HIRANUMA APPLICATION DATA	Automatic Titrator	Data No.	L14	Oct.23 2024
Lubricant petroleum products	**Base number in Petroleum products (Hydrochloric acid method)**			

1. Abstract

The base number of petroleum products are one of the important index for judging its quality.

Measurement of base number is defined in several standard test methods. It is indicated by "milligrams of potassium hydroxide equivalent weight to acid required to neutralize basic components contained in 1 g of the sample". There are two methods of base number, hydrochloric acid method and perchloric acid method. The international standard methods for base number are shown as bellow.

- ASTM D 4739 : Standard Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration
- ASTM D 2896 : Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration
- JIS K2501 : Petroleum products and lubricants - Determination of neutralization number
- ISO 3771 : Potentiometric titration method for base number (perchloric acid method)

This data sheet presents an example of how the base number of a petroleum product is measured by the hydrochloric acid method (ASTM D 4739).

The potentiometric titration process is as follows:

1) Weigh sample exactly corresponding to base number and dissolve it in a titration solvent.
2) Immerse glass electrode and reference electrode.
3) Start titration with alcoholic hydrochloric acid solution.

Inflection point is defined as the end point if it obtained sharply. If it's not clear, the endpoint is the potential mV indicated by the pH 3 standard. This data sheet shows examples of base number measurements for samples with well-defined and unclear inflection points.

2. Configuration of instruments and reagents

(1) Configuration of instruments

Main unit	:	Automatic Titrator	COM Series
Electrode	:	Glass electrode	GE-103B
	:	Reference electrode	RE-201Z
		(Inner solution: 1-3 mol/L lithium chloride ethanol solution)	

* Instead of glass and reference electrodes, the following glass-reference combination electrodes can also be used.

: GR-513BZ (for non-aqueous titration, movable sleeve type)

(2) Reagents

Titrant : 0.1 mol/L hydrochloric acid in 2-propanol standard solution

Titration solvent : Mixture of 500 mL of chloroform, 500 mL of toluene, 500 mL of 2-propanol, and 15 mL of water.

pH 3 buffer solution : Used to determine endpoint potentials when inflection points are not available.

3. Measurement procedure

(1) Determination of the end point mV

i) Put the stirrer bar in pH 3 buffer solution and immerse electrodes. Read the mV value after the 5 minutes and is taken as the endpoint mV.

(2) Measurement of Base number

i) A sample is taken in a 200 mL tall beaker and weighed to the nearest 0.1 mg digit. The volume of sample taken is determined by the expected base number.

ii) Add 75 mL of titration solvent and dissolve sample by stirrer.
The stirrer speed must be adjusted to avoid the scattering of contents or taking the air into the solution.

iii) Immerse the electrodes and titrated with 0.1 mol/L 2-propanol hydrochloric acid standard solution. The inflection point that appears between the potential indicated by the pH3 buffer solution (212.3 mV in this example) and its +100 mV above is detected as the endpoint. Otherwise the potential indicated by the pH3 buffer solution is detected as the endpoint. Also, perform the blank test with the same procedure of sample measurement.

4. Measurement conditions and results

Examples of titration conditions

Measurement of endpoint potentials

Cndt No.	1	
Method	pH Meas.	
AMP No.	1	
D. Unit	mV	
S. Timer	300	sec

Measurement of blank

Cndt No.	2							
Method	Auto/Set		ConstantNo.	2		Mode No.	20	
Buret No.	1		Size	0	g	Pre Int	0	sec
Amp No.	1		Blank	0	mL	Del K	0	
D. Unit	mV		Molarity	0	mol/L	Del Sens	0	mV
S- Timer	0	sec	Factor	0		Int Time	12	sec
C.P. mV	-2000	mV	K	0		Int Sens	0	mV
Direction	↓		L	0		Brt Speed	2	
T- Timer	0	sec				Pulse	8	
D.P. mV	212.2	mV	Unit	mL				
End Sens	50		Formula	D				
End Point	212.3	mV	Digits	3				
Over mL	332.2	mV						
Max.Vol.	2	mL						

Measurement of sample

Cndt No.	3							
Method	Auto/Set		ConstantNo.	3		Mode No.	21	
Buret No.	1		Size	0	g	Pre Int	0	sec
Amp No.	1		Blank	0.005	mL	Del K	0	
D. Unit	mV		Molarity	0.1	mol/L	Del Sens	0	mV
S-Timer	0	sec	Factor	0.985		Int Time	90	sec
C.P. mV	-2000	mV	K	56.1		Int Sens	0	mV
Direction	↓		L	0		Brt Speed	2	
T- Timer	0	sec				Pulse	80	
D.P. mV	212.2	mV	Unit	mg/g				
End Sens	50		Formula	(D-B)*K*F*M/S				
End Point	212.3	mV	Digits	3				
Over mL	332.3	mV						
Max.Vol.	20	mL						

Measurement results

Measurement of blank

Number of measurement	Size (g)	Titrant volume (mL)
1	—	0.005
2	—	0.005
	Avg.	**0.005**

Measurement of sample No.1 (Endpoint: Inflection)

Number of measurement	Size (g)	Titrant volume (mL)	Base number (mgKOH/g)
1	4.9738	0.762	0.841
2	4.9852	0.777	0.856
		Avg.	**0.849**
Difference between repetitive results		:	0.015
Repeatability limit		:	0.099

Reproducibility（Inflection）$= 0.11(X+0.0268)^{0.79}$

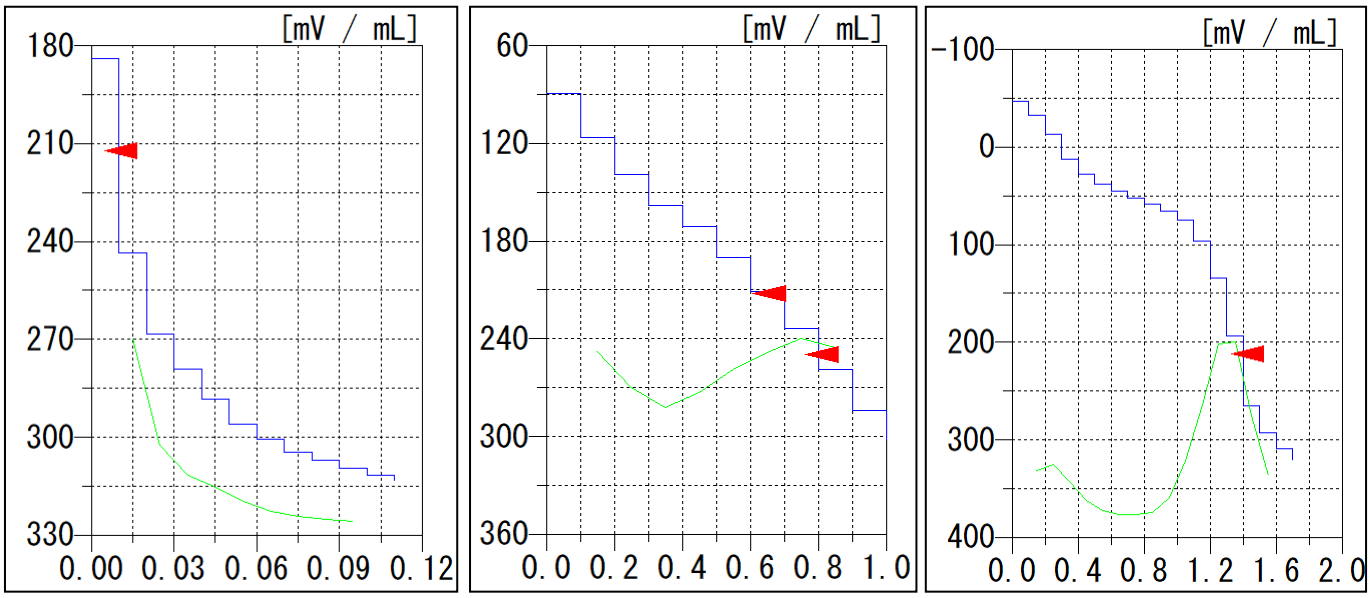
X：The average of the two test results

Measurement of sample No.2 (Endpoint: pH3)

Number of measurement	Size (g)	Titrant volume (mL)	Base number (mgKOH/g)
1	0.9508	1.303	7.544
2	0.9610	1.327	7.602
		Avg.	**7.573**
Difference between repetitive results		:	0.058
Repeatability limit		:	0.570

Reproducibility（Buffer EP）$= 0.22X^{0.47}$

X：The average of the two test results



Measurement of blank | Measurement of sample No.1 | Measurement of sample No.2

Examples of titration curves

5. Note

(1) About endpoint detection

There are two methods for detecting endpoints.

1) If an inflection occurs in the potential region between the pH 3 buffer potential and a point 100 mV past this potential, mark this inflection as the end point. If more than one inflection points are observed, use the last well-defined inflection point.

2) If no well-defined inflection occurs in the above mentioned potential region, mark as the end point the point on the curve that corresponds to the acidic aqueous pH 3 buffer potential.

(2) About titration control

In ASTM D 4739, 0.01 mL of titrant is titrated at 12-second intervals for blank measurement. For sample measurement, 0.1 mL of titrant is titrated at 90 second intervals. To control the above titration, set the parameters as shown in the control mode in the titration condition example shown above.

(3) Electrode

In this titration, a glass electrode (GE-103B) with a low-resistance glass membrane was used. This electrode has improved response due to its reduced internal resistance, and is expected to provide more stable results especially for non-aqueous neutralization titrations.

In addition, a movable sleeve type glass-reference combination electrode (GR-513B) can also be used in this titration instead of the glass electrode and reference electrode. Note that the internal solution must be replaced with a 1-3 mol/L lithium chloride ethanol solution as described in ASTM D4739, and it is recommended to leave it to stand overnight after replacement.

Repeated titrations over a long period of time reduce the response and electromotive force to the glass electrode, so the electrode should be periodically immersed in water to activate it.

(4) Standardization of 0.1 mol/L hydrochloric acid in 2-propanol titrant

2-Propanol used as a solvent for the titrant has a relatively larger thermal expansion coefficient than water, and when the temperature changes by 1 °C, the titrant causes a volume change of 0.1 %. For accurate measurement, factor titration and sample measurement should be performed at the same room temperature as much as possible.

Keyword : ASTM D4739, Petroleum products, Base number, Potentiometric titration, Non-aqueous neutralization titration

※Depend on the configuration of instrument, ,some of measurement may not possible