Application Note

Determination of the total acid number in petroleum products

Industry	Petrochemicals
Instrument	Automatic potentiometric titrator
Measurement method	Potentiometric titration / Neutralization titration
Standards	ASTM D664

1. Scope

The total acid number of a petroleum product is important in evaluating its quality, such as checking for organic acids resulting from degradation. This Application Note introduces an example of the determination of the total acid number of petroleum products in accordance with ASTM D664 (9. Notes). The measurement sample was a standard with a known total acid number.

2. Precautions

1) To prevent the loss of sensitivity of the glass electrode, an operation to restore sensitivity is required. The electrode should be immersed in pure water for about 5 minutes at the end of each titration.
2) Potassium hydroxide in 2-propanol solution should be standardized at intervals where the change in concentration does not exceed 0.0005 mol/L.
3) If the measurement results are not repeatable or the titration curve is unclear, it is possibly due to the influence of carbon dioxide in the air. To avoid this effect, it is recommended to blow nitrogen gas on the surface of the sample solution.
4) To control the effect of carbon dioxide in the air, stirring with a stirrer should be controlled at a rotational speed that does not create a vortex on the liquid surface.
5) To avoid the influence of carbon dioxide in the air, add the titration solvent immediately before the measurement.

3. Post-measurement procedure

After the measurement is completed, the sensitivity of the glass electrodes may have decreased, so perform the sensitivity recovery operation described in "2. Precautions 1)".
Once done, store the electrode in accordance with the following:

- For short-term storage (less than one month) store immersed in pure water.
- For long-term storage (longer than one month) store immersed in a solution of pH 4 standard solution and 3.3 mol/L KCl solution mixed in an equal volume ratio.

4. Apparatus

Equipment	Automatic potentiometric titrator (preamplifier STD)
Electrode	Nonaqueous titration combined glass electrode (Electrode liquid 1 mol/L Lithium chloride in ethanol).

5. Reagents

Titrant	0.1 mol/L Potassium hydroxide in 2-propanol
Titration solvent	A solution of 500 mL of toluene, 5 mL of water, and 495 mL of 2-propanol

6. Procedure

-Blank test-

1) Add 125 mL or 60 mL of the titration solvent into a 200 mL tall beaker.
2) Titrate with 2-propanol solution of 0.1 mol/L potassium hydroxide to measure the blank level.
3) After measurement, the electrode is cleaned with titration solvent and immersed in pure water for 5 minutes.

-Measurement-

1) Depending on the expected acid value, a specified quantity of sample (outlined in ASTM D644) is introduced into a beaker and the mass is measured.
2) Add 125 mL or 60mL of titration solvent, purge with nitrogen, and titrate with 0.1 mol/L potassium hydroxide in 2-propanol solution.
3) After measurement, the electrode is cleaned with titration solvent and immersed in pure water for 5 minutes.

7. Calculation

Acid number (mgKOH / g) = (EP1 – BL1) × TF × C1 × K1 / S

EP1	Titration amount of sample (mL)	
BL1	Blank test (mL)	Described in Table of measurement results
TF	Factor of titrant	Described in Table of measurement results
C1	Concentration conversion coefficient	= 5.61 mg/mL
K1	Unit conversion factor	= 1
S	Quantity of sample (g)	

8. Example

—Titration parameter—

<Titr. Mode> Auto Int.
<Titr. Form> EP Stop

<Titr. Para.>		**<Ctrl. Para.>**	
Burette No.	1	Number of EP	1
Max. Volume	10 (mL)	End Sense	Auto
Channel/Unit(Ctrl.)	Ch1, mV	Gain	1
Channel/Unit(ref.)	off	Data Sampling	Auto
pH Polarity	Standard	Ctrl. Speed Mode	Standard*
Type of Titration	Not check	Unit Volume (mL)	1st Volume 0.2 2nd Volume 0.1 3rd Volume 0.075 4th Volume 0.05
EP Direction	Auto	1st>2nddvdiff.	20 (dE/dmL)
Wait Time	0 (s)	2nd>3rddvdiff.	60 (dE/dmL)
Dose Mode	Non	3rd >4thdvdiff.	100 (dE/dmL)
		Other Control	Standard
		Stirrer Speed	2

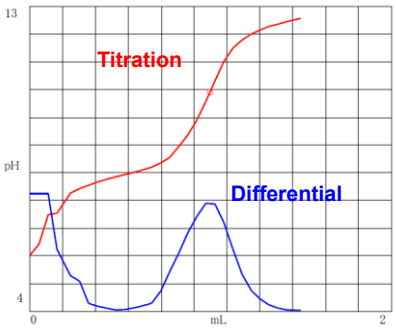
* Only for label value 0.11 mg KOH/g, 60 mL solvent volume Ctrl. Speed Mode: set, 4th titration volume: 0.02 mL.
(Listed above are example settings. Availability of settings may vary by instrument model.)

—Measurement results—

＜Titration solvent 125mL＞

・Label Value 1.03 mg KOH/g

- Titration curve -



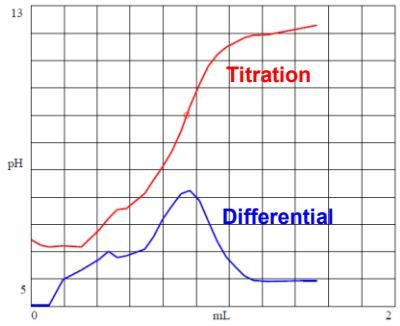
-Measurement results-

	Sample (g)	Blank (mL)	Titration amount (mL)	Acid number (mgKOH/g)
1	5.0028	0.1131	1.0011	1.03
2	5.0123	0.0975	0.9979	1.04
3	5.0080	0.0975	0.9959	1.04
Mean				1.04
SD				0.01
RSD(%)				1.0

* Factor of titrant= 1.0297

・Label Value 0.11 mg KOH/g

- Titration curve -



-Measurement results-

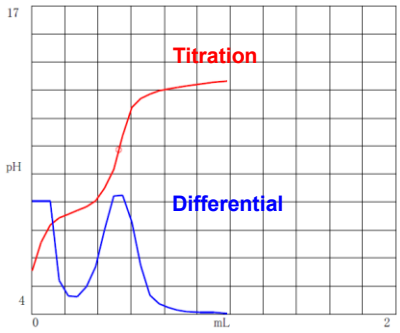
	Sample (g)	Blank (mL)	Titration amount (mL)	Acid number (mgKOH/g)
1	40.0393	0.0657	0.8578	0.12
2	40.0491	0.0657	0.8313	0.11
3	40.0144	0.0561	0.8596	0.12
Mean				0.12
SD				0.01
RSD(%)				8.3

＊Factor of titrant= 1.0297

＜Titration solvent 60mL＞

・Label Value 1.03 mg KOH/g

- Titration curve -



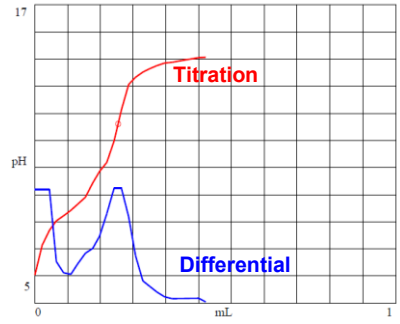
-Measurement results-

	Sample (g)	Blank (mL)	Titration amount (mL)	Acid number (mgKOH/g)
1	2.5073	0.0657	0.4792	0.95
2	2.5086	0.0657	0.4615	0.91
3	2.5027	0.0561	0.4585	0.93
Mean				0.93
SD				0.02
RSD(%)				2.2

＊Factor of titrant= 1.0297

・ Label Value 0.11 mg KOH/g

- Titration curve -



-Measurement results-

	Sample (g)	Blank (mL)	Titration amount (mL)	Acid number (mgKOH/g)
1	10.0261	0.0662	0.2310	0.10
2	10.0432	0.0662	0.2233	0.09
3	10.0050	0.0662	0.2088	0.08
Mean				0.09
SD				0.01
RSD(%)				11.1

＊Factor of titrant= 1.0543

9. Reference

ASTM D664 Standard Test Methods for Acid Number of Petroleum Products by Potentiometric Titration.