

AQUACOUNTER Application Sheet	COM series	DATA No. L2	1st edition
Petroleum Products	Measurement of total base value in lubricants (hydrochloric acid method)		

## 1. Measurement outline

The total base value for lubricants is one of the important indices for evaluating the quality of lubricants. The method for measuring the total base value is stipulated in JIS K 2501, and it is expressed as the milligram (mg) value of potassium hydroxide (KOH) equivalent for the hydrochloric acid or perchloric acid required for neutralizing the total basic components contained in 1g of sample. The components for total base value are organic bases, inorganic bases, amino compounds, weak acid salts (soaps), basic salts of polybasic substances, heavy metal salts, and additives such as antioxidants and cleansers. The methods for measuring total base value are hydrochloric acid method and base value-perchloric acid method (abbreviated as perchloric acid method hereafter). The following lists the related measurement method:

- JIS K 2501: Total base value
  - Hydrochloric acid
  - Perchloric acid method
- ASTM D4739-1996: Base value test method by potentiometric titration method (hydrochloric acid method)
- ISO 3771-1994: Base value test method by potentiometric titration method (perchloric acid method)
- ASTM D2896-1998: Base value test method by potentiometric titration method (perchloric acid method)

This section introduces an example in which the total base value of diesel engine oil (used) was measured by hydrochloric acid method.

In this method, the sample volume corresponding to total acid value is weighed precisely to be added and dissolved in solvent mixture of toluene : 2-propanol. Electrodes are then immersed for titration with 2-propanol-type hydrochloric acid titrant. While the inflection point is considered the end point for samples which clearly show inflection points at titration end point, the pH indicated by non-aqueous basic buffer is considered as the end point for samples with unclear inflection points

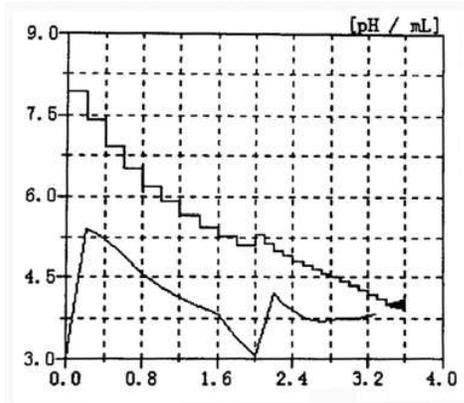
**2. Reagents and Electrodes**

(1) Reagents	Titrant	0.1mol/L Hydrochloric acid (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 A Add 10mL to 100mL titration solvent and mix.
(2) Electrodes	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
*standard accessories		

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

<b>Master File 1</b>				<b>Master File 2</b>			
<b>Condition 1 (for BLANK)</b>				<b>Condition 2 (for TBN measurement)</b>			
Method	Set			Method	Oil 1		
Buret No.	1	Mode No.	19	Amp No.	1	Mode No.	5
Meas Unit	pH	Pre Int	0 sec	Meas Unit	pH	Del mL 1	0.20 mL
S-Timer	180 sec	Del K	0	S-Timer	120 sec	Int Time 1	60 sec
CP pH	0.00 mL	Del Sens	0 mV	CP pH	4.50 pH	Tran Timer	180 sec
Direction	Down	Int Time	120 sec	Direction	Down	Del mL 2	0.10 mL
DP pH	0 mL	Int Sens	0 mV	DP pH	4.00 pH	Int Time 2	120 sec
End pH	3.69 pH	Brt Speed	2	End pH	3.69 pH	Int Time	0 sec
Over mL	0.20 mL	Pulse	80	Over mL	0.20 mL	Int Sens	0 mV
Max volume	1mL			Max Volume	20 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	0.1 mol/L			Molarity	0.1 mol/L		
K	0			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



**Total base value measurement results**

Sample No.	Sample volume (g)	Titration value (mL)	Total base value (mg/g)
1	5.0074	3.396	3.7245
2	5.0253	3.544	3.8741
3	5.0045	3.502	3.8438
<b>Avg.</b>			<b>3.81 mg/g</b>
<b>Std. Dev.</b>			<b>0.08 mg/g</b>
<b>C.V.</b>			<b>2.07 %</b>

#### 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 used oil samples do not show clear inflection points while new oil samples show clear inflection points, and thus the end point detection method shall be selected depending on the sample.

(2) Dropping control

In general, the measurement of total base value in oils by 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 the 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 a dropping volume of 0.05 – 0.1mL (dropping volume 2) at a certain interval (waiting period 2) until 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 the 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 for restore the performance.

## (4) 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 regard 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 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<sub>0</sub> : Titer at the time of titer evaluation  
α : Volumetric expansion coefficient for the titrant  
t : Temperature for sample titration  
t<sub>0</sub> : Temperature for titer evaluation

**Key words**

Lubricants, total base value, neutralization value test, JIS K 2501

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