AQUACOUNTER Application Sheet	COM series	DATA No. L6	1st edition

Petroleum Products — Measurement of total acid value in turbine oils

1. Measurement outline

The method for measuring total acid value in turbine oils is stipulated in JIS K 2213, and it is an important test item. JIS K 2213 adopts the total acid value measurement method stipulated in JIS K 2501. The total acid value expressed as the milligram (mg) value of potassium hydroxide (KOH) required to neutralize the total acidic components contained in 1g of sample.

This section introduces an example of total acid value measurement for a turbine oil (used) by acid value measurement method in conformance to JIS K 2501.

The total acid value for turbine oils are at the level of 0.3mg/g for new oils, and individual errors tend to occur in end point detection by visual inspection. In this section, total acid value of a turbine oil was measured using potentiometric titration method instead of titration by visual inspection.

In this method, the sample volume corresponding to total acid value is collected and weighed according to JIS K 2501 and is added and dissolved in toluene：2-propanol titration solvent. Then the electrodes are immersed for titration with 0.1mol/L potassium hydroxide titrant.

2. Reagents and Electrodes

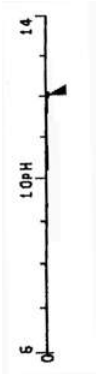
(1) Reagents	Titrant	0.1mol/L potassium hydroxide (2-propanol type)
	Titration solvent	Toluene 500mL 2-propanol 495mL DI Water 5mL } 1L…125mL used for 1 measurement
	Non-aqueous basic buffer	Commercial buffer stock solution B Add 10mL to 100mL titration solvent and mix.
(2) Electrodes * standardaccessories	Indicator electrode	*Glass electrode GE-101B to IE-1 jack
	Reference electrode	*Reference electrode RE-201 to RE-1 jack
	Thermistor electrode	*Thermistor electrode TE-401 to TE jack

3. Measurement conditions example (for COM-1600S)

Master File 1 **Condition 1** (for BLANK)				**Master File 2** **Condition 2** (for TAN measurement)			
Method	Set			Method	Set		
Buret No.	1	Mode No.	12	BURET No.	1	Mode No.	11
Meas Unit	pH	Pre Int	20 sec	Meas Unit	pH	Pre Int	20 sec
S-Timer	10 sec	Del K	0	S-Timer	10 sec	Del K	0
CP pH	0.00 pH	Del Sens	0 mV	CP pH	00.0 pH	Del Sens	0 mV
Direction	UP	Int Time	10 sec	Direction	UP	Int Time	10 sec
DP pH	0.00 pH	Int Sens	0 mV	DP pH	00.00 pH	Int Sens	0 mV
End pH	12.05 pH	Brt Speed	2	End Point	12.05 pH	Brt Speed	2
Over mL	0.1 mL	Pulse	10	Over mL	0.1 mL	Pulse	20
Max volume	20 mL			Max Volume	20 mL		
Size	0 g			Unit	mg/g		
Blank	0 mL			Size	-- g		
Factor	Titre of the titrant			Blank	BLANK result value		
Molarity	0.1 mol/L			Factor	Titre of the titrant		
K	56.1 (as KOH)			Molarity	0.1 mol/L		
L	0			K	56.1 (as KOH)		
Formula	D			L	0		
				Formula	(D-B)*K*F*M/S		
					to be set automatically.		

4. Measurement example

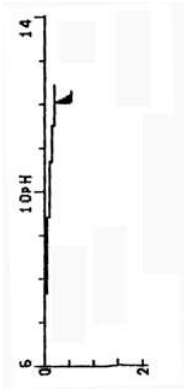
(1) Blank measurement



Blank measurement results

Sample No.	Titration value (mL)	Average value (mL)
1	0.0781	0.0810
2	0.0839	

(2) Sample measurement



Measurement results on total acid value of turbine oils

Sample No.	Sample volume (g)	Titration value (mL)	Total acid value (mg/g)
1	20.291	0.2091	0.0356
2	20.014	0.2067	0.0354
	Avg.		0.0355 mg/g

5. Outline

(1) Maintenance of electrode performance

While this measurement used a glass electrode and a reference electrode for titration, the response of glass electrode may deteriorate or the electromotive force may deteriorate when titration is repeated for a long period. Thus it can be restored by immersing in water for 5 minutes when one measurement is completed. In addition, the inner KCl solution may precipitate on the liquid junction block of the reference electrode and cause a potential difference fluctuation. It is important to immerse the glass electrode in water periodically to restore the performance.

(2) Buret maintenance

Since alcoholic KOH is used as the titrant for total acid value measurement, crystals form within the buret cylinder or the sliding block between the buret cylinder and plunger. It is important that they are rinsed with water regularly. If the buret is not to be used for a long period, remove the titrant and wash well before putting into storage.

(3) The effect of temperature change on titer of the titrant

Organic solvent (2-propanol) is used in the titrant of this measurement, and caution is required due to the change in volume with respect to temperature change (approximately 0.11% change at 1°C). This is larger compared to normal titrants with aqueous solution. It is important that measurement is taken at a temperature as constant as possible.

If the temperature for titer evaluation of the titrant and the temperature for titration vary, it can be corrected by substituting the following titer correction formula into concentration calculation formula.

$$F = \frac{F_0}{1 + \alpha(t - t_0)}$$

F : Titer for sample titration (corrected)
F_0 : Titer at the time of titer evaluation
α : Volumetric expansion coefficient for the titrant
t : Temperature for sample titration
t_0 : Temperature for titer evaluation

(4) Effect of carbon dioxide gas during measurement

Since the total acid value is measured by titration using potassium hydroxide titrant, the pH of the titrated solution stays basic. Therefore, it tends to absorb carbon dioxide gas in the air and then increases in the measurement value. For measurement conditions in which the measurement may take a long period, measures to titrate while purging with nitrogen gas, etc. are necessary.

(5) Total acid value measurement using an automatic titration system (introduction of Japan Petroleum Institute)

Besides the total acid value measurement method by visual inspection stipulated in JIS K 2501, another method of total acid value measurement in which individual errors at end point detection are reduced is stipulated as Total acid value measurement method "Japan Petroleum Institute Lubricating oils – Neutralization value test method – The method for total acid number – Color indicator – Transmissivity Titration (JPI-5S-48-97)." As an outline of this standard, change in indicator during titration process is detected photometrically to measure the end point, and it has an advantage of being capable of obtaining measurement results without individual errors.

Key words

Turbine oils, total acid value, neutralization value test

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