

HIRANUMA APPLICATION DATA		Automatic Titrator	Data No.	L16	Oct.24. 2024
Lubricant petroleum products	Base number in Petroleum products (Perchloric acid / Back-titration)				

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 2896 : Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration
- ASTM D 4739 : Standard Test Method for Base Number Determination by Potentiometric Hydrochloric 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 perchloric acid back titration method (ASTM D 2896).

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) Add fixed amount of perchloric acid in acetic acid solution to the sample.
- 4) Start titration with sodium acetate in acetic acid solution.

There are two procedures for perchloric acid titration with back-titration, A and B on ASTM D2896. Procedure A and B use different titration solvent volume and sample weight. In this article, measurement with procedure B will be applied. In this example, by adding an optional buret, dispensing of perchloric acid-acetic acid standard solution and titration with sodium acetate-acetic acid standard solution are continuously performed.

2. Configuration of instruments and reagents

(1) Configuration of instruments

Main unit	:	Automatic Titrator	COM Series
		One buret	Optoion
Electrode	:	Glass electrode	GE-103B
	:	Reference electrode	RE-201Z
		(Inner solution: Saturated sodium perchlorate in glacial acetic acid)	
	*	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 sodium acetate acid in glacial acetic acid standard solution
Additive	:	0.1 mol/L perchloric acid in glacial acetic acid standard solution

Titration solvent : Mixture of 500 mL of glacial acetic acid and 1 L of chlorobenzene.

3. Measurement procedure

- (1) Take 1 g of sample into 100 mL beaker and weigh accurately to 0.1 mg digits.

Note that the weight of sample will be changed depending on the base number.

- (2) Add 60 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.

- (3) Immerse the electrode and start titration. After 4 mL of 0.1 mol/L perchloric acid-acetic acid standard solution is dispensed, titration with 0.1 mol/L sodium acetate-acetic acid standard solution is performed. Also, perform the blank test with the same procedure of sample measurement.

4. Measurement conditions and results

Examples of titration conditions

- (1) Measurement of blank

- i) Dispense 0.1 mol/L perchloric acid in acetic acid standard solution.

Cndt No.	1
Method	Disp
Buret No.	1
S- Timer	0 sec
Disp Vol.	4 mL

- ii) Titration with 0.1 mol/L sodium acetate in acetic acid standard solution.

Cndt No.	2	ConstantNo.	2	Mode No.	19
Method	Auto	Size	0 g	Pre Int	0 sec
Buret No.	2	Blank	0 mL	Del K	0
Amp No.	1	Molarity	0 mol/L	Del Sens	0 mV
D. Unit	mV	Factor	0	Int Time	5 sec
S- Timer	10 sec	K	0	Int Sens	3 mV
C.P. mL	0 mL	L	0	BrT Speed	2
T- Timer	0 sec			Pulse	40
D.P. mL	0 mL	Unit	mL		
End Sens	300	Formula	D		
Over mL	0.2 mL	Digits	3		
Max. Vol.	20 mL				

(2) Measurement of sample

i) Dispense 0.1 mol/L perchloric acid in acetic acid standard solution.

Cndt No.	1
Method	Disp
Buret No.	1
S- Timer	0 sec
Disp Vol.	4 mL

ii) Titration with 0.1 mol/L sodium acetate in acetic acid standard solution.

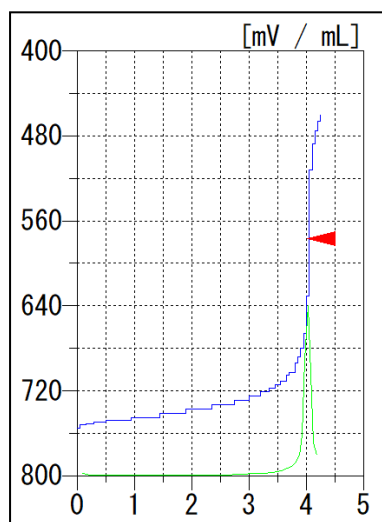
Cndt No.	3	ConstantNo.	3	Mode No.	8
Method	Auto	Size	0 g	Pre Int	0 sec
Buret No.	2	Blank	4.022 mL	Del K	5
Amp No.	1	Molarity	0.1 mol/L	Del Sens	0 mV
D. Unit	mV	Factor	1.005	Int Time	5 sec
S-Timer	10 sec	K	56.1	Int Sens	3 mV
C.P. mL	0 mL	L	0	Brt Speed	2
T- Timer	0 sec	Unit	mg/g	Pulse	40
D.P. mL	0 mL	Formula	(D-B)*K*F*M/S		
End Sens	300	Digits	3		
Over mL	0.2 mL				
Max.Vol.	20 mL				

Measurement results

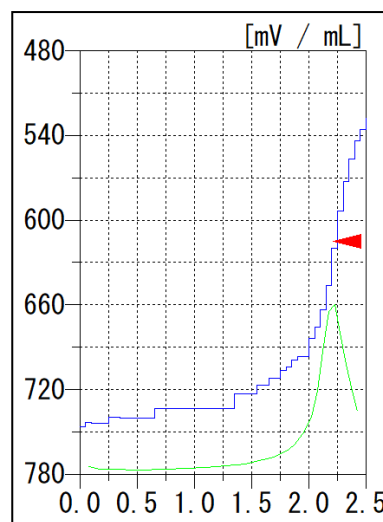
Measurement of blank			Measurement of sample			
Number of measurement	Size (g)	Titrat volume (mL)	Number of measurement	Size (g)	Titrat volume (mL)	Base number (mgKOH/g)
1	—	4.022	1	0.9846	2.210	10.376
2	—	4.022	2	0.9564	2.257	10.405
	Avg.	4.022			平均值	10.391
				Difference between repetitive results	:	0.029
				Repeatability limit	:	0.520

Reproducibility (Inflection)= $X \times 0.05$ (Within 5% of average)

X : The average of the two test results



Measurement of blank



Measurement of sample

Examples of titration curves

5. Note

(1) 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-513BZ) 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 saturated sodium perchlorate glacial acetic acid solution as described in ASTM D2896, 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.

(2) Experiment temperature

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

(3) Preparation of inner solution for reference electrode

The inner solution of the reference electrode RE-201Z and the combination electrode GR-513BZ are filled with saturated KCl aqueous solution when purchased. For this measurement, it is necessary to replace inner solution to saturated sodium perchlorate in acetic acid solution. Replacement procedure is described below.

- i) Prepare the saturated solution of sodium perchlorate in acetic acid with reagent grade of these.
- ii) Discharge inner solution from reference electrode RE-201Z (or GR-513BZ) and wash inside it with water and then acetic acid.
- iii) Fill the prepared inner solution into reference electrode from the supply port.
- iv) Leave the electrode for one day before use.

Keyword : ASTM D 2896, Petroleum products, Base number, Potentiometric titration, Perchloric acid titration, Back-titration

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