

AQUACOUNTER Application Sheet	COM series	DATA No. L4	1st edition
Petroleum Products		Measurement of total acid value in transformer oils	

1. Measurement outline

The methods for evaluating the level of degradation for electrical insulation oils used in transformers is stipulated in JIS C 2101 “Testing methods of electrical insulating oils.” Among these evaluation items for degradation level, measurement of total acid value for insulation oils is an important test and evaluation item. The total acid value is expressed as the milligram (mg) value of potassium hydroxide (KOH) required to neutralize the total acidic components contained in 1g of sample. Oxidation advances as degradation advances in transformer oils, and the oils become gradually colored in red brown. The test method stipulated in JIS C 2101 is a photometric titration method using alkali blue 6B indicator. The acid value of transformer oils is at the level of 0.1mg/g or smaller for new oils and about 0.5mg/g for most degraded oils, and individual errors tend to occur in end point detection by visual inspection.

This section introduces an example in which the total acid value of transformer oil was measured by potentiometric titration method instead of photometric titration with visual inspection.

In this method, the sample volume corresponding to total acid value is collected and weighed precisely according to JIS C 2101 and is added and dissolved in toluene : ethanol (3 : 2) solvent mixture. Then the electrodes are immersed for titration with 0.05mol/L potassium hydroxide titrant. The titration end point was set in the system by measuring the pH for the point of color change in the indicator at the end point in advance.

2. Reagents and Electrodes

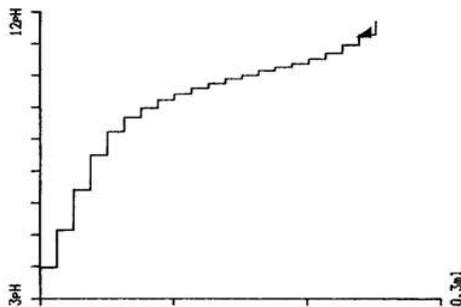
(1) Reagents	Titrant	0.05mol/L potassium hydroxide (ethanol solution)
	Titration solvent	Toluene : ethanol (3 : 2) mixture, 100mL used for 1 measurement Note) For silicone oils, toluene : 2-propanol (1 : 1) solvent mixture
(2) Electrodes * standard accessories	Indicator electrode	*Glass electrode GE-101B to IE-1 jack
	Reference electrode	*Reference electrode RE-201 to RE-1 jack

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

Master File 1				Master File 2			
Condition 1 (for BLANK)				Condition 2 (for TAN measurement)			
Method	Set			Method	Set		
Buret No.	1	Mode No.	20	BURET No.	1	Mode No.	3
Meas Unit	pH	Pre Int	0 sec	Meas Unit	pH	Del mL 1	0.05 mL
S-Timer	0 sec	Del K	0	S-Timer	0 sec	Int Time 1	60 sec
CP mL	0 mL	Del Sens	0 mV	CP mL	0 mL	Tran Timer	180 sec
Direction	UP	Int Time	30 sec	Direction	UP	Del mL 2	0.05 mL
DP mL	0 mL	Int Sens	0 mV	DP mL	0 mL	Int Time 2	60 sec
End pH	11.25 pH	Brt Speed	2	End Point	11.25 pH	Int Time	0 sec
Over mL	0.01 mL	Pulse	40	Over mL	0.01 mL	Int Sens	0 mV
Max volume	5 mL			Max Volume	5 mL		
Unit	mL			Unit	mg/g		
Size	0 g			Size	-- g		
Blank	0 mL			Blank	BLANK result value		
Factor	Titre of the titrant			Factor	Titre of the titrant		
Molarity	0.05 mol/L			Molarity	0.05 mol/L		
K	56.1 (as KOH)			K	56.1 (as KOH)		
L	0			L	0		
Formula	D			Formula	(D-B)*K*F*M/S to be set automatically.		

4. Measurement example

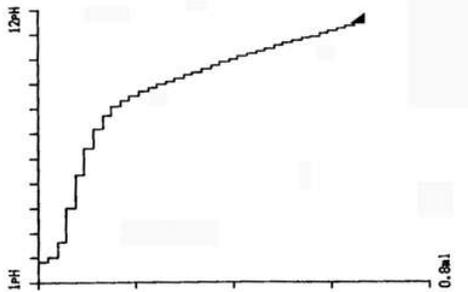
(1) Blank measurement



Blank measurement results

Sample No.	Titration value (mL)	Average value (mL)
1	0.235	0.237
2	0.239	

(2) Sample measurement



Measurement results on total acid value of transformer oil

Sample No.	Sample volume (g)	Titration value (mL)	Total acid value (mg/g)
1	20.321	0.649	0.0512
2	20.111	0.634	0.0507
3	20.061	0.633	0.0507
Avg.			0.0512 mg/g
Std. Dev.			0.0008 mg/g
C.V.			1.5 %

5. Outline

(1) Maintenance of electrode performance

While this measurement 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 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 (ethanol) 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)
- F₀ : Titer at the time of titer evaluation
- α : Volumetric expansion coefficient for the titrant
- t : Temperature for sample titration
- t₀ : 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, 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 C 2101, 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 electrical insulating oils – Neutralization value test method – Determination of total acid value (JPI-5S-57-99).” 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

Transformer oils, electrical insulation oils, total acid value, neutralization value test

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