

AQUACOUNTER Application Sheet	COM series	DATA No. L5	1st edition
Petroleum Products		Measurement of total acid value in freezer oils	

1. Measurement outline

The lubricants for freezers are used by mixing with the coolant (chlorofluorocarbon-type or ammonia-type). Evaluation tests for freezer oils are stipulated in JIS K 2211, and they are important test items. 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.

In JIS K 2211, the total acid value measurement method stipulated in JIS K 2501 is adopted.

This section introduces an example in which the total acid value in a freezer oil (used) was measured by photometric titration with an automatic titration system using the measurement unit for photometric titration by applying the indicator titration in JIS C 2101 “Testing methods of electrical insulating oils.”

The test method stipulated in JIS C 2101 is a photometric titration method using alkali blue 6B indicator. The acid value of freezer oils is at the level of 0.2mg/g for most degraded oils, and individual errors tend to occur in end point detection by visual inspection. In this section, total acid value of a freezer oil was measured using an automatic titration system incorporating a measurement unit for photometric titration instead of photometric titration by 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 determined by the point of color change for the indicator.

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
	Indicator	0.15g alkali blue 6B dissolved in 100mL ethanol and filtered.
(2) Electrodes	Photometric probe with 650 nm filter	

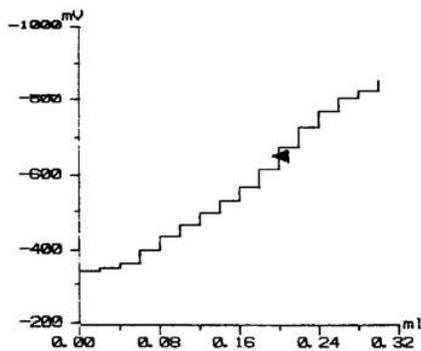
3. Measurement conditions example (for COM-1600M)

Master File No.1	
Condition file: 1	
Parameters for Condition file 1	
Method	AUTO
Buret No.	1
Meas Unit	mV
S-Timer	20 sec
CP mL	0 mL
DP mL	0 mL
Direction	N/A
End Sens	1500
Over mL	0.10 mL
Max Vol	20 mL
Mode No.	23
Unit	mg/g
Formula	$(D-B) \times K \times F \times M / S$
Blank	BLANK measurement value
Molarity	0.05
Factor	Titre of the titrant
K	56.1 (as KOH)

Mode No.23	
Pre Int	0 sec
Del K	0
Del Sens	0 mV
Int Time	15 sec
Int Sens	0 mV
Brst Speed	2
Pulse	64

4. Measurement example

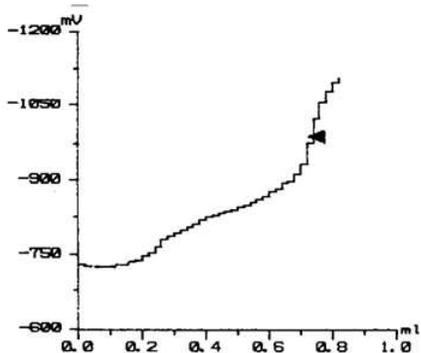
(1) Blank measurement



Blank measurement results

Sample No.	Titration value (mL)	Average value (mL)
1	0.1940	0.1935
2	0.1930	

(2) Sample measurement



Measurement results on total acid value of freezer oils

Sample No.	Sample volume (g)	Titration value (mL)	Total acid value (mg/g)
1	20.0163	0.726	0.0724
2	20.0042	0.725	0.0723
Avg.			0.0724 mg/g

5. Outline

(1) Maintenance of the liquid immersion type probe electrode

Indicator, etc. gradually adheres to the lens, mirror, etc. and the change in transmittance decreases as the liquid immersion type probe electrode is repeatedly used. Therefore it is important that the attached substances be wiped off regularly with soft paper, etc.

(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) About 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 taken 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

Freezer oils, total acid value, neutralization value test

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