

Application Note

Total acid number of petroleum products

Industry	:	Petroleum
Instrument	:	Automatic potentiometric titrator
Measurement method	:	Potentiometric titration / Neutralization titration
Related standard	:	ASTM D664, JIS K2501

1. Scope

Measurement of total acid number of petroleum products is specified in “ASTM D664 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration”.

A test sample is potentiometrically titrated with 0.1mol/L potassium hydroxide 2-propanol solution, and an inflection point on the titration curve is regarded as the endpoint (if no inflection appears, the point at the meter reading corresponding to that obtained with the appropriate buffer specified by each standard.). Total acid number is calculated from the volume of potassium hydroxide 2-propanol solution used to titrate sample to endpoint.

Test samples are usually dissolved in mixed solvent of toluene and 2-propanol with a small amount of water. Petroleum products dissolved in the mixed solvent contain such components as organic acids, inorganic acids, esters, phenol compounds, lactones, resins, heavy metal salts, ammonium salts, weak acids and polybasic acid chlorides.

2. Precautions

- 1) To prevent sensitivity reduction of glass electrode, it is necessary to regenerate sensitivity of the electrode by soaking in pH 4.5-5.5 hydrochloric acid for about 5 min after each measurement.
- 2) Potassium hydroxide 2-propanol solution should be standardized at an interval not shorter than the concentration changes by more than 0.0005mol/L.
- 3) In case repeatability of results is wrong or an inflection point is ill defined, N₂ purge is recommended in order to reduce the influence of CO₂ in air.
- 4) To eliminate the influence of CO₂ in air, titration solvent should be added to a beaker just before titration.
- 5) To eliminate the influence of CO₂ in air, set the stirring speed to “2”.

3. Post-measurement procedure

The sensitivity of glass electrode is deteriorated after a series of measurements for the day, and the electrode needs regeneration by the method described in 2. Precautions.

4. Apparatus

- Main unit : Automatic potentiometric titrator (preamplifier : STD)
Electrode : Combined glass electrode for nonaqueous titration
(inner solution : 1mol/L LiCl ethanol)

5. Reagents

Reagent : 0.1mol/L potassium hydroxide 2-propanol solution
 Titration solvent : toluene : pure water : 2-propanol = 500 : 5 : 495 (volumetric ratio)

6. Procedure

-Blank test-

- 1) Add 125mL of the titration solvent into a 200mL beaker.
- 2) Blowing N₂ gas to the surface of the sample solution with flow rate of 200L/min, and titrate with 0.1mol/L potassium hydroxide 2-propanol solution to measure blank level.

-Measurement-

- 1) Weigh regulated quantity of the sample into a 200mL beaker.
- 2) Add 125mL of the titration solvent.
- 3) Blowing N₂ gas to the surface of the sample solution with flow rate of 200L/min, and titrate with 0.1mol/L potassium hydroxide 2-propanol solution to measure the total acid number.

7. Calculation

Total acid number (mgKOH/g) = (EP1 - BL1) × TF × C1 × K1 / S

EP1	:	Titer (mL)
BL1	:	Blank level = 0.1262mL (Sample ①) = 0.1039mL (Sample ②) = 0.1060mL (Sample ③)
TF	:	Factor of reagent = 0.9606 (Sample ①) = 0.9340 (Sample ②) = 0.9324 (Sample ③)
C1	:	Concentration conversion coefficient = 5.61mg/mL
K1	:	Unit conversion coefficient = 1
S	:	Sample (g)

8. Example

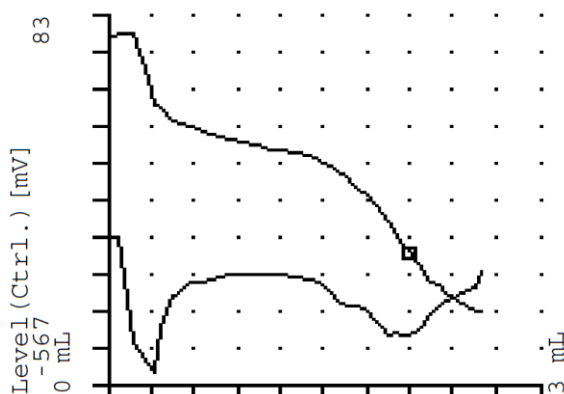
-Titration parameter-

<u>< Titr. Mode ></u>	: Auto Int.	<u>< Ctrl. Para. ></u>	Number of EP : 1
<u>< Titr. Form ></u>	: EP Stop	End Sense	: Set
<u>< Titr. Para. ></u>		dE	: 125.0 (dE) (Sample ①,②) : 100.0 (dE) (Sample ③)
Max. Volume	: 20 (mL)	dE/dmL	: 100.0 (dE/dmL)
Channel/Unit(Ctrl.)	: Ch1, mV	Gain	: 1
Channel/Unit(Ref.)	: Off	Data Sampling	: Auto
pH Polarity	: Standard	Ctrl. Speed	: Slow (Sample ①) : Standard (Sample ②,③)
Tit. Type Check	: No Check	Other Ctrl.	: Standard
Direction	: Negative	Auto Int. Mode	: Blank (Blank test) : Standard (Sample ①~③)
Wait Time	: 10 (s)	Stirrer Speed	: 2
Dose Mode	: None		

(The measurement parameter and the titration curve are an example of our automatic potentiometric titrator. In some titrators, parameter item may be different or another parameter item may be added.)

Sample ①

-Titration curve-



-Measurement results-

	Sample (g)	Titer (mL)	Total acid number (mgKOH/g)
1	19.9999	2.0805	0.527
2	20.0075	2.0909	0.529
Mean	-	-	0.528
The difference of the two results	-	-	0.002
Repeatability limit (ASTM)*	-	-	0.067
Repeatability limit (JIS)**	-	-	0.032

Sample ②

-Measurement results-

	Sample (g)	Titer (mL)	Total acid number (mgKOH/g)
1	4.9964	1.1024	1.047
2	4.9874	1.0986	1.045
Mean	-	-	1.046
The difference of the two results	-	-	0.002
Repeatability limit (ASTM)*	-	-	0.090
Repeatability limit (JIS)**	-	-	0.063

Sample ③

-Measurement results-

	Sample (g)	Titer (mL)	Total acid number (mgKOH/g)
1	4.9583	5.1002	5.269
2	4.9679	5.0982	5.256
Mean	-	-	5.263
The difference of the two results	-	-	0.013
Repeatability limit (ASTM)*	-	-	0.276
Repeatability limit (JIS)**	-	-	0.316

* Repeatability limit (ASTM) = 0.044 (X + 1)

** Repeatability limit (JIS) = 0.06X

X: Mean of the two results

9. Summary

In each samples, the differences of the two results were within the repeatability limits regulated by ASTM D664 and JIS K2501.

In some samples, verification of the measurement capability is required. In such case, please contact us.

10. References

- 1) ASTM D664-11a Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration
- 2) JIS K2501: 2003 Petroleum products and lubricants – Determination of neutralization number