

Sheet No.

GT-310-PE-031E Energy &amp; Petroleum Products

# Base Number Analysis of Petroleum Products - Perchloric Acid Titration (JIS K2501) Back Titration

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

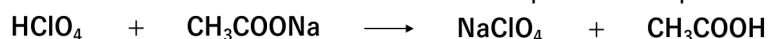
## Outline

"9. Potentiometric titration (Base number, perchloric acid titration) in JIS K 2501 states that if no clear inflection point can be detected using direct titration, back titration should be performed. The testing method is divided into Procedure A (120 mL) and Procedure B (60 mL) depending on the amount of titration solvent used. For this application sheet, commercial hydraulic oil for which no clear inflection point could be obtained using direct titration was subjected to base number analysis using automatic back titration according to Procedure B.

## Principle

The basic constituents in the sample are made to react by adding an excess amount of perchloric acid. The unreacted perchloric acid is then neutralized with sodium acetate. Titration is performed while recording the potential difference between a glass electrode and the reference electrode.

4 mL of 0.1 mol/L perchloric acid solution in acetic acid is added to react with the sample, then the titration by 0.1 mol/L sodium acetate solution in acetic acid) is performed 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, 0.1 mol/L perchloric acid solution and the volume of titrant used up to the end point.



## 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)

## Reagents

[Titrant]	■ Sodium acetate solution in acetic acid 0.1 mol/L (for non-aqueous titration)
[Reagents]	■ Titration solvent: 1 part acetic acid (special grade) mixed with 2 parts chlorobenzene (special grade)
	■ Perchloric acid solution in acetic acid 0.1 mol/L (for non-aqueous titration)
	■ Sodium perchlorate electrolyte: saturated solution of sodium perchlorate (NaClO <sub>4</sub> ) in glacial acetic acid
	■ Potassium hydrogen phthalate (certified reference material): Dried at 120 °C for 2 hours, then cooled to room temperature in a desiccator

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**Analytical Procedure****[Testing of electrodes]**

- 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).
- The electrode was rinsed with chlorobenzene, to which 0.75 mL of 0.1 mol/L perchloric acid solution in acetic acid was added to 50 mL of acetic acid by the GT-310BRT. The potential was then recorded (the potential was recorded when it changed less than 5 mV/min).
- It was confirmed that the potential difference between steps 1 and 2 was at least 300 mV.

**[Blank titration]**

- 60 mL of titration solvent was added into a 150 mL beaker.
- 4 mL of 0.1 mol/L perchloric acid solution in acetic acid was added using the GT-310BRT and stirred for 2 to 3 minutes. \*1
- It was titrated with a solution of sodium acetate in acetic acid. \*2

**[Sample titration]**

- A sample was weighed into a 150 mL beaker, referring to Table 1, and 60 mL of titration solvent was added. \*3
- 4 mL of 0.1 mol/L perchloric acid solution in acetic acid was added using the GT-310BRT and stirred for 2 to 3 minutes. \*1
- It was titrated with a solution of sodium acetate in acetic acid. \*2

Table 1 Sample weighing (Procedure B) \*4

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

\*1: By using two GT-310BRT units, the blank titration and sample titration in step 2 was performed automatically.

When using just one GT-310BRT unit, replace the cassette after adding 4 mL of 0.1 mol/L perchloric acid solution in acetic acid using the GT-310BRT with a cassette of 0.1 mol/L sodium acetate solution in acetic acid.

\*2: The electrode was rinsed and immersed in purified water for at least 5 minutes before each titration.

\*3: If the sample is difficult to dissolve, first add 40 mL of chlorobenzene to dissolve it, then add 20 mL of acetic acid.

\*4: The maximum sample weight is 2.5 g. If no inflection point is observed at 2.5 g, reduce to 1.25 g.

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[Calculation]

$$\text{Base number (mgKOH/g)} = (B - A1) \times Q \times f \times FW / W$$

With temperature correction\*1

$$\text{Base number (mgKOH/g)} = [B \times \{1 + 0.001 \times (X1 - X2)\} - A1 \times \{1 + 0.001 \times (X1 - t)\}] \times Q \times f \times FW / W$$

- B: Volume of 0.1 mol/L sodium acetate solution in acetic acid used up to the end point for blank titration (= 3.9625 mL)
- A1: Volume of 0.1 mol/L sodium acetate solution in acetic acid used up to the end point for sample titration (mL)
- Q: Concentration of 0.1 mol/L sodium acetate solution in acetic acid (= 0.1 mol/L)
- f: Factor of 0.1 mol/L sodium acetate solution in acetic acid (= 1.003)<sup>\*2</sup>
- FW: Molar weight of potassium hydroxide (= 56.1 g/mol)
- W: Sample weight (g)
- X1: Temperature of 0.1 mol/L sodium acetate solution in acetic acid at standardization (°C)
- X2: Temperature of 0.1 mol/L sodium acetate solution in acetic acid at blank titration (°C)
- t: Temperature of 0.1 mol/L sodium acetate solution in acetic acid at sample titration (°C)

\*1: Use this formula when the temperature difference of the titrant exceeds 5 °C between the time of standardization and use. Connect the buret sensor for the sodium acetate solution in acetic acid to the TEMP connector during titration. If the temperature of the perchloric acid solution in acetic acid differs at blank titration and sample titration, also add the following correction expression derived from the temperature difference of the perchloric acid solution in acetic acid:

$$4 \times 0.001 \times (X3 - X4) \times Qp1 \times fp1 \times FW / W$$

X3 and X4, respectively, are the temperatures of the perchloric acid solution in acetic acid at blank titration and sample titration, while Qp1 and fp1, respectively, are the concentration and factor of the perchloric acid solution in acetic acid. The calculation formula with temperature correction was not used in this application sheet because the difference in temperature was within 5 °C.

\*2: Standardization was performed in accordance with JIS K 2501 (see application sheet no. GT-310-PE-033E).

**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 sampling 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.

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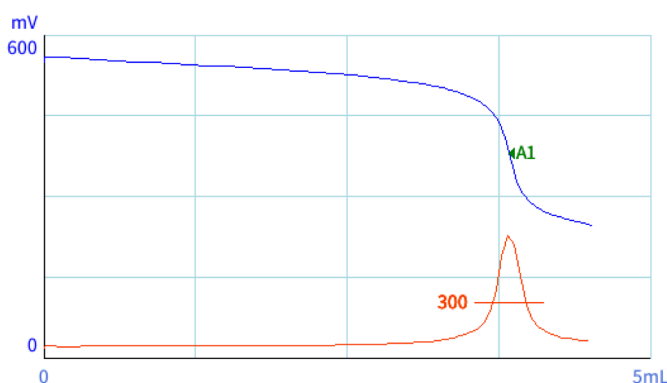
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**Measurement Results**

Sample	Sample amount (g)	Titration volume (mL)	Base number (mgKOH/g)	Average (mgKOH/g)	RSD (%)
Hydraulic oil	2.480	3.8252	0.31	<b>0.30</b>	<b>7.2</b>
	2.480	3.8415	0.27		
	2.470	3.8253	0.31		



Sample name: Hydraulic oil  
 End point: 3.8252 mL 381.0 mV  
 Start of measurement: 0.000 mL 559.6 mV  
 End of measurement: 4.510 mL 248.1 mV  
 Measurement time: 18 min 09 s  
 Start temperature: 22.6 °C

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■ 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
Preset <sup>1*</sup> :	Volume	Volume
P1 titrant:	0.1 mol/L HClO <sub>4</sub> /AcOH	0.1 mol/L HClO <sub>4</sub> /AcOH
P1 buret number.:	1	1
P1 injection volume:	4 mL	4 mL
Titrant:	0.1 mol/L AcONa/AcOH	0.1 mol/L AcONa/AcOH
Buret number:	2	2
Initial wait time:	120 s	120 s
Drop control:	Individual	Individual
Max. drop volume:	200 μL	150 μL
Min. drop volume:	50 μL	50 μL
Stability criteria:	Individual	Individual
Delta potential:	1 mV	1 mV
Delta time:	12 s	12 s
E1:	Inflection/Set-Potential	Inflection/Set-Potential
E1 potential:	480 mV	480 mV
E1 potential width:	250 mV	250 mV
E1 derivative threshold:	300 mV/mL	300 mV/mL
E1 evaluation points:	5	5
Max. titration volume:	20 mL	20 mL
End derivative:	50 mV/mL	50 mL/mV

\* "Preset" was used for automatic blank titration and sample titration in step 2 using two GT-310BRT units.

\* 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.