

Application Note

Bromine numbers of petroleum distillates and aliphatic olefins by potentiometric titration

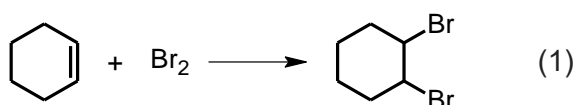
Industry	Chemicals
Instrument	Automatic potentiometric titrator
Measurement method	Potentiometric titration
Standards	ASTM D1159-07

1. Scope

Caution

This measurement is performed using organic solvents and strong acids. When you follow this application note, wear masks, gloves, protective equipments, etc. The automatic potentiometric titrator should be installed and used in fume hoods where local exhaust ventilation is possible.

The bromine number is the number of grams of bromine added to carbon-carbon unsaturated bonds in 100 g of petroleum fraction, expressed as $\text{gBr}_2/100 \text{ g}$, and is measured as a value indicating the number of unsaturated components contained in petroleum products. This application shows an example of bromine number measurement based on ASTM D1159-07 (Note 1). The measurement sample was prepared by dissolving cyclohexene in dichloromethane to a known concentration (approximately $30 \text{ gBr}_2/100 \text{ g}$) (reaction formula (1)).



2. Precautions

- 1) To suppress side reactions during titration, cool the solution to $5 \text{ }^\circ\text{C}$ or less during measurement.
- 2) Before starting measurements each day, purge the titrant several times between the reagent bottle and the burette to equalize the titrant concentration, then discharge about 10 mL of the titrant between the burette and the titration nozzle.

3. Apparatus

Main unit	Automatic potentiometric titrator (Preamplifier POT)
Electrode	Blank test and measurement Twin platinum electrode (M-511) Temperature compensation electrode (T-171)

4. Reagents

Titrant	0.25 mol/L Bromide-bromate standard solution (potassium bromide and potassium bromate) Dissolve 51.0 g of potassium bromide (KBr) and 13.92 g of potassium bromate (KBrO_3) each dried at $105 \text{ }^\circ\text{C}$ for 30 min, in pure water and dilute to 1 L.
Titration solvent	A solution consisting of a mixture of 714 mL of acetic acid, 134 mL of dichloromethane, 134 mL of methanol, and 18 mL of sulfuric acid (1 + 5).

5. Procedure

-Preparation of sample solution-

- 1) Add 10 mL of dichloromethane into a 50 mL volumetric flask.
- 2) Add around 4-5 g of cyclohexene into the flask and measure the mass of it (approximately 30 gBr₂/100 g).
- 3) Add dichloromethane to the mark of the flask and mix it.

-Setting of the constant current value-

- 1) Cool the solution to 0 - 5 °C, then press [Calibration] button.
- 2) Set Channel/Unit to “Ch3/Pol”.
- 3) Press [Details] button and set as follows.

Calibration Mode	Current
Polar Current	10.00 μA
- 4) Immerse the twin platinum electrode in titration solvent and perform calibration.

-Blank test-

- 1) Collect 5 mL of dichloromethane and mix with 110 mL of the titration solvent.
- 2) Cool the solution to 0 - 5 °C, then titrate with 0.25 mol / L Bromide-bromate standard solution.

-Measurement-

- 1) Collect 5 mL of the sample solution*¹ and mix with 110 mL of titration solvent.
- 2) Cool the solution to 0 - 5 °C, then titrate with 0.25 mol / L Bromide-bromate standard solution.

*¹ To avoid phase separation, adjust the sample collection volume so that the titration volume is less than 20 mL.

6. Calculation

$$\text{Bromine number (gBr}_2\text{/100 g)} = (\text{EP1} - \text{BL1}) \times \text{TF} \times \text{C1} \times \text{K1} \times \text{R/S}$$

EP1	Titration amount (mL)
BL1	Titration amount (mL) of blank test = 0.0377(mL)
TF	Factor of titrant = 1.005
C1	Concentration conversion coefficient = 39.95
K1	Unit conversion factor = 0.1
S	Sample size = 4.6716 (g)
R	Dilution coefficient (10)

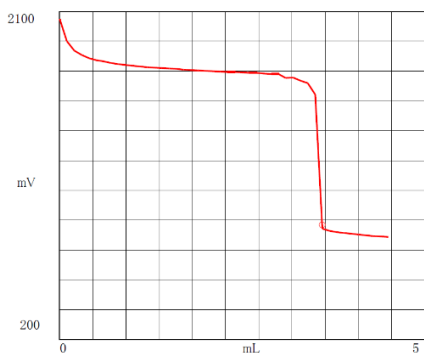
7. Example

— Parameter —

<Titr. Mode>	Intermit	<Ctrl. Para.>	
<Titr. Form>	Level Stop	End Point No.	1
		End Level (mV)	1110.0
<Titr. Para.>		Gain	1
Max Volume	0.15 (mL) (blank test)	Data Sampling	Set
	4.5 (mL) (sample)	Data Sampling Pot.(mV)	999.0
Channel/Unit(Ctrl.)	Ch3, mV	Data Sampling Vol. (mL)	0.0050 (blank test)
Channel/Unit (Ref.)	Off		0.1000 (sample)
pH Polarity	Standard	Control Speed Mode	Set
Titr. Type Check	No Check	Cut-Off time	10
Direction	Auto	Unit Volume	0.0050 (blank test)
Wait Time	0 (blank test)		0.1000 (sample)
	30 (sample)	Dispense Speed	1
Dose Mode	None	Other Control	Set
		Titr. over vol.	2.00 (blank test)
		End Time(s)	30
		Stirrer Speed	4

(The above condition is an example. The setting condition depends on the model.)

— Example of titration curve —



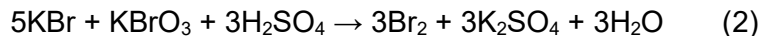
— Measurement results —

Table 1 Measurement result

	Sample (g)	Titration (mL)	Bromine number (gBr ₂ /100 g)
1	4.6716	3.4699	29.50
2	4.6716	3.5615	30.29
3	4.6716	3.5653	30.32
Average	-	-	30.04
SD	-	-	0.38
RSD (%)	-	-	1.26

8. Notes

Note 1) The bromine produced at reaction formula (2) below is reacted with the carbon-carbon unsaturated bonds of the sample (formula (1) above).



According to the standard, the endpoint of the titration is defined as the potential stable point where the titration is stopped for 30 seconds after a drastic potential change at the equivalence point.

9. Reference

ASTM D1159-07 Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration