AQUACOUNTER Application Sheet	COM series	DATA No. L1	1st edition

Petroleum Products — Measurement of total acid value in lubricants

1. Measurement outline

The total acid value of lubricants is one of the important indices for evaluating the quality of lubricants. The method for total acid value is stipulated in JIS K 2501, and it is expressed as milligrams (mg) of potassium hydroxide (KOH) required to neutralize the total acidic components contained in 1g of sample. The components for total acid value are organic and inorganic acids, esters, phenolic compounds, lactones, resins, salt of heavy metals, and additives such as antioxidants and detergents. Test methods for total acid value are mainly classified into the color indicator titration methods (p-naphthol benzene indicator) and the potentiometric titration method. The following lists the related measurement methods:

- JIS K 2501: Total acid value
  - Color Indicator titration method
  - Potentiometric titration method
- ISO 6618-1997: Neutralization value test method by indicator titration method
- ISO 6619-1988: Neutralization value test method by potentiometric titration method
- ASTM D664-1995: Acid Number of Petroleum Products by potentiometric titration
- ASTM D974-1997: Neutralization value test method by color indicator titration method
- The Japan Petroleum Institute Standard JPI-58-48-97: Indicator photometric titration method (automatic titration method)

In the indicator titration method, the sample is titrated by potassium hydroxide titrant using p-naphthol benzene indicator. Though this method has the advantage of a short measurement period, it is limited to light color oils or oils with relatively few additives. Meanwhile, the potentiometric titration method has the advantage of not being limited in measurement subject oils including colored or used oils though it requires time in measurement. This section introduces an example in which the total acid value of diesel engine oil (used) was measured by potentiometric titration method.

In this method, the sample volume corresponding to total acid value is weighed precisely to be added and dissolved in a mixture of toluene and propan-2-ol. Electrodes are then immersed for titration with 2-propanol-type potassium hydroxide titrant. For samples which have well-defined inflection points, end points are taken only at well-defined inflections. When no definite inflections are obtained, the pH indicated by non-aqueous basic buffer is considered as the end point for samples with unclear inflection points.

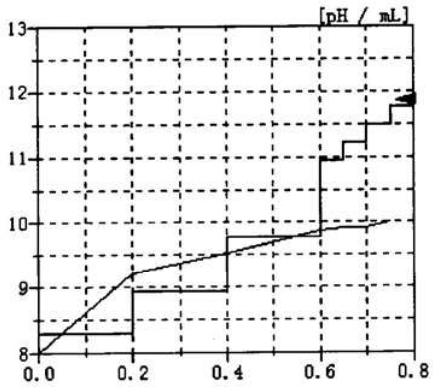
2. Reagents and Electrodes

(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 *standard accessories	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	Oil 1		
Buret No.	1	Mode No.	18	BURET No.	1	Mode No.	3
Meas Unit	pH	Pre Int	0 sec	Meas Unit	pH	Del mL 1	0.05 mL
S-Timer	120 sec	Del K	0	S-Timer	120 sec	Int Time 1	60 sec
CP pH	10.00 pH	Del Sens	0 mV	CP pH	10.0 pH	Tran Timer	180 sec
Direction	UP	Int Time	120 sec	Direction	UP	Del mL 2	0.05 mL
DP pH	10.00 pH	Int Sens	0 mV	DP pH	10.00 pH	Int Time 2	60 sec
End pH	11.86 pH	Brt Speed	2	End Point	11.86 pH	Int Time	0 sec
Over mL	0.5 mL	Pulse	40	Over mL	0.5 mL	Int Sens	0 mV
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



Total acid value measurement results

Sample No.	Sample size (g)	Titration value (mL)	Total acid value (mg/g)
1	5.0110	0.764	0.6706
2	5.0154	0.768	0.6744
3	5.0099	0.778	0.6861
Avg. (Average value)			0.680 mg/g
Std. Dev. (Standard deviation)			0.008 mg/g
C.V. (Coefficient of variation)			1.2 %

5. Outline

(1) The end point detection method

The method in which the inflection point of the titration curve is considered the end point and the method in which a certain pH preset on the titration curve (pH indicated by non-aqueous basic buffer) is considered the end point are possible. The former can be used for samples that show clear inflection points on the titration curves. The latter is applied for samples that do not show inflection points on the titration curves. In general, many of the samples for measurement of total acid value do not show clear inflection points, and the latter measurement method is used.

(2) Dropping control

In general, measurement of total acid value in oils by the potentiometric titration method has a slow reaction speed as well as electrode response speed, and it is necessary that the titration be conducted fast in the beginning and slowly near the end point. For the purpose of reducing the measurement period, 0.1 – 0.2mL (dropping volume 1) is titrated at a certain interval (waiting period 1) in the beginning of titration then dropping is paused at the point where potential difference becomes large. It is then paused for a certain period (transition period) until the reaction between the titrant added so far and the sample completes. Titration is resumed when the transition period has passed with dropping volume of 0.05 – 0.1mL (dropping volume 2) at a certain interval (waiting period 2) until the titration end point is reached.

(3) Maintenance of electrode performance

While this titration used a glass electrode and a reference electrode for titration, the response of the 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 periodically. 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.

(4) 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.

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

Organic solvent 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 1ºC). This is larger compared to normal titrants with aqueous solution. It is important that measurement is taken at a temperature that is 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

Key words

Lubricants, total acid value, neutralization value test

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