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# DETERMINATION THE ACIDITY OF COLOURED OILS BY CATALYZED THERMOMETRIC TITRIMETRY

*Jian-Qiang Hu* [1], *Yong-Guo Zhang* [2], *Huan-Qinqin Zhu* [3], Shi-Zhao Yang [2]

[1] Air Force logistic college, Xuzhou, China, hjq555918@sohu.com
[2] Department of Aviation oil, Air Force logistic college, Xuzhou, Xuzhou, China, hongwen825@sohu.com
[3] Air Force logistic college, Xuzhou, China, huanqz@163.com

***Abstract*** Catalytic thermometric titrition has been developed for the determination of the acidity of oils. The amounts of oil, concentration and delivery rate of titrant, volumes and types of thermometric indicator were investigated. The results show that mixture of acetone and chloroform used as indicator exhibits strongly exothermic effects to reflect end point obviously. The method is fast, easy to use, accurate, and highly reproducible to measure lower acidity in non-coloured and coloured oils.

***Keywords***: acidity, coloured oil, catalytic thermometric titrimetry, determination

## 1. INTRODUCTION

The acidity of oils is an important quality control parameter to evaluate corrosion, by which we can estimate the properties and deteriorationof oils during usage and storage. The standard methods employed for the determination of acidity of oils are based either on visual indicators titrimetry or potentiometric titrimetry. However, accuracy of visual titrimetry is strongly influenced by the skill and color perception of the analyst, and variations between analysts can be considerable for coloured oils. Potentiometric titrimetry by employing a glass pH electrode in nonaqueous solutions can be unreliable owing to unobservation of end-point, and subject to the noxious effect of the sample solutions. In order to resolve quickly and efficiently determination of the end point in titrations, there is a need for a simple, fast, accurate, and precise automated titrimetric procedure that is substantially independent of the analyst's skill and that is suitable for routine process and quality control.

Catalytic thermometric titrimetry as a new method The has several attractive features: (1) the apparatus is simple, all that is required is a temperature measuring probe such as a thermometer or a thermistor as the sensing element; (2) the thermometric probes are inert to most solutions, the temperature changes in highly colored can be measured without difficulty; (3) the range of indicator reactions is unlimited because all reactions are accompanied by temperature change, the magnitude of which can be adjusted by changing the concentrations of the reagents[1]. The basic principle of the method is catalytic initiation of an exothermic or endothemic reaction by an excess of titrant, as a consequence, the end points in titrations is indicated by obvious temperature change of the solution[2]. It has been successfully applied to the determination of acidic substances in vegetable oils, and aluminumion concentration in wastewater[3-6].

When small amounts of weakly acidic species are titrated in nonaqueous solution with a titrant of strong alkali, the heat produced from the neutralization reactions may be quite small and easy to be confused by solvent evaporation and the mixing heat of the titrant with sample solution. If the special thermometric indicator was added to sample solution, excess hydroxide ions would react quickly with them endothermicly or exothermicly, the end-point can be easy to determine by a temperature increase or decrease of the solution.

However, practical experience has demonstrated that the end-point in thermometric titrition showed excessive rounding, with consequent loss of precision and accuracy for some oils with lower acidity, such as aviation oil,

hydraulic oil and fuel oils. Greenhow[6] have shown that titration error or the sharpness of the end-point can be related to the concentration and delivery rate of titrant, volumes and types of thermometric indicator.

In this paper, we report herein our results on the determination of the acidity of some coloured oils by catalytic thermometric titrimetry employing the mixture of acetone and chloroform as the end-point indicator, and compared with potentiometric and visual titration, the accuracy and repeatability of the thermometric titration was futher tesified.

## 2. EXPERIMENTAL

### *2.1. Reagents*

Potassium hydroxide and isopropanol were of analytical reagent (A.R.) quality. The grades of acetone and chloroform were chosen for their minimal water contents. A 0.10 mol/L potassium hydroxide isopropanol solution was prepared and standardized with potassium hydrogen phthalate by the usual procedures. Hydraulic oil, aviation lubricating oils, and diesel oil were employed in this investigation. The oil samples used in this work were commercial samples obtained from lubricant manufacturers. Standard acid solution was prepared from approximately 37.8 mg benzoic acid dissolved with 250 mL isooctane, and acid value of standard acid is 0.10 mgKOH/g.

### *2.2. Apparatus*

In thermometric titrations, two motor-driven micrometer syringe were employed to add the titrant to samples at a constant delivery rate, and a magnetic stirrer was provided to dissolve oil solutions, the temperature changes were detected by locating the themistor in one arm of a weatstone bridge and were recorded with a strip chart recorder. At the end of each titration, sample and titration data were automatically sent for identification and computation, the acidity of oil samples was obtained from auto-calculation. In potentiometric titrations, a pH probe containing both a glass and a reference electrode in the same body was employed.

### *2.3. Procedures*

In visual titrations, the amount of oil was chosen in accordance with the ASTM D974 method, 8 g oil samples was dissolved in 125 mL ethanol solvent, 0.5 mL 2% ethanol solution of alkali blue 6B was added and the solution was titrated with 0.1 mol/L KOH ethanol solution.

In the case of catalytic thermometric titrition, oil samples were accurately weighed into clean, dry 125 mL silvered Dewar flask, then 25 mL acetone and 4 mL chloroform were homogenized by using a magnetic stirrer. The 0.10 mol/L KOH titrant solution is added at a constant delivery rate of 0.5 mL/min to the stirred solution. End points were determined using a peak-picking algorithm applied to the second derivative curve computed from the smoothed temperature data. During titrations, there is a blank to be determined. The blank is a summation of all delays inherent in the titration solution under defined experimental conditions. These delays include contributions from kinetics of the chemical reaction between titrant and titrand, sensor response, mixing inefficiencies, electronic transfer and computation of data. The volumes of the titrant obtained in the blank solution titration were subtracted from those the initial titration data of oil samples. Each titration experiments were performed in four times.

In the case of potentiometric titrations, except for oil samples were dissolved in 125 mL of the solvent mixture (isopropanol and toluene), the oil samples stirring, dissolution and titrant addition procedures were employed accordance with the ASTM D664 method.

## 3. RESULTS AND DISCUSSION

### *3.1. Thermometric titration in oil samples*

The titration of coloured samples of hydraulic oil, aviation lubricating oil and diesel oil was investigated by catalytic thermometric titrimetry, employing acetone and chloroform as end-point indicator. By comparison, potentiometric titration and visual titration methods were employed to anylyze with the same oil samples. The thermometric titration curves obtained from three oil samples are shown in Figure 1, 2 and 3, from which we can see clearly that there were obvious temperature changes in thermometric titration curves, where the second-derivative plot is presented along with the solution temperature plot. According to sharper end-point inflection we can calculate

Table 1 Results from the acid number of oil samples by

thermometric, potentiometry and visual titrimetry

| Oil Samples | Thermometric Titrimetry | | Potentiometric Titrimetry | Visual Titrimetry |
|---|---|---|---|---|
| | Acid number, mgKOH/g | relative SD, % | Acid number, mgKOH/g | Acid number, mgKOH/g |
| aviation oil | 0.288 | 0.48 | 0.272 | 0.31 |
| hydraulic oil | 0.055 | 0.62 | 0.058 | 0.63 |
| diesel oil | 0.032 | 1.15 | 0.031 | 0.029 |

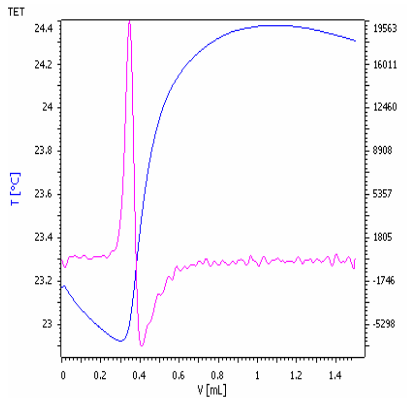


Figure 1 Thermometric titration curve of 5g aviation oil

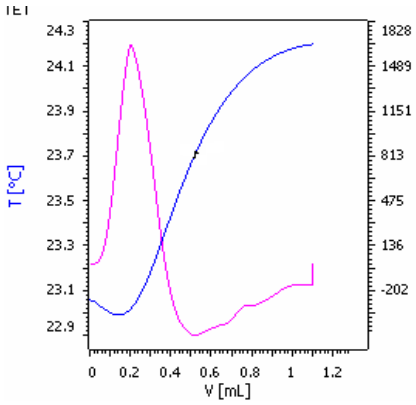


Figure 2 Thermometric titration curve of 10g hydraulic oil

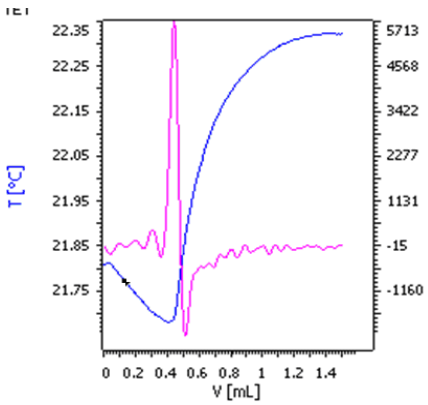


Figure 3 thermometric titration curve of 20g diesel oil

the results of the acidity of the oil samples which are listed in Table 1. In this table the results obtained for the acid numbers by the proposed method are compared with those obtained by potentiometric and visual titration. The indicator system with acetone and chloroform gives highly reproducible results.

In the case of hydraulic and aviation lubricating oils, the results from catalytic thermometric titrimetry present a better agreement with those obtained by potentiometric titrimetry than those obtained by visual titrations. The large discrepancy between the results from catalytic thermometric and visual titration, may be related to the difficulty in observing the colour change of alkali blue indictor at the end point of the visual titration, owing to the said oils with dark colour. In the case of diesel oil, the results obtained by catalytic thermometric titrimetry agree quite well with those obtained with either potentiometric or visual titrimetry. Therefore, the catalytic thermometric titrimetry method may be choosen as an alternative method for determining the acidity of oils. In fact it has advantages over both of potentiometric and visual methods, because it can be applied to coloured oils, and over the potentiometric method as regard to the sample processing speed and simplicity, the whole measuring process only 3-5 min, even the range of acid numbers included in the precision statement is lower than 0.1 mg/g KOH.

### *3.2. Thermometric titration in standard acid samples*

In order to testify the accurity of the method of catalytic thermometric titrimetry, different mass of benzoic standard acid samples was investigated, the results are listed in Table 2. The coefficient of correlation ($R^2$) for the linear calibration curve was found to be 0.99965, which was shown in Figure 2. The system offset was determined to be 0.069 mL. From which we can see clearly that the acid numbers of five standard acid samples were very similar to real acid number (0.10 mgKOH/g). These obsevations confirm that thermometric titrimetry is an accurate and highly reproducible method, which was easy to determine acidity of colored or additive-containing petroleum oils in titrations.

In thermometric titrations, the titrant must be added to solution at a constant delivery rate, which could bring about constant heat absorbtion and radiation, so as to make sure constant temperature changes in solution before the end-point. The concentration and delivery rate of

titrant may be adjusted the delivery rate of KOH titrant according to acid number and size of oil samples. It was found that acceptably sharp end-point inflections were achieved by using 0.10 mol/L potassium hydroxide isopropanol with constant delivery rate of 0.5 mL/min.

Table 2 The determination results of different mass of standard acid samples

| m(Oil)/g | V[1](KOH)/mL | Acid number/(mgKOH·g$^{-1}$) |
|---|---|---|
| 5.0 | 0.1679 | 0.09942 |
| 7.5 | 0.2141 | 0.09935 |
| 10.0 | 0.2633 | 0.09964 |
| 12.5 | 0.3113 | 0.09916 |
| 15.0 | 0.3587 | 0.09922 |

1) The volume containing blank value

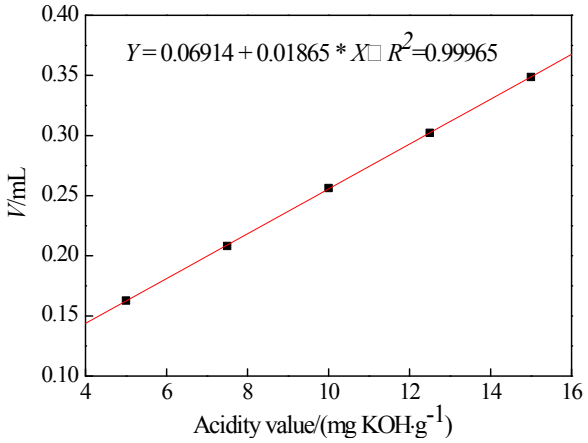


Figure 2 Linear regression equation for benzoic acid samples

The mixtures of acetone and chloroform are known to react vigorously when basified, the results show that two reagents were added separately, and chloroform was delivered after oil samples dissolved in acetone. However, there was no evidence of uncontrolled exothemic effects either during or after the titration. In fact, the exothemic rate of the sample solution increased shortly after the end point. In addition, the amount of acetone and chloroform play an important role on determination of end-point. In preliminary experiments, it was found that relatively sharp end-point could still be obtained by using 25 mL acetone and 4 mL chloroform for oils with lower acidity. Increasing or decreasing the amount also caused end-point rounding and loss in precision of the determination.

It may also be noted that the titration is performed in a dewar flask with a closely fitted lid, through which the titrant delivery buret and thermometric probe are inserted. Apart from preventing heat exchange from environment, loss of volatile components is also minimized.

## 4. CONCLUSIONS

The catalytic thermometric titrition is a fast, easy to use, accurate, and highly reproducible method to determine lower acidity in coloured oils by using the mixture of acetone and chloroform as the end point indicators. The method has more advantages than the potentiometric and visual titration as regard to speed and simplicity and accuracy for dark coloured oils. It is very suitable for the routine process and quality control of non-coloured and coloured oils, among other applications.

The mixture of acetone and chloroform used as the end point indicators can exhibits strongly exothermic base catalyzed reaction in thermometric titrition, which has good agreement with standard acid samples.

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