The results of comparisons of the modified and standardized methods allowed us to draw the following conclusions when the modified method is used: the results are more precise; the voltage stabilizing time is shorter; it avoids back titration; and it allows the TBN determination in used lubricating oil samples from marine engines with many working hours, which is not possible with the standardized method. Consequently, the proposed method can be suggested as an alternative to the IP and ASTM methods.

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