Sheet No.
GT-310-PE-041E Energy & Petroleum Products

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

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

Outline

ASTM D2896 specifies the test method for determination of basic constituents in petroleum products such as fresh oils and used oils. 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 engine oils were measured using automatic recording titration with Procedure B, and results were achieved with a relative standard deviation (RSD) of less than 1 %.

Principle

The basic constituents in the sample are neutralized using perchloric acid. Titration is performed at a speed of 1.0 mL/min maximum while recording the potential difference between a glass electrode and the reference electrode.
Then the inflection point is detected as the end point. When there is no inflection point or only a very poor one, back-titration should be performed. (see application sheet No. GT-310-PE-042E)

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 Perchloric acid standard solution in acetic acid

[Reagents]
- Titration solvent: Add one part of glacial acetic acid to two parts of chlorobenzene.
- 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. A well-stirred mixture of 60 mL of glacial acetic acid plus 0.1 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 less than 5 mV/min).
2. The electrode was rinsed with chlorobenzene. 0.75 mL of 0.1 mol/L perchloric acid solution in 50 mL of 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.

[Blank titration]

1. 60 mL of titration solvent was added into a 150 mL beaker.
2. It was titrated with 0.1 mol/L perchloric acid solution in acetic acid.*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 0.1 mol/L perchloric acid solution in acetic acid.*1

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: The electrode was rinsed and immersed in purified water for at least 5 minutes before each titration.
*2: If the solution of the sample proves difficult, dissolve it in 40 mL of chlorobenzene in the titration beaker, then add 20 mL of glacial acetic acid.
*3: For procedure B, maximum of 10 g should be taken for analysis.

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[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: Perchloric acid solution used to titrate the sample to the inflection point on the titration curve (mL)
B: Volume of 0.1 mol/L perchloric acid solution used to titrate the solvent to the end point for blank titration of same potential as sample (Automotive engine oil: 0.0076 mL, 4-stroke motorcycle engine oil: 0.0080 mL)
Q: Concentration of 0.1 mol/L perchloric acid solution (= 0.1 mol/L)
f: Factor of 0.1 mol/L perchloric acid solution (= 0.993)
FW: Molar mass of potassium hydroxide (= 56.1 g/mol)
W: Sample weight (g)
X1: Temperature of 0.1 mol/L perchloric acid solution at standardization (°C)
t: Temperature of 0.1 mol/L perchloric acid solution at sample titration (°C)
X2: Temperature of 0.1 mol/L perchloric acid solution 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 in this application sheet, as the temperature difference was within 5 °C.
*2: Standardization was performed in accordance with ASTM D2896 (see application sheet no. GT-310-PE-043E).

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.
- It was confirmed that the buret with temperature sensor had a specified accuracy of ± 0.02 mL.

Measurement Results

Sample	Sample amount (g)	Titration volume (mL)	Base number (mgKOH/g)	Average (mgKOH/g)	RSD (%)
Automotive engine oil	0.997	1.8364	10.2	**10.2**	**0.2**
	0.958	1.7681	10.2		
	0.964	1.7720	10.2		
4-stroke motorcycle engine oil	1.780	1.8317	5.71	**5.72**	**0.4**
	1.730	1.7807	5.71		
	1.720	1.7833	5.75		

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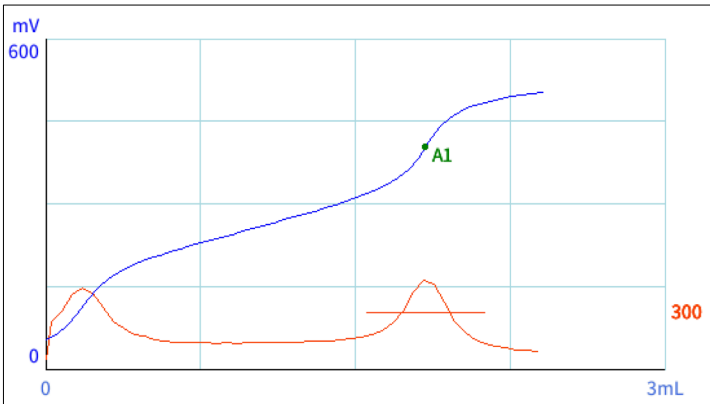

Sample name:	Automotive engine oil	
End point:	1.8364 mL	405.0 mV
Start of measurement:	0.000 mL	55.5 mV
End of measurement:	2.405 mL	503.1 mV
Measurement time:	14 min 54 s	
Start temperature:	23.1 °C	

■ Default values were used for parameters not listed below.

	Blank titration	Sample titration
Stirrer speed:	2.5	2.5
Titration mode:	TAN/TBN standard method: OIL-A	TAN/TBN standard method: OIL-A
Detector:	mV1	mV1
Initial wait time:	60 s	90 s
Drop volume control:	Individual	Individual
Max. drop volume:	50 µL	150 µL
Min. drop volume:	10 µL	50 µL
Stability criteria:	Individual	Individual
Delta potential:	1.0 mV	1.0 mV
Delta time :	12 s	12 s [s]
E1:	Inflection/Set-Potential	Inflection/Set-Potential *2
E1 potential:	End point potential of sample titration*1	480 mV
E1 potential width:	0 mV	130 mV
E1 derivative threshold:	2,000 mV/mL	300 mV/mL*3
E1 evaluation points:	3	5
Max. titration volume:	10 mL	20 mL
End derivative:	50 mV/mL	50 mL/mV

*1: Because the blank titration volume is defined as “the volume corresponding to E ($HClO_4$ solution used to titrate the sample to the inflection point on the titration curve) for blank titration at same potential as sample.”
*2: If no inflection point is detected, the E1 potential is used to detect the end point. If the potential of end point (A1) is the same as the E1 potential, the titration amount should be treated as 0.
*3: Adjust as necessary.