Sheet No.
GT-310-PE-046E Energy & Petroleum Products

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

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. Titration is performed by dissolving a sample in chlorobenzene and adding acetic acid as original method in the standard. The appendix states that xylene can be used instead of chlorobenzene. It also notes that the addition of approximately 10 % acetone to the alternative titration solvent reduces electrode noise. Testing can be performed as manual titration using a buret or automatic recording titration using an automatic buret in accordance with Procedure A (120 mL).
For this application sheet, commercial lubricating oil was measured using automatic titration with an alternative solvent.

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.
8 mL of 0.1 mol/L perchloric acid solution in acetic acid is reacted with the sample, then titrate with 0.1 mol/L sodium acetate solution in acetic acid at a speed of 1.0 mL/min maximum. The inflection point is detected as the end point. The base number is calculated from the amount of the sample and 0.1 mol/L perchloric acid solution together with volume of titrant used up to the end point.

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

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] ■ Sodium acetate solution in acetic acid 0.1 mol/L (for non-aqueous titration)

Sheet No.
GT-310-PE-046E

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

[Reagents]

- Acetic acid (special grade)
- Xylene (special grade)
- Acetone (special grade)
- Perchloric acid solution in acetic acid 0.1 mol/L (for non-aqueous titration)
- Sodium perchlorate electrolyte: saturated solution of sodium perchlorate ($NaClO_4$) in glacial acetic acid
- Potassium hydrogen phthalate (certified reference material)

Analytical Procedure

[Testing of electrodes]

1. A well-stirred mixture of 100 mL of glacial acetic acid plus 0.2 g of potassium hydrogen phthalate was prepared. 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 by less than 5 mV/min).
2. The electrode was rinsed with xylene. 1.5 mL of 0.1 mol/L perchloric acid solution in acetic acid was added to 100 mL of acetic acid by using the GT-310BRT. The electrode was immersed in the mixture, and the potential was then recorded (the potential was recorded when it changed by 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 dissolved in 80 mL of xylene. 40 mL of acetic acid and 10 mL of acetone was also added.
2. 8 mL of 0.1 mol/L perchloric acid solution was added using the GT-310BRT and stirred for 2 to 3 minutes. *1
3. It was titrated with a solution of sodium acetate. *2

Table 1 Sample weighing (Procedure A)*3

Approximate weight of sample (g)	Sample weight (g)	Precision of weighing (g)
28/Expected base number	10 to 20	0.05
	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: Two GT-310BRT units were used. The sample titration in step 2 was performed automatically. When using just one GT-310BRT unit, replace the cassette after adding 8 mL of 0.1 mol/L perchloric acid solution with a cassette of 0.1 mol/L sodium acetate solution. Add more than 8 mL, if necessary, but use the same quantity of 0.1 mol/L perchloric acid solution and titrate by the 0.1 mol/L sodium acetate solution as a blank.
*2: The electrode was rinsed and immersed in purified water for at least 5 minutes before each titration.
*3: The maximum sample weight is 5 g. If no inflection point is observed at 5 g, reduce to 3 g.

Sheet No.
GT-310-PE-046E

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

[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 of the 0.1 mol/L sodium acetate solution (= 7.9165 mL)*2

A1: Volume of 0.1 mol/L sodium acetate solution 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 (= 1.0025)

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 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 standardization and sample titration, also add the following correction term derived from the temperature difference of the perchloric acid solution in acetic acid.

$$8 \times 0.001 \times (X3 - X4) \times Qp1 \times fp1 \times FW / W$$

X3 and X4, respectively, are the temperatures of the perchloric acid solution in acetic acid at 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-048E).

Other Requirements

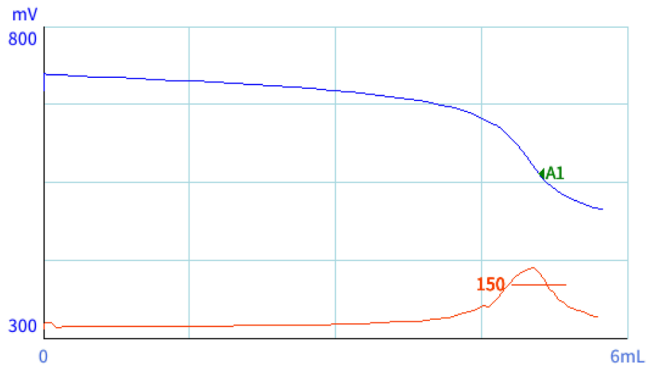
- Confirm reagent labels and safety data sheets for safety.
- Wear safety goggles, gloves, and/or other safety equipment when handling reagents.
- Replace the reference electrode inner and outer solutions at regular intervals (at least once a week).
- The particular methods for collection and preparation may be stipulated for certain samples. For details, refer to the standard.
- The standard states that precision of alternative solvent is worse than original. However, it does not mention the accuracy when acetone is added.

Sheet No.
GT-310-PE-046E

Base Number Analysis of Petroleum Products - Perchloric Acid Titration (ASTM D2896) Back Titration - Alternative Solvent – 4/5

Measurement Results

Sample	Sample amount (g)	Titration volume (mL)	Base number (mgKOH/g)	Average (mgKOH/g)	RSD (%)
4-stroke motorcycle engine oil	2.960	5.0789	5.39	**5.4**	**0.8**
	2.960	5.0497	5.45		
	2.970	5.0812	5.47		
Hydraulic oil	4.970	7.6568	0.29	**0.3**	**8.9**
	4.960	7.6913	0.26		
	4.960	7.6956	0.25		



Sample name:	4-stroke motorcycle engine oil	
End point:	5.0789 mL	564.8 mV
Start of measurement:	0.000 mL	724.9 mV
End of measurement:	5.727 mL	507.8 mV
Measurement time:	17 min 36 s	
Start temperature	25.8 °C	

Sheet No.
GT-310-PE-046E

Base Number Analysis of Petroleum Products - Perchloric Acid Titration (ASTM D2896) Back Titration - Alternative Solvent – 5/5

■ 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:	Volume
P1 titrant:	0.1 M HClO4/AcOH
P1 buret number:	1
P1 injection volume:	8 mL
Titrant:	0.1 M AcONa/AcOH
Buret number:	2
Initial wait time:	120 s
Drop control:	Individual
Max. drop volume:	200
Min. drop volume:	50 µL
Stability criteria:	Individual
Delta potential:	1 mV
Delta time:	12 s
E1:	Inflection/Set-Potential*2
E1 potential:	550 mV
E1 potential width:	250 mV
E1 derivative threshold*2:	150 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 end point. If the potential for the end point 1(A1) is the same as the E1 potential, the inflection point cannot be detected, so the E1 derivative threshold should be adjusted.