Application Note
Mercaptan sulfur of petroleum products

Industry	:	Petroleum
Instrument	:	Automatic potentiometric titrator
Measurement method	:	Potentiometric titration / Precipitation titration
Standards	:	UOP Method 163

1. Scope

Mercaptan sulfur in test samples were measured based on "UOP Method 163　Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration". Test samples were prepared to almost 100 ppm and 1 ppm by dissolving octanethiol in toluene.

A test sample and concentrated ammonia solution were dissolved in 2-propanol, and then the solution was potentiometrically titrated with 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) Handle the reagents in a well ventilated room or a draft chamber.
2) Rinse electrodes with suitable solvent and then pure water after each measurement.
3) Immerse the silver/silver-sulfide electrode into 100　mL of titration solvent containing 0.5 mL of 0.1 mol/L silver nitrate solution for 5 minutes, after washing electrodes.
4) Prepare silver sulfide coating on the surface of silver electrode again by the method described in "6. Procedure, -Preparation of silver/silver-sulfide electrode-", when the coating becomes rough or the titration curves become noisy.
5) 0.1　mol/L silver nitrate 2-propanol solution is standardized at an interval not shorter than the concentration changes by more than 0.0005　mol/L.

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. 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

・0.1 mol/L silver nitrate solution
・0.01 mol/L silver nitrate 2-propanol solution
　Prepare this solution daily by diluting 0.1 mol/L silver nitrate solution with 2-propanol.
・0.001 mol/L silver nitrate 2-propanol solution
　Prepare this solution daily by diluting 0.01 mol/L silver nitrate solution with 2-propanol.
・Concentrated ammonia solution (28%)
・1% sodium sulfide (Na_2S) solution
　Dissolve 1 g of anhydrous Na_2S or 3 g of $Na_2S \cdot 9H_2O$ in water and dilute to 100 mL with water.

6. Procedure

-Preparation of silver/silver-sulfide electrode-
1) Burnish detection part of electrode with polishing paper included with the product.
2) Wash the electrode with pure water and wipe dry.
2) Immerse the electrode in mixture of 96 mL of 2-propanol, 1 mL of concentrated ammonia solution and 8 mL of 1% Na_2S solution, and heat the mixture to 60°C*.
3) Keep the temperature of the solvent at 60°C * and add 10 mL of 0.01 mol/L silver nitrate 2-propanol solution for 10 minutes with stirring.
4) Wash the electrode with water and wipe off surplus silver sulfide.
　*Though heating operation is not described in the standard, good silver sulfide coating is formed by this operation.

-Measurement of 100 ppm sample-
1) Add 100 mL of 2-propanol into a 200mL tall beaker.
2) Add approximately 1 mL of concentrated ammonia solution.
3) Add approximately 50 g of sample and measure mass of it to the nearest 0.1 mg.
4) Titrate with 0.01 mol/L silver nitrate 2-propanol solution.

-Measurement of 1 ppm sample-
1) Add 150 mL of 2-propanol into a 300mL tall beaker.
2) Add approximately 1 mL of concentrated ammonia solution.
3) Add approximately 100 g of sample and measure mass of it to the nearest 0.1 mg.
4) Titrate with 0.001 mol/L silver nitrate 2-propanol solution.

7. Calculation

$$\text{Mercaptan sulfur (mass-ppm)} = EP1 \times TF \times C1 \times K1 / S$$

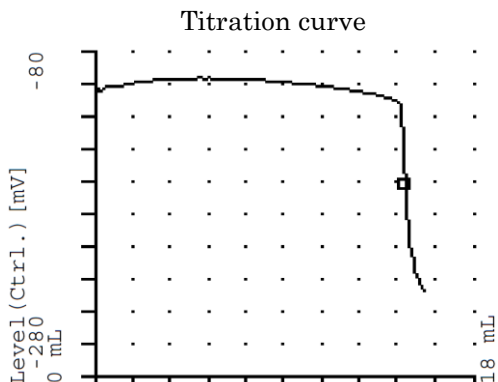|		
EP1	:	Titer (mL)
TF	:	Factor of titrant = 0.9990
C1	:	Concentration conversion coefficient = 0.32 mg/mL (100 ppm sample)
		0.032 mg/mL (1 ppm sample)
K1	:	Unit conversion coefficient = 1000
S	:	Mass of sample (g)

8. Example

-Titration parameter-

＜Titr. Mode＞	: Auto Intermit	**＜Ctrl. Para.＞**	
＜Titr. Form＞	: EP Stop	Number of EP	: 1
		End Sense	: Auto
＜Titr. Para.＞		Gain	: 1
Max. Volume	: 20 (mL)	Data Sampling	: Auto
Channel/Unit(Ctrl.)	: Ch1, mV	Ctrl. Speed	: Standard
Channel/Unit(Ref.)	: Off	Other Ctrl.	: Standard
pH Polarity	: Standard	Auto Int. Mode	: Standard
Titr. Type Check	: No Check	Stirrer Speed	: 4
Direction	: Negative		
Wait Time	: 30 (s)		
Dose Mode	: None		

(The measurement parameter and the titration curve are an example of our automatic potentiometric titrator.
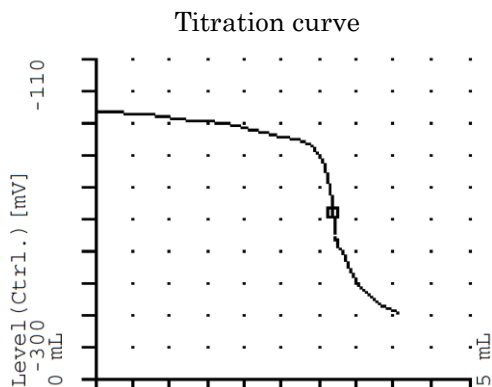For other models, parameter item may be different or other parameter items may be added.)

京都電子工業株式会社
KYOTO ELECTRONICS
MANUFACTURING CO.,LTD.

-Results-

100 ppm Sample

Titration curve

	Results		
	Mass of sample	Titer	Mercaptan sulfur
	(g)	(mL)	(mass-ppm)
1	49.1585	14.4340	94
2	49.5134	14.6195	94
3	49.1704	14.5369	95
Mean	-	-	94
SD	-	-	0.6
RSD (%)	-	-	0.6

1 ppm Sample

Titration curve

	Results		
	Mass of sample	Titer	Mercaptan sulfur
	(g)	(mL)	(mass-ppm)
1	98.7940	3.1435	1.0
2	98.4737	3.1301	1.0
3	98.4903	3.1613	1.0
Mean	-	-	1.0
SD	-	-	0.0
RSD (%)	-	-	0.0

9. Summary

   Two test samples were measured three times respectively, and the results of them showed a good repeatability.
   In some samples, verification of the measurement capability is required. In such case, please contact us.

10. References

1) UOP Method 163-10   Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration