

Application Note

Mercaptan sulfur of petroleum products

| | | |
|--------------------|---|----------------------------------------------------|
| Industry | : | Petroleum |
| Instrument | : | Automatic potentiometric titrator |
| Measurement method | : | Potentiometric titration / Precipitation titration |
| Related standard | : | ASTM D3227, JIS K2276 |

1. Scope

Test samples were prepared by dissolving octanethiol in toluene and mercaptan sulfur in the samples were measured based on “ASTM D3227 Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosene, Aviation Turbine, and Distillate Fuels (Potentiometric Method)”.

A test sample dissolved in sodium acetate 2-propanol solution was potentiometrically titrated with 0.01mol/L silver nitrate 2-propanol solution. An inflection point on the titration curve was regarded as the endpoint. The quantity of mercaptan sulfur was calculated from the volume of silver nitrate 2-propanol solution used to titrate sample to endpoint.

2. Precautions

- 1) Prepare a fresh silver sulfide coating on the silver electrode each day by the method described in “6. Procedure, -Preparation of silver/silver-sulfide electrode-“.
- 2) After each measurement, soak the silver/silver-sulfide electrode into 100mL of titration solvent containing 0.5mL of 0.1mol/L silver nitrate 2-propanol solution for 5 minutes.
- 3) Clean the glass electrode at least once a week by stirring in cold chromic acid solution.
- 4) 0.1mol/L silver nitrate 2-propanol solution is standardized at an interval not shorter than the concentration changes by more than 0.0005mol/L.
- 5) Prepare 0.01mol/L silver nitrate 2-propanol solution daily by diluting 0.1mol/L silver nitrate 2-propanol solution by 10 times with 2-propanol.
- 6) If sample contains hydrogen sulfide (H₂S), remove H₂S by the method described in ASTM D3227.

3. Post-measurement procedure

- 1) Clean the glass electrode with alcohol and keep lower half of the electrode immersed in water.
- 2) Clean the silver electrode with alcohol and wipe with a soft, clean tissue. Then, keep in a dry condition.

4. Apparatus

| | | |
|-----------|---|----------------------------------------------------------------------|
| Main unit | : | Automatic potentiometric titrator (preamplifier : STD) |
| Electrode | : | Silver electrode (with silver sulfide coating) pH glass electrode |

5. Reagents

- 0.1mol/L silver nitrate 2-propanol solution
- 0.01mol/L silver nitrate 2-propanol solution (titrant)
- Sodium acetate 2-propanol solution (titration solvent)
Dissolve 1.6g of anhydrous sodium acetate in 25mL of water and pour into 975mL of 2-propanol.
- 10g/L sodium sulfide(Na₂S) aqueous solution
Dissolve 10g of anhydrous Na₂S or 30.6g of Na₂S·9H₂O in water and dilute to 1L with water.

6. Procedure

-Preparation of silver/silver-sulfide electrode-

- 1) Burnish detection part of electrode with polishing paper.
- 2) Immerse the electrode in 100mL of titration solvent containing 8mL of sodium sulfide solution, and then heat the solvent up to 60°C*.
- 3) Keep the temperature of the solvent at 60°C* and add slowly from a burette, with stirring, 10mL of 0.1 mol/L silver nitrate 2-propanol solution over a period from 10 to 15min.
- 4) Wash the electrode with water and wipe off surplus silver sulfide with a soft, clean tissue.

*Though heating operation is not described in the standard, good silver sulfide coating is formed by this operation.

-Blank test-

- 1) Add 100mL of the titration solvent into a 200mL beaker.
- 2) Titrate with 0.01mol/L silver nitrate 2-propanol solution to measure blank level.

-Measurement-

- 1) Measure 20~50 mL of the sample with pipet and pour into a 200mL beaker.
- 2) Add 100mL of the titration solvent.
- 3) Titrate with 0.01mol/L silver nitrate 2-propanol solution to measure mercaptan sulfur concentration.

7. Calculation

$$\text{Mercaptan sulfur (wt\%)} = (\text{EP1} - \text{BL1}) \times \text{TF} \times \text{C1} \times \text{K1} / \text{S}$$

| | | |
|-----|---|-----------------------------------------------------|
| EP1 | : | Titer (mL) |
| BL1 | : | Blank level = 0.0000mL |
| TF | : | Factor of titrant = 0.9128 |
| C1 | : | Concentration conversion coefficient = 0.32065mg/mL |
| K1 | : | Unit conversion coefficient = 0.1 |
| S | : | Sample (g) |

8. Example

-Titration parameter-

< Titr. Mode > : Auto Int.

< Titr. Form > : EP Stop

< Titr. Para. >

Max. Volume : 20 (mL)

Channel/Unit(Ctrl.) : Ch1, mV

Channel/Unit(Ref.) : Off

pH Polarity : Standard

Titration Type Check : No Check

Direction : Negative

Wait Time : 30 (s)

Dose Mode : None

< Ctrl. Para. >

Number of EP : 1

End Sense : Auto

Gain : 1

Data Sampling : Auto

Ctrl. Speed : Standard (Blank test, Sample ①)

: Slow (Sample ②)

Other Ctrl. : Standard

Auto Int. Mode : Blank (Blank test)

: Micro (Sample ①,②)

Micro Titr. Max. Vol. : 1 (mL)

Micro Titr. dE : 50.0 (dE)

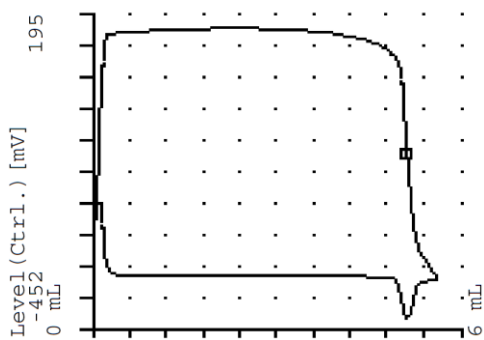
Micro Titr. dE/dmL : 100.0 (dE/dmL)

Stirrer Speed : 3

(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-

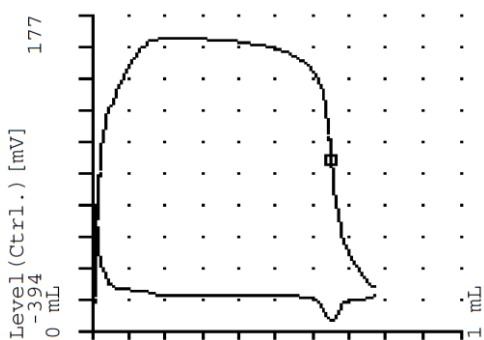


-Measurement results-

| | Sample* | | Titer (mL) | Mercaptan sulfur (wt%) |
|------------|---------|--------|---------------|---------------------------|
| | (mL) | (g) | | |
| 1 | 20 | 17.338 | 5.0813 | 0.00858 |
| 2 | 20 | 17.338 | 5.0865 | 0.00859 |
| 3 | 20 | 17.338 | 5.1184 | 0.00864 |
| Mean | - | - | - | 0.00860 |
| SD | - | - | - | 0.00003 |
| RSD (%) | - | - | - | 0.37364 |

Sample ②

-Titration curve-



-Measurement results-

| | Sample* | | Titer (mL) | Mercaptan sulfur (wt%) |
|------------|---------|--------|---------------|---------------------------|
| | (mL) | (g) | | |
| 1 | 50 | 43.345 | 0.6242 | 0.00042 |
| 2 | 50 | 43.345 | 0.6317 | 0.00043 |
| 3 | 50 | 43.345 | 0.6430 | 0.00043 |
| Mean | - | - | - | 0.00043 |
| SD | - | - | - | 0.00001 |
| RSD (%) | - | - | - | 1.35316 |

*Sample : Sample was collected in fixed volume, and sample volume was converted into weight by the density of sample.

9. Summary

Each sample was measured three times and good repeatability was obtained. In some samples, verification of the measurement capability is required. In such case, please contact us.

10. References

- 1) ASTM D3227-13 Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosene, Aviation Turbine, and Distillate Fuels (Potentiometric Method)
- 2) JIS K2276: 2003 Petroleum products – Testing methods for aviation fuels