Nittoseiko Analytech

Application Sheet

Sheet No.
GT-310-PE-042E

Energy & Petroleum Products

Base Number Analysis of Petroleum Products - Perchloric Acid Titration (ASTM D2896) Back titration

Related standard: ASTM D2896-15 Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration

Outline

ASTM D2896 states that back titration should be performed if the inflection point cannot be clearly detected via direct titration. It describes two procedures with different titration solvent volumes: Procedure A (120 mL) and Procedure B (60 mL). Testing can be performed as manual titration using a buret or automatic recording titration using an automatic buret.
For this application sheet, commercial hydraulic oil for which the inflection point was unclear with direct titration was measured using automatic recording titration with Procedure B.

Principle

The basic constituents in the sample are made to react with 4 mL of 0.1 mol/L perchloric acid solution in acetic acid. The unreacted perchloric acid is then neutralized with 0.1 mol/L sodium acetate solution in acetic acid. Titration is performed while recording the potential difference between a glass electrode and the reference electrode. Then the inflection point is detected as the end point. Typically in back titration, the analytical values are calculated from the difference in titration volumes between blank titration and sample titration. However, in this standard, the titration volume obtained during the standardization of the 0.1 mol/L sodium acetate solution in acetic acid is used as the blank titration volume.

$$HClO_4 + CH_3COONa \longrightarrow NaClO_4 + CH_3COOH$$

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)

Reagents

[Titrant]
- 0.1 mol/L Sodium acetate solution in acetic acid solution

[Reagents]
- Acetic acid (special grade)
- Chlorobenzene (special grade)
- 0.1 mol/L Perchloric acid solution in acetic acid
- Sodium perchlorate electrolyte: saturated solution of sodium perchlorate ($NaClO_4$) in glacial acetic acid
- Potassium hydrogen phthalate (certified reference material)

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Analytical Procedure

[Testing of electrodes]

1. 0.1 g of potassium hydrogen phthalate was dissolved in 60 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, then immersed in 50 mL of acetic acid, to which 0.75 mL of 0.1 mol/L perchloric acid solution in acetic acid was added using the GT-310BRT. The 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.

[Sample titration]

1. A sample was weighed into a 150 mL beaker, referring to Table 1, and 40 mL of chlorobenzene was added to dissolve it. 20 mL of acetic acid was also added.
2. 4 mL of 0.1 mol/L perchloric acid solution in acetic acid was added using the GT-310BRT and stirred for 2 minutes. *1
3. It was titrated with sodium acetate solution in acetic acid. *2

Table 1 Sample weighing (Procedure B)*3

Approximate weight of sample (g)	Sample weight (g)	Precision of weighing (g)
10/Expected base number	5 to 10	0.02
	1 to 5	0.005
	0.25 to 1.0	0.001
	0.1 to 0.25	0.0005

*1: In this application sheet, the sample titration in step 2 was performed automatically with two GT-310BRT units. 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. Add more than 4 mL, if necessary, but standardize the 0.1 mol/L sodium acetate solution in acetic acid by using the same quantity of 0.1 mol/L perchloric acid solution in acetic acid.
*2: The electrode was rinsed and immersed in purified water for at least 5 minutes before each titration.
*3: The maximum sample weight is 2.5 g. If no inflection point is observed at 2.5 g, reduce to 1.5 g.

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[Calculation]

Base number (mgKOH/g) = (X1 − A1) × Q × f × FW / W

With temperature correction*1

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

X1: Volume of 0.1 mol/L sodium acetate solution used up to the end point for standardization (= 3.9621 mL)*2

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 (= 0.1 mol/L)

f: Factor of 0.1 mol/L sodium acetate solution (= 1.002)

FW: Molar mass of potassium hydroxide (= 56.1 g/mol)

W: Sample weight (g)

X2: Temperature of 0.1 mol/L sodium acetate solution at standardization (°C)

t: Temperature of 0.1 mol/L sodium acetate solution 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 to the TEMP connector during titration. If the temperature of the perchloric acid solution differs at standardization and sample titration, also add the following correction derived from the temperature difference of the perchloric acid solution.

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

X3 and X4, respectively, are the temperatures of the perchloric acid solution at standardization and sample titration, while Qp1 and fp1, respectively, are the concentration and factor of the perchloric acid solution. No correction was applied in this application sheet because there was no temperature difference.

*2: Standardization was performed in accordance with ASTM D2896 (see application sheet No. GT-310-PE-044E).

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 solution at regular intervals.
- Before use, it was confirmed that the buret with temperature sensor had a accuracy of ± 0.02 mL.

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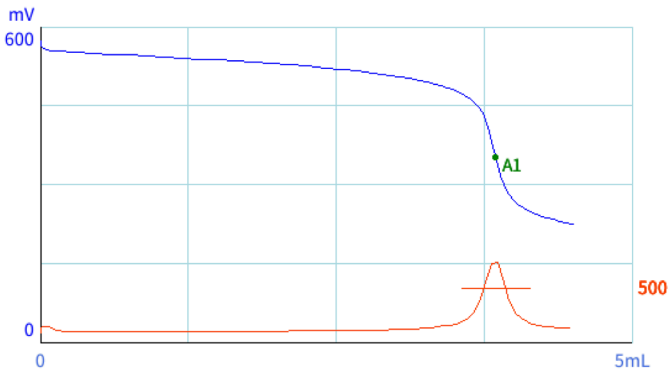
Measurement Results

Sample	Sample amount (g)	Titration volume (mL)	Base number (mgKOH/g)	Average (mgKOH/g)	RSD (%)
	2.480	3.8434	0.27		
Hydraulic oil	2.490	3.8336	0.29	**0.3**	**8.7**
	2.490	3.8208	0.32		



Sample name:	Hydraulic oil	
End point:	3.8434 mL	352.7 mV
Start of measurement:	0.000 mL	563.7 mV
End of measurement:	4.495 mL	226.4 mV
Measurement time:	14 min 15 s	
Start temperature:	25.5 °C	

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■ Default values were used for parameters not listed below.

Stirrer speed:	2.5
Titration mode:	TAN/TBN standard method: OIL-A
Detector:	mV1
Preset 1*1:	Preset-A
P1 titrant:	0.1 M HClO4/AcOH
P1 buret number:	1
P1 injection volume:	4 mL
Titrant:	0.1 M AcONa/AcOH
Buret number:	2
Initial wait time:	120 s
Drop control:	Individual
Max. drop volume:	150
Min. drop volume:	50 µL
Stability criteria:	Individual
Delta potential:	1 mV
Delta time:	12 s
E1:	Inflection/Set-Potential*2
E1 potential:	480 mV
E1 potential width:	250 mV
E1 derivative threshold*2:	500 mV/mL
E1 evaluation points:	5
Max. titration volume:	20 mL
End derivative:	50 mL/mV

*1: Set because step 2 was automated using two GT-310BRT units
*2: If no inflection point is detected, the E1 potential is used to detect the endpoint. If the potential for end point 1 (A1) is the same as the E1 potential, the inflection point cannot be detected, so the E1 derivative threshold must be adjusted.