Sheet No.
GT-310-PE-030E Energy & Petroleum Products

Base Number Analysis of Petroleum Products - Perchloric Acid Titration (JIS K 2501)

Related standard: JIS K 2501: 2003 Petroleum products and lubricants - Determination of neutralization number 9. Potentiometric titration (Base number, perchloric acid titration)

Outline

The base number is used as an estimate of the amount of basic constituents, such as detergent dispersants, in petroleum products and lubricating oils.
The base number is defined in the standard as: “the amount in milligrams (mg) of potassium hydroxide equivalent to the hydrochloric acid or perchloric acid required to neutralize the basic constituents* contained in 1 g of a sample.” The basic constituents contained in petroleum products and lubricating oils are measured by dissolving in acetic acid and chlorobenzene. The testing method is divided into Procedure A (120 mL) and Procedure B (60 mL) depending on the amount of titration solvent used. In this sheet, Procedure B was used with automatic recording titration to measure commercial lubricating oil. Results were obtained with a relative standard deviation (RSD) of around 1 %.

* Basic constituents include: organic bases, inorganic bases, amino compounds, salts of weak acid (soaps), basic salts of polyacid bases, heavy metal salts, and additives such as antioxidants and cleaning agents.

Principle

The basic constituents in the sample are neutralized using perchloric acid. Titration is performed while recording the potential difference between a glass electrode and the reference electrode.
The titrant 0.1 mol/L perchloric acid solution in acetic acid is dripped at a speed of 1.0 mL per minute maximum, the inflection point is detected as the end point. The base number is calculated from the amount of the sample and the titrant used up to the end point. If no clear inflection point is observed, the end point should be detected by back-titration (see application sheet no. GT-310-PE-031E).

Apparatus

Automatic titrator:	GT-310
Electrodes:	GLASS ELECTRODE, L=105 (GTPH1B), REFERENCE ELECTRODE SLEEVE L=105 (SLEEVE TYPE) (GTRS10B) (Inner solution: sodium perchlorate electrolyte)
Buret cassette:	BURET CASSETTE UNIT WITH TEMPERATURE SENSOR, 20mL (GTECST)
Titration vessel:	A vessel with approx. 150 mL capacity (A 150 mL tall beaker was used)

Sheet No.
GT-310-PE-030E

Base Number Analysis of Petroleum Products - Perchloric Acid Titration

Reagents

[Titrant]
- 0.1 mol/L Perchloric acid solution in acetic acid (for non-aqueous titration)

[Reagents]
- Titration solvent: 1 part acetic acid (special grade) mixed with 2 parts chlorobenzene (special grade)
- Sodium perchlorate electrolyte: saturated solution of sodium perchlorate monohydrate (special grade) in acetic acid
- Potassium hydrogen phthalate (certified reference material): Dried at 120 °C for 2 hours, then cooled to room temperature in a desiccator

Analytical Procedure

[Testing of electrodes]

1. 0.1 g of potassium hydrogen phthalate was dissolved in 50 mL of acetic acid. The screen of multi controller was switched to the potential monitor. The electrodes were dipped into the solution, and the potential was recorded (the potential was recorded when it changed less than 5 mV/min).
2. The electrode was rinsed with chlorobenzene. 0.75 mL of 0.1 mol/L perchloric acid solution in acetic acid was added into 50 mL of acetic acid by using the GT-310BRT. The electrode was immersed in the solution, potential was then recorded (the potential was recorded when it changed less than 5 mV/min).
3. It was confirmed that the potential difference between steps 1 and 2 was at least 300 mV.

[Blank titration]

1. 60 mL of titration solvent was added to a 150 mL beaker.
2. It was titrated with a titrant. *1

[Sample titration]

1. A sample was weighed into a 150 mL beaker, referring to Table 1, and 60 mL of titration solvent was added to dissolve it. *2
2. It was titrated with a titrant. *1

Table 1 Sample weighing (Procedure B)

Approximate weight of sample (g)	Sample weight* 3 (g)	Precision of weighing (g)
10/Expected base number*4	Over 0.10 to 0.25	0.0005
	Over 0.25 to 1.0	0.001
	Over 1.0 to 5.0	0.005
	Over 5.0 to 10	0.02

*1: The electrode was rinsed and immersed in purified water for at least 5 minutes before each titration.
*2: If the sample is difficult to dissolve in mixed solution, dissolve it in 40 mL of chlorobenzene in the titration beaker, then add 20 mL of glacial acetic acid.
*3: For procedure B, maximum sample amount is 10 g.
*4: If the expected base number is unknown, weigh out 0.1 to 0.2 g of the sample, and titrate it to 570 mV. Use this

value to calculate the base number to determine the approximate mass to be weighed out.

[Calculation]

Base number (mgKOH/g) = (A1 − B) × Q × f × FW / W

With temperature correction*1

Base number (mgKOH/g) = [A1 × {1+0.001× (X1 − t)} − B × {1+0.001 × (X1 − X2)}] × Q × f × FW / W

A1: Volume of 0.1 mol/L perchloric acid solution in acetic acid used up to the end point (mL) for sample titration
B: Volume of 0.1 mol/L perchloric acid solution in acetic acid used up to the end point for blank titration (= 0 mL)
Q: Concentration of 0.1 mol/L perchloric acid solution in acetic acid (= 0.1 mol/L)
f: Factor of 0.1 mol/L perchloric acid solution in acetic acid (= 0.994)*2
FW: Molar mass of potassium hydroxide (= 56.1 g/mol)
W: Sample weight (g)
X1: Temperature of 0.1 mol/L perchloric acid solution in acetic acid at standardization (°C)
t: Temperature of 0.1 mol/L perchloric acid solution in acetic acid at sample titration (°C)
X2: Temperature of 0.1 mol/L perchloric acid solution in acetic acid at blank titration (°C)

*1: Use this formula when the temperature difference of the titrant exceeds 5 °C between the time of standardization and use. The calculation formula with temperature correction was not used here, as the temperature difference was within 5 °C
*2: Standardization was performed in accordance with JIS K 2501 (see application sheet no. GT-310-PE-032E).

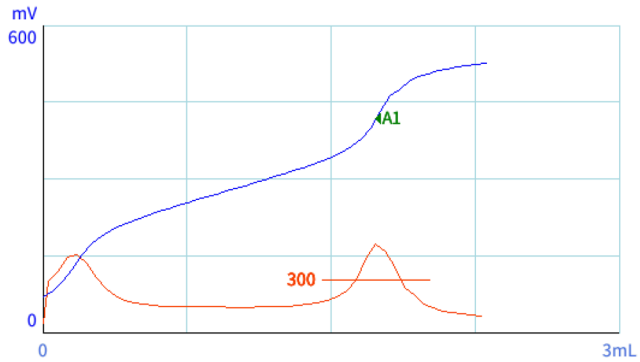
Other Requirements

- Confirm reagent labels and safety data sheets for safety.
- Wear safety goggles, gloves, and/or other safety equipment when handling reagents.
- Replace the reference electrode inner and outer solutions at regular intervals (at least once a week).
- The particular methods for collection and preparation may be stipulated for certain samples. For details, refer to the standard.
- Before use, it was confirmed that the buret with temperature sensor had a accuracy of 20 mL ± 0.02 mL.

Measurement Results

Sample	Sample amount (g)	Titration volume (mL)	Base number (mgKOH/g)	Average (mgKOH/g)	RSD (%)
Automotive engine oil	0.948	1.7292	10.2	**10.3**	**0.8**
	0.941	1.7327	10.3		
	0.957	1.7748	10.3		
4-cycle motorcycle engine oil	1.810	1.8794	5.79	**5.78**	**0.4**
	1.805	1.8785	5.80		
	1.820	1.8797	5.76		

Base Number Analysis of Petroleum Products - Perchloric Acid Titration



Sample name:	Automotive engine oil	
End point:	1.7292 mL	418.4 mV
Start of measurement:	0.000 mL	71.6 mV
End of measurement:	2.306 mL	527.2 mV
Measurement time:	19 min 59 s	
Start temperature:	22.4 °C	

■ Default values were used for parameters not listed below.

	Blank titration	Sample titration
Stirrer speed:	2.5	2.5
Detector:	mV1	mV1
Titration mode:	TAN/TBN standard method: OIL-A	TAN/TBN standard method: OIL-A
Initial wait time:	60 s	90 s
Drop control:	Individual	Individual
Max. drop volume:	50 µL	150 µL
Min. drop volume:	10 µL	50 µL
Stability criteria:	Individual	Individual
Delta potential:	1 mV	1 mV
Delta time:	12 s	12 s
E1:	Inflection/Set-Potential*1	Inflection/Set-Potential*1, *2
E1 potential:	500 mV	500 mV
E1 potential width:	250 mV	130 mV
E1 derivative threshold:	300 mV/mL	300 mV/mL
E1 evaluation points:	3	5
Max.:	10 mL	20 mL
End derivative:	50 mV/mL	50 mV/mL

*1: If no inflection point is detected, the E1 potential is used to detect the end point. If the potential for the end point 1 (A1) is the same as the E1 potential, the titration amount is treated as 0.
*2: When determining the expected base number, should be the E1 potential to 570 mV and set the E1 potential width to 0 mV.

* This application sheet is provided as reference, and does not assure the measurement results. Please consider the analysis environment, external factors and sample nature for optimal conditions before the measurement.